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3,5Bd	3,5-dihydroxyphenol acid
BSTFA	N,O -Bis(trimethylsilyl)trifluoroacetamide
BP	Before present
C	Carbon
°C	Celsius degree
^{13}C	Carbon-13
CH_4	Methane
cm	Centimetre
CO_2	Carbon dioxide
COMERN	Collaborative Mercury Research Network
CuO	Copper oxidation
CVA-FS	Cold vapour atomic fluorescence spectrometry detection
DA/LA	Drainage area / Lake area
DOC	Dissolved organic carbon
dw	Dry weight
Fd	Ferulic acid
g	Gram
GC/MS	Gas chromatograph / Mass spectrometer
GIS	Geographical information system
GRASS	Geographic Resources Analysis Support System
HCl	Hydrochloric acid
HNO_3	Nitric acid
Hg	Mercury
km	Kilometre
km^2	square kilometre
m	Meter
mg	Milligram
min	Minute
ml	Millilitre
mm	Millimetre

N	Nitrogen
n	Size of statistical sample
NaOH	Sodium hydroxide
NRCAN	Natural Resources Canada
O_2	Dioxygen
OC	Organic carbon
P	P-hydroxyphenol
PCA	Principal component analysis
pH	Potential Hydrogen
p-Cd	*p*-coumaric acid
Pd	*p*-hydroxybenzoic acid
Pl	*p*-hydroxybenzaldehyde
Pn	*p*-hydroxyacetophenone
POC	Particulate organic carbon
ppb	Part per billion
R^2	Coefficient of determination
S	Syringyl
Sd	Syringic acid
Sl	Syringin
Sn	Acetosyrigon
SOM	Soil organic matter
THg	Total mercury
TMCS	Trimethylchlorosilane
TOM	Terrestrial (or terrigenous) organic matter
Vd	Vanillic acid
Vl	Vanillin
Vn	Acetovanillone
X	X-axis
Y	Y-axis
λ	Lambda
Σ	Sum
[...]	Concentration

RÉSUMÉ

Dans le cadre du « Collaborative Mercury Research Network »(COMERN), la problématique de la contamination des écosystèmes boréaux par le mercure (Hg) a été abordée sous forme d'approche écosystémique. Cette approche a notamment été utilisée dans le cadre du projet dit « des lacs de la forêt boréale » pour comprendre l'origine et le devenir du Hg présent dans ces milieux. Cette thèse fait partie intégrante du volet « interaction lac – bassin versant » et a pour but de comprendre les mécanismes qui influencent l'apport de Hg des bassins versants vers les lacs. L'objectif spécifique est de déterminer pourquoi les concentrations en Hg ([Hg]) dans les sédiments récents varient entre les lacs de l'écosystème boréal. De nombreuses études démontrent que le devenir du Hg dans les écosystèmes lacustres est associé aux apports de matière organique terrigène (MOT). Pour comprendre et préciser cette interaction, une double approche a été utilisée. L'analyse de biomarqueurs spécifiques de la MOT dans les sédiments de lacs et la caractérisation des propriétés des bassins versants par système d'information géographique (SIG). Les biomarqueurs de la MOT ont été choisis car ils sont spécifiquement d'origine terrigène et procurent une information sur la source et la qualité de la MOT.

Dans un premier temps et après une revue de la littérature, il est apparu nécessaire de bien définir le cadre de référence et les valeurs sources des biomarqueurs utilisés. Les biomarqueurs de la lignine obtenus par oxydation à l'oxyde de cuivre des végétaux et de matière organique partiellement décomposée sont souvent utilisés pour décrire les sources et l'état de dégradation de la matière organique terrestre (MOT). La plupart des études utilisant ces biomarqueurs font référence aux sources pures (échantillons de plantes fraîches) mais plusieurs recherches récentes démontrent que les sols jouent un rôle prépondérant sur les signatures de biomarqueurs de lignine. Il était donc nécessaire d'établir un milieu de référence plus adapté à cette problématique.

Nous avons ainsi démontré que la matière organique des sols de trois grands écosystèmes terrestres du paysage boréal (tourbières et les peuplements dominés par les gymnospermes ou par les angiospermes) est caractérisée par des signatures de biomarqueurs distinctes. De plus, la pédogenèse réduit la variation des signatures de référence de ces biomarqueurs. Finalement, nous avons été en mesure de confirmer le potentiel d'utilisation des indicateurs de dégradation et d'humification de la matière organique des sols.

Dans la deuxième partie de cette thèse l'influence du bassin versant sur la composition de biomarqueurs spécifiques de la MOT mesurés dans les sédiments, est analysée. La caractérisation d'un bassin versant est souvent ardue, coûteuse et longue et les biomarqueurs de la lignine représentent d'excellents indicateurs des processus qui ont lieu à l'échelle d'un bassin versant. Les systèmes d'information géographique permettent également d'intégrer et de décrire les caractéristiques morpho édaphiques des bassins versants. En combinant ces deux approches, nous avons observé une relation positive et significative entre la pente moyenne du bassin versant et les

apports de MOT estimé par $\lambda8$ dans les sédiments récents (R^2=0.65). La pente moyenne est également corrélée avec la composition de la MOT. En effet, les rapports P/(V+S) et 3,5Bd/V diminuent significativement avec l'augmentation de la pente moyenne (R^2=0.57 and R^2=0.71 respectivement). La composition de la végétation influence également la composition des sédiments des lacs étudiés. L'augmentation de la présence d'angiospermes dans le bassin versant favorise l'apport de MOT dans les sédiments de lacs tel qu'estimé par $\lambda8$ (R^2=0.44). Une relation similaire est observée avec le rapport S/V, indicateur de ce type de source. Dans cette étude, nous avons donc pu déterminer : que les zones de faibles pentes jouent le rôle de zone tampon pour les apports de lignine et donc par extension sur les apports de MOT vers les sédiments lacustres et que la contribution relative de la MOT des horizons de sols organiques augmente dans les bassins versant plus escarpés. Cette étude a des implications significatives pour la compréhension du devenir de la MOT dans les écosystèmes lacustres.

Dans un troisième temps nous avons caractérisé la MOT au niveau moléculaire pour déterminer précisément les conditions du transfert de Hg vers les sédiments. Quinze lacs ont été échantillonnés au Québec et au Labrador. Dans chaque lac, les sédiments récents de la zone focale du lac ont été échantillonnés et analysés en laboratoire pour déterminer la concentration en Hg total et celles des différents biomarqueurs terrigènes. Nos résultats mettent en évidence trois régions distinctes déterminées par des apports de MOT et de Hg différents. L'Outaouais et le Témiscamingue (région A) sont caractérisés par des concentrations en Hg très variables et des teneurs élevées en MOT. L'Abitibi (région B) est caractérisée par des taux de Hg intermédiaires et des teneurs de MOT très faibles. Le Labrador (région C) est caractérisé par des niveaux de Hg très faibles et des teneurs de MOT également très faibles. Dans les lacs de la région A, la variation des teneurs en Hg est bien expliquée par l'augmentation du rapport 3,5Bd/V et la diminution du rapport C/V. Dans la région B, les sédiments sont enrichis en Hg lorsque comparés aux apports de MOT. Une contamination locale due à l'activité minière explique cet enrichissement relatif. Finalement au Labrador, la dynamique de la MOT est dominée par les gymnospermes et la végétation arbustive ou rase et induit une production primaire faible dans le bassin versant. Cette spécificité entraîne un apport très faible de Hg des bassins versants vers les lacs. Notre étude montre donc que la source et la qualité de la MOT sont déterminantes pour comprendre les variations d'apports en Hg dans les sédiments récents. Plus précisément, l'augmentation des apports de MOT dérivés des horizons humifiés des sols explique une grande part des apports de Hg dans les sédiments.

Finalement, dans la partie 4 de cette thèse, nous nous sommes intéressés à la problématique du cycle du Hg dans un complexe hydroélectrique boréal. En effet, la mise en eau d'un réservoir entraîne des impacts environnementaux considérables sur les écosystèmes initiaux comme la modification drastique du cycle du carbone, ainsi que celle de la dynamique des éléments nutritifs et des contaminants. Les sédiments des lacs Gabbro et Sandgirt, inondés, et du lac Atikonak ont été échantillonnés pour

déterminer les sources du Hg observé dans le complexe hydroélectrique de Churchill Falls au Labrador. Les biomarqueurs de la lignine ont été utilisés comme indicateur de source de la matière organique terrigène (TOM). Dans le lac Atikonak, qui n'a pas été modifié par l'inondation, les niveaux de Hg total ([THg]) dans les sédiments ont augmenté progressivement dans le temps. Par opposition, dans les lacs Gabbro et Sandgrit inondés, des augmentations drastiques de [THg] ont été observées depuis l'inondation. Contrairement au lac Atikonak, ces augmentations de [THg] dans les lacs inondés sont associées à un changement de la nature de la MOT. À la suite de la mise en eau, la proportion de MOT dans les sédiments a augmenté significativement. La composition de la MOT montre qu'elle est également moins dégradée et présente une signature typique des horizons organiques de sols forestiers. Les résultats obtenus dans cette étude démontrent que l'augmentation de niveaux de Hg dans les sédiments de réservoir est causée par l'inondation des sols forestiers et l'érosion de leurs horizons de surface. Il est également important de remarquer que les [THg] restent élevées 38 ans après la mise en eau.

En conclusion, le travail réalisé dans cette thèse permet de démontrer qu'il est possible d'intégrer des paramètres du bassin versant par l'analyse moléculaire de la matière organique terrigène. En associant des analyses moléculaires et des SIG, il est également possible de mettre en place un indicateur de la contamination des sédiments récents par le mercure. Finalement, nous confirmons le rôle primordial des versants dans l'apport de mercure vers les milieux aquatiques. Cette thèse démontre la nécessité du couplage bassin versant milieu aquatique dans les études environementales mais aussi géochimique notamment pour la compréhension des cycles des contaminants et du carbone dans ces milieux.

Mots clés : bassin versant, biomarqueur, lignine, matière organique, mercure, lac, réservoir, sédiment, SIG, terrigène.

INTRODUCTION GÉNÉRALE

Depuis le début de l'ère industrielle, l'activité humaine globale a considérablement augmenté. Sous la double impulsion du progrès technologique et de l'accroissement de la population mondiale, l'activité anthropique s'est globalisée. Cette accélération de l'activité d'une espèce à l'échelle de la planète a été rendue possible par l'augmentation du prélèvement des ressources naturelles disponibles. L'utilisation des ressources en espace a apporté des changements drastiques de l'utilisation du territoire. De plus, la pression sur les ressources biologiques a entraîné une baisse de la biodiversité. Finalement, le prélèvement des ressources naturelles et énergétiques a contribué à la modification de l'ensemble des cycles biogéochimiques (Vitousek et al 1997, Western 2001, Foley et al 2005).

Face à ces enjeux environnementaux, les équipes de recherche ont développé des approches globales à l'échelle de l'écosystème intégrant l'expertise de plusieurs champs disciplinaires. L'étude du cycle du mercure (Hg) n'échappe pas à cette logique écosystémique. Elle peut même être considérée comme un « cas d'école » de l'étude environnementale à l'échelle globale. En effet, le Hg est un métal naturellement présent dans l'environnement et plus particulièrement dans la croûte terrestre. Des phénomènes naturels comme le volcanisme ou l'érosion favorisent la mobilité et la dispersion du Hg dans les milieux atmosphériques, terrestres et aquatiques. L'activité humaine comme par exemple l'extraction des énergies fossiles implique également une modification drastique du cycle naturel du Hg et un déplacement important de son réservoir terrestre vers les autres sphères environnementales (Fitzgerald 1995, Pacyna et al 2006, Lindberg et al 2007).

Le COMERN (Collaborative Mercury Research Network) a ainsi abordé la question du cycle du Hg dans l'environnement de façon transdisciplinaire et intégré à l'échelle écosystémique (Lucotte et al 2005). Ce réseau de recherche pancanadien regroupe plusieurs universités, des organismes gouvernementaux et des groupes représentants les communautés concernées par cette problématique. Les objectifs du COMERN sont : i) de déterminer les sources de Hg présent dans l'environnement, ii) de comprendre les mécanismes de transfert du Hg atmosphérique vers les milieux aquatiques, iii) de déterminer les facteurs qui influencent la contamination des poissons et iv) d'optimiser la consommation de poissons tout en réduisant les risques pour les populations locales.

Les recherches à l'intérieur du réseau sont articulées autour de deux études de cas : le fleuve St-Laurent et l'environnement côtier de la baie de Fundy, et d'une approche écosystémique de la problématique dans les lacs de la forêt boréale.

Ainsi, la présente thèse s'inscrit dans le cadre de l'étude de la contamination des lacs de la forêt boréale par le Hg et plus spécifiquement fait partie intégrante d'un ensemble de projets de recherche sur la dynamique du Hg entre les lacs et leurs bassins versants (figure 0.1).

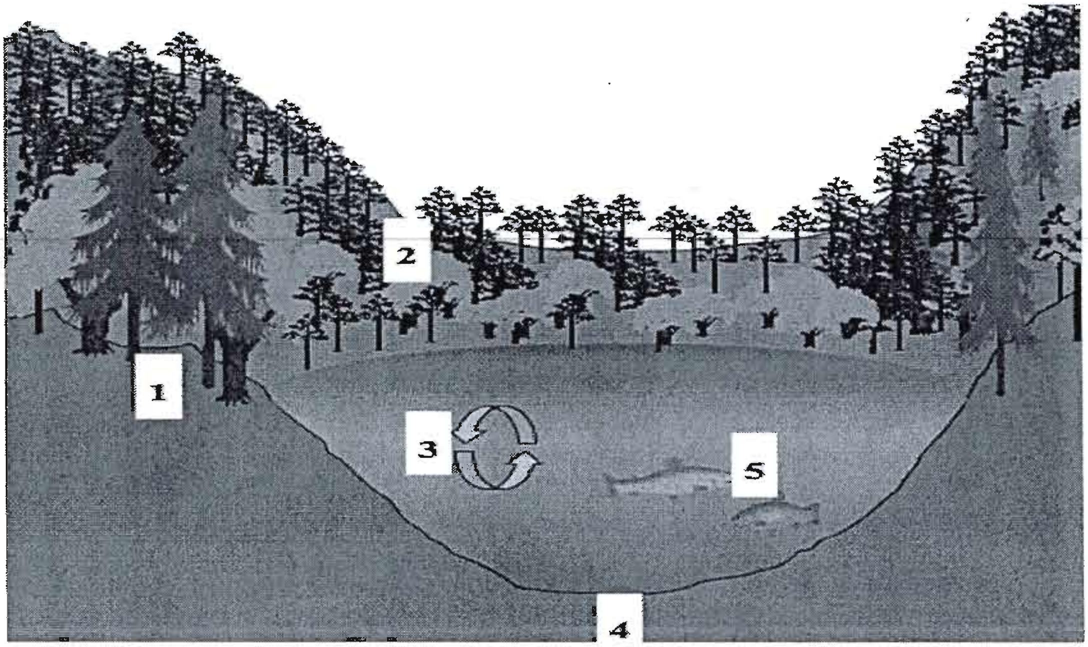

Figure 0.1 Schéma représentant chacun des projets de recherche menés par le COMERN dans le cadre de l'étude écosystémique des lacs de la forêt boréale : Étude de la dynamique du Hg et de la matière organique terrigène dans un système « lac - bassin versant ». **1**- Caractéristion de la matière organique dans les sols : chapitre I ; **2**- Analyse des bassin-versants : Chapitre II, Beaulne et al 2009 ; **3**- Dynamique du Hg dans la colonne d'eau : Dufour 2005, Ouellet et al 2009 ; **4**- Dynamique de la MOT et du Hg dans les sédiments : chapitres II et III ; **5**- Hg dans la chaine alimentaire : Roué-Legall et al 2005, Simoneau et al 2005, Lavigne et al 2009, Ouellet et al 2009

La présente étude a pour objectif spécifique de préciser les conditions de transfert du Hg des bassins versants vers les milieux aquatiques et ainsi résoudre la question des variations de teneurs en Hg des sédiments récents dans des lacs a priori très similaires (situation géographique, couverture végétale du bassin versant, lac de tête et peu ou pas perturbé). Dans l'environnement boréal, le Hg est à la fois d'origine naturelle et anthropique. Naturellement présent dans tous les écosystèmes, l'activité humaine, notamment la combustion des énergies fossiles et les activités de l'industrie minière, a contribué à l'augmentation du Hg dans l'atmosphère et la biosphère. Ainsi plusieurs études démontrent que les taux de Hg dans les sédiments lacustres ont augmenté de deux à cinq fois depuis le début de l'ère industrielle (Lucotte et al 1995, Jackson 1997, Rognerud et Fjeld 2001). Le Hg est transporté dans l'atmosphère sur de très longues distances et la contamination par le Hg anthropique peut s'étendre à des écosystèmes très éloignés des sources d'émissions. Le Hg atmosphérique se dépose par précipitations sèche ou humide sur les écosystèmes terrestres. En région boréale, la densité des lacs et cours d'eau est une des plus importante de la Planète (Downing et al 2006). L'impact du Hg sur ces environnements est particulièrement important puisqu'au Hg qui se dépose directement sur la surface du lac s'ajoute le Hg lessivé depuis la végétation et les sols du bassin versant (Porvari et Verta 2003, Lamborg et al 2002). Le Hg qui entre dans les lacs peut sédimenter, être réémis vers l'atmosphère, ou être méthylé pour former du méthylmercure (MeHg) et être ainsi potentiellement bioaccumulé par les organismes vivants (Lindqvist et al 1991). Si l'on considère la concentration en Hg total ([T-Hg]) dans les sédiments récents de lacs de la forêt boréale québécoise, des variations de 50 ppb à 500 ppb sont observées (Lucotte et al 1995, Kainz et Lucotte 2006). Ces variations s'observent également à l'échelle continentale en Amérique du Nord et en Europe (Jackson 1997). Celles-ci peuvent être expliquées par un gradient Nord-Sud de contamination par le Hg anthropique plus on s'éloigne des sources d'émission (figure 0.2a, Fitzgerald 1995, Jackson 1997). Mais, à l'échelle du Québec, ce facteur n'est pas déterminant (figure 0.2b, Lucotte et al 1995).

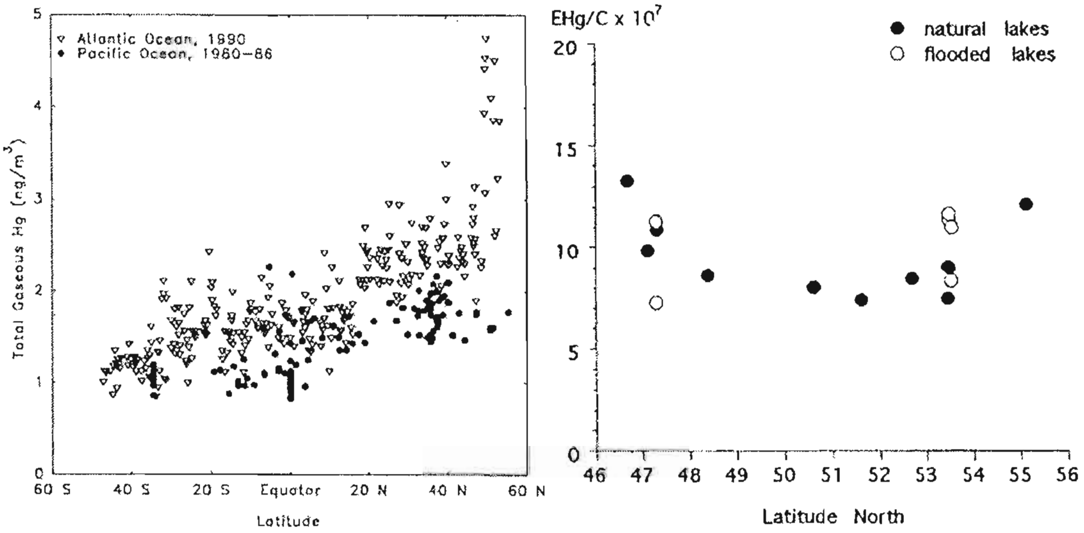

Figure 0.2 a : Concentrations en Hg gazeux dans l'atmosphère au dessus des océans Atlantique et Pacifique en fonction de la latitude. **b** : Concentrations en Hg normalisées par la teneur en carbone organique dans les sédiments récents de plusieurs lacs de la forêt boréale en fonction de leur latitude (d'après Fitzgerald 1995, Lucotte et al 1995).

Un autre facteur expliquant ces variations réside ~~dans le lien qui existe entre le Hg et~~ la matière organique (MO). En particulier, la matière organique terrigène (MOT) joue un rôle prépondérant dans le transport de nombreux composés des systèmes terrestres vers les systèmes aquatiques et son transfert dépend en partie des caractéristiques du bassin versant (Mierle et Ingram 1991, Scherbatskoy et al 1998, Porvari et Verta 2003). La MOT est essentiellement trouvée dans les sols et provient des dégradations chimique et biologique de résidus d'êtres vivants et des activités synthétiques des microorganismes. C'est un mélange complexe de produits végétaux et animaux dans des états de décomposition variables. Malgré son hétérogénéité, la MO possède des caractéristiques générales particulières comme la capacité de se lier avec de nombreux composés organiques et inorganiques par des processus de sorption (Huang et al 2003) ou de chélation (Drever 1997). Ainsi l'adsorption et l'absorption par la MOT de contaminants sont des processus majeurs régissant leur transport et leur devenir (Kan et al 1994). Ces processus sont largement étudiés notamment dans la problématique du Hg dans les lacs démontrant un lien entre les apports en Hg et la MOT (figure 0.3, Mierle et Ingram 1991, Meili 1991, Kolka et al 1999 , Kainz et al 2003, Ravichandran 2004, Sanei et Goodarzi 2006). Par exemple, Mierle et Ingram (1991) ont montré que la MOT d'un bassin versant était un vecteur potentiel du transfert du Hg vers le milieu aquatique. Certains auteurs ont également montré que l'évaluation des flux de carbone organique dissous (COD) est un meilleur indicateur du transport du Hg et du MeHg vers un lac que les calculs des dépôts humides du Hg dans le bassin versant du lac considéré (Driscoll et al 1995, Lee et al 1995). Cependant, des études démontrent que ce lien n'est pas systématique et qu'au-delà de la quantité de MOT retrouvée dans le lac, il est nécessaire de connaître sa qualité (source et composition; Lucotte et al 1995, Kainz et Lucotte 2006, Sanei et Goodarzi 2006). En effet, le rôle de la composition de la MOT dans les lacs apparaît comme crucial puisque plusieurs études récentes démontrent : que la MO des sols et les concentrations en Hg varient selon les types de sols, que le dépôt atmosphérique de Hg sur les sols dépend de la composition de la végétation, et que le régime hydrologique d'un bassin versant varie selon cette composition (Grondin et al 1995, Schroeder et Munthe 1998, Branfireum et Roulet 2002, Demers et al 2007). Le transport de la MOT vers les lacs, aussi bien d'un point de vue quantitatif que qualitatif, est variable. Il est influencé par plusieurs paramètres dépendant de la physiographie du bassin versant (pente, rapport entre la surface de drainage et celle du lac) (D'arcy et Carignan 1997, Lee et Iverfeld 1991), de la compositions des peuplements végétaux, du type de sol (Bishop et al 1995, Lee et al 1995, Meyers et Ishiwatari 1993) et du degré de perturbation physique du bassin versant (action anthropique, feu de forêt, etc.; Farella et al 2001, Caldwell et al 2000, Balogh et al 1997).

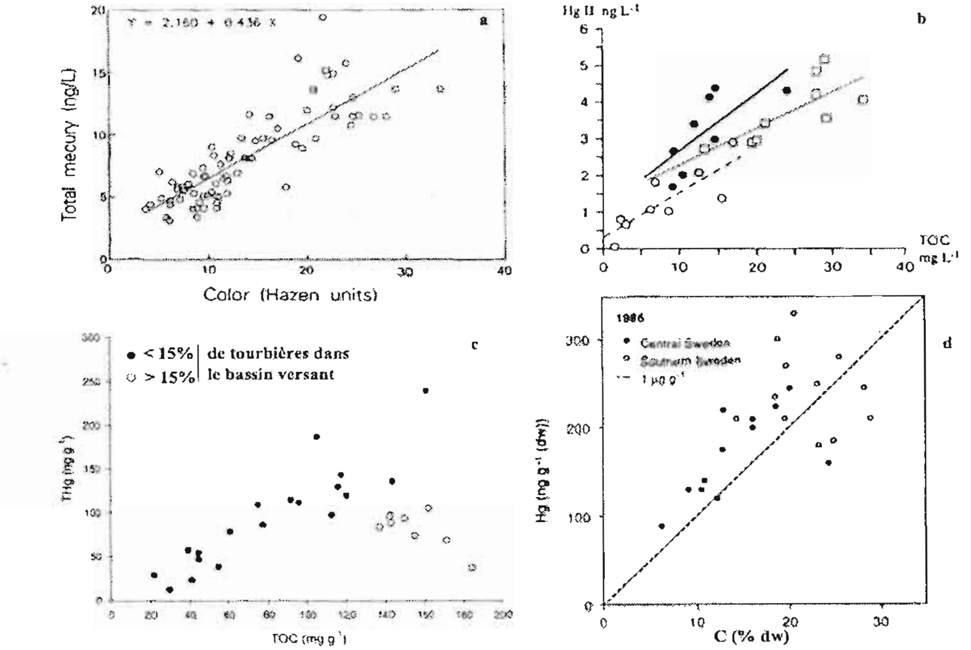

Figure 0.3 Relations entre le mercure total (THg) la concĕntration en matière organique estimée (couleur de l'eau) ou mesurée (TOC) dans l'eau (a et b) et dans les sédiments récents de lac (c et d). **a** : Mierle et Ingram 1991. **b** et **d** : Lindqvist et al 1991. **c** : Kainz et Lucotte 2006.

Dans l'optique de mieux comprendre la dynamique du Hg dans un système « lac – bassin versant », nous avons décidé d'adopter une approche méthodologique utilisant l'analyse d'indicateurs spécifiques de la MO dans des enregistrements sédimentaires. Il existe une série d'indicateurs potentiels pour décrire la MOT (e.g. isotopes stables, lipides, pollens, pigments ou phénols dérivés de la lignine; Cifuentes 1991, Hedges 1992, Meyers et Ishiwatari 1993, Meyers 1997, Hedges et al 1997, Goñi et al 2005). Dans cette étude, nous privilégions l'utilisation de biomarqueurs dérivés de la lignine car exclusifs à la végétation terrestre et permettant de décrire à la fois la source et l'état de dégradation de la MOT. La macromolécule ligneuse de par sa spécificité aux différents groupes de plantes terrestres, sa haute stabilité chimique, son abondance naturelle et sa large distribution sur la planète représente un marqueur d'activité biologique de premier plan pour les études biogéochimiques. Les composés dérivés de la lignine sont très résistants aux dégradations biologiques et chimiques (Hedges et Ertel 1982) et sont trouvés dans les milieux aquatiques d'eau douce et océanique (marge continentale et estuaire). Il en résulte que les biomarqueurs dérivés de la lignine sont d'excellents traceurs des sources de la MOT dans ces milieux. Leur omniprésence dans la plupart des compartiments terrestres et aquatiques a mené à de nombreuses études dans divers environnements comme les estuaires et les rivières (Louchouarn et al 1999, Farella et al 2001, Dittmar et Lara 2001), les sédiments lacustres (Houel et al 2006), les sols (Ertel et Hedges 1984, Amelung et al 1999), ou encore les tourbières (Williams et al 1998). Même si les phénols dérivés de la lignine ne représente qu'une fraction infime de l'ensemble de la MOT, leur grande stabilité chimique et leurs signatures spécifiques en font d'excellents biomarqueurs de cette MOT, particulièrement en milieu aquatique.

En laboratoire, ces biomarqueurs moléculaires spécifiques de la MOT proviennent de l'oxydation de la lignine par l'oxydation alcaline par l'oxyde de cuivre (CuO; Goñi et Montgomery 2000). L'oxydation alcaline permet entre autres d'obtenir une estimation de la contribution relative de la lignine à un échantillon. En milieu aquatique, cette estimation permet d'estimer la fraction d'origine terrigène de la MO. Les phénols identifiés permettent également d'obtenir de l'information sur la source de la MOT puisque leur composition varie selon le type de plante (angiosperme vs gymnosperme) et le type de tissu végétal (boisé vs non-boisé; Hedges et Mann 1979). Finalement, plusieurs indicateurs permettent d'estimer l'état de dégradation et d'humification de la MOT trouvée en milieu aquatique (Houel et al 2006, Dickens et al 2007). Toutes ces indications sont donc potentiellement importantes pour aider à la compréhension du cycle du Hg dans les milieux aquatiques de la forêt boréale.

Ainsi, des études ont utilisé les biomarqueurs ligneux pour décrire la dynamique de la MO associée au Hg (Louchouarn et Lucotte 1998, Caron et al 2008, Ouellet et al 2009). En ce qui a trait aux sédiments estuariens, on observe une corrélation positive entre les apports en MOT et les concentrations en Hg lorsque l'écosystème est perturbé par l'activité humaine. En revanche, dans les enregistrements sédimentaires pré et post-contamination, aucune relation n'est observée (figure 0.4) (Louchouarn et Lucotte 1998).

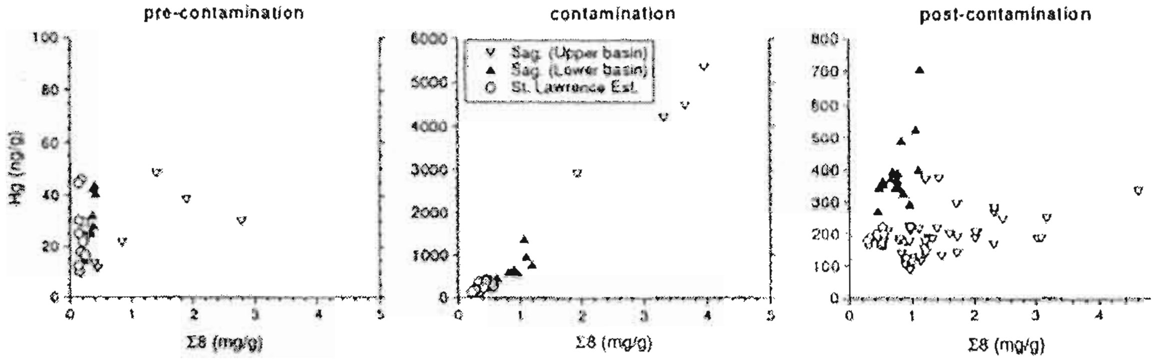

Figure 0.4 Relations entre Σ8 (indicateur de la contribution relative en lignine d'un échantillon normalisé par gramme d'échantillon) et la [Hg] dans les sédiments du fjord du Saguenay et de l'estuaire du Saint-Laurent (Louchouarn et Lucotte 1998).

Caron et al (2008) démontrent que le Hg trouvé dans la colonne d'eau du Saint-Laurent et de rivières drainant des sols agricoles est associé à une augmentation des apports en composés organiques dérivés de la lignine (figure 0.5). La MOT associée à ce Hg provient de l'érosion des horizons de surface des sols agricoles de la région (Caron et al 2008).

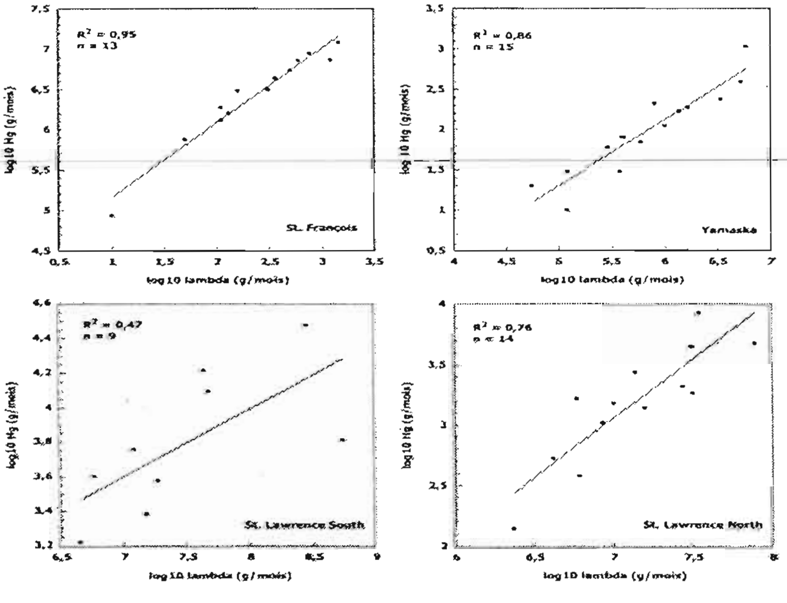

Figure 0.5 Relations entre les apports de MOT estimés par λ8 (indicateur de la contribution relative en lignine d'un échantillon) et les [Hg] dans la matière particulaire en suspension pour différents cours d'eau de la région du lac St-Pierre, Québec (Caron et al 2008).

Finalement, la dernière étude publiée démontre qu'il existe un lien entre les concentrations en Hg et les apports de MOT dans la colonne d'eau (carbone organique dissous et particulaire; Ouellet et al 2009). Au-delà des apports, la qualité et l'origine de la MO semblent également influencer les teneurs en Hg. En effet, plus la MOT est dégradée, moins les apports en Hg sont importants. Ces apports sont généralement reliés à une MOT dérivée des horizons de surface des sols boréaux (figure 0.6; Ouellet et al 2009).

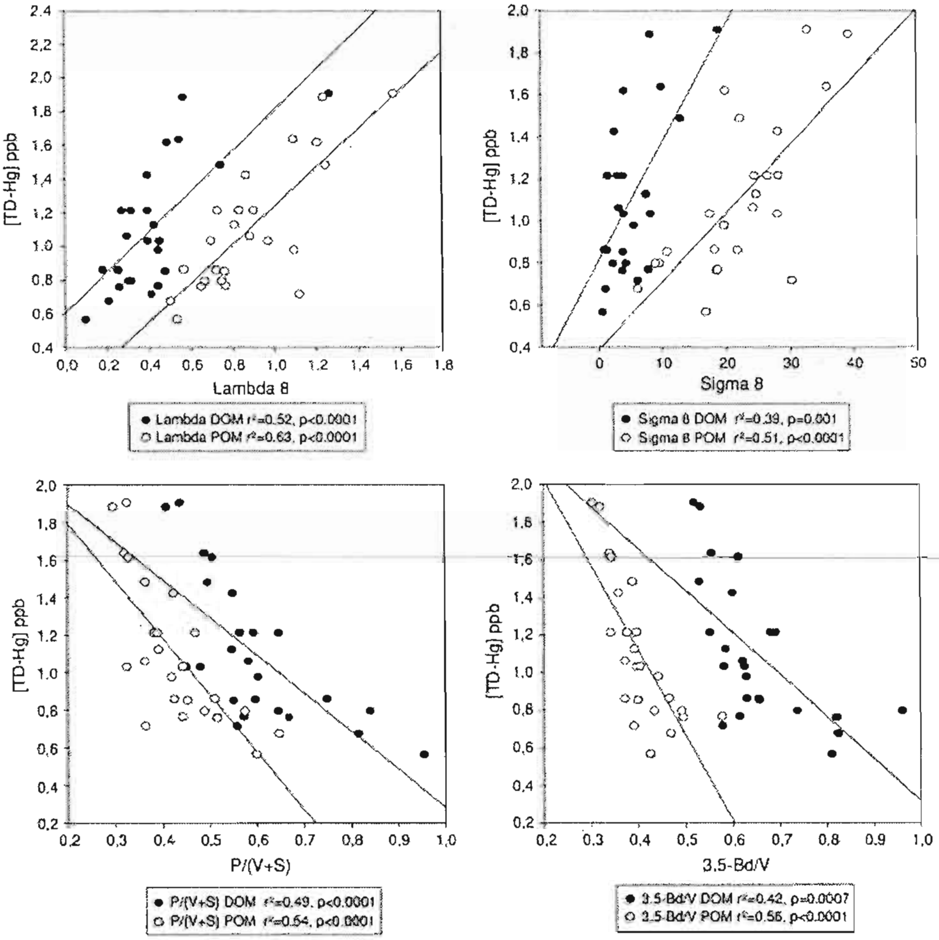

Figure 0.6 Relations entre la [Hg] et les biomarqueurs dérivés de la lignine dans les colonnes d'eau de six lacs du moyen nord du Québec (Ouellet et al 2009).

Dans cette thèse, nous avons étudié comment la nature de la MOT et sa dynamique peuvent expliquer les variations de contamination en Hg dans les écosystèmes aquatiques boréaux. Pour atteindre cet objectif, cette étude a été réalisée en quatre parties interdépendantes qui ont permis d'intégrer et d'identifier les principales composantes de l'écosystème impliquées dans la dynamique combinée de la MOT et du Hg.

Dans un premier temps, nous avons caractérisé la matière organique de sols boréaux par l'analyse des biomarqueurs dérivés de la lignine. Les biomarqueurs de la lignine ont longtemps été utilisés en faisant référence aux sources pures mesurées par Hedges et Mann (1979) dans les premiers travaux exploratoires sur le sujet. Sous l'impulsion d'une étude réalisée par Opsahl et Benner (1995), la question de l'évolution des signatures de biomarqueurs dans l'environnement a été soulevée. En effet, généralement utilisés dans les milieux aquatiques, les biomarqueurs de la lignine proviennent, comme la majeure partie de la MOT, des sols et non directement des sources pures que sont les plantes vasculaires. Les modifications de la MO dérivée des plantes vasculaires dans les sols ont été identifiées comme une problématique cruciale dans l'utilisation des biomarqueurs de la lignine dans les échantillons environnementaux (Opsahl et Benner 1995).

Les deux mécanismes principaux du fractionnement des différents composés ligneux dans les sols sont le lessivage et la sorption différentiels des différents phénols. Le lessivage entraîne une partie des composés les plus solubles vers les horizons inorganiques des sols où ils vont s'adsorber sur des particules minérales (Kaiser et Guggenberger 2000, Houel et al 2006). Ces processus ont une influence importante sur l'interprétation des valeurs de biomarqueurs de la lignine. En effet, même si les indicateurs de source mesurés dans les sols et les sédiments ont un très grand potentiel pour enregistrer et préserver l'information à long terme des sources végétales, notamment entre angiospermes et gymnospermes, les indicateurs de dégradation mesurés dans la colonne d'eau ou dans des sédiments marins peuvent être modifiés principalement par les processus de fractionnement et de sorption (Hernes et al 2007). Cependant, peu d'études se sont intéressées à développer des critères spécifiques permettant d'identifier les apports de MO des sols vers les milieux aquatiques et ainsi développer une base de données des biomarqueurs de la lignine dans les sols utilisables dans les milieux aquatiques (Houel et al 2006, Kuo et al 2008). Les sols jouent pourtant un rôle intégrateur et d'interface de la MOT depuis les végétaux supérieurs vers les milieux aquatiques (Lal 2003). Dans le cadre d'une étude des milieux sédimentaires lacustres de la forêt boréale, le premier objectif était donc de constituer une banque d'indicateurs (biomarqueurs de la lignine) qui caractérisent la matière organique des principaux types de peuplements végétaux et leurs sols associés de la forêt boréale du Nord Est de l'Amérique.

La définition de ce nouveau cadre de référence pour l'étude du devenir de la MOT dans les lacs a permis de réaliser le deuxième volet de l'étude. Celui-ci consiste à réaliser l'intégration des transferts de matière organique terrigène des bassins versants vers les lacs. Le couplage d'une approche holistique par l'analyse des systèmes d'information géographique et d'une approche réductionniste par l'analyse sédimentaire permet de réaliser cette intégration.

Ainsi, les biomarqueurs de la lignine ont été mesurés dans les sédiments récents de plusieurs lacs boréaux. Ces analyses permettent d'intégrer en un point focal les caractéristiques de la MOT entrant dans le lac. Les signatures spécifiques des phénols dérivés de la lignine sont comparées aux caractéristiques morpho-édaphiques des bassins versants (chapitre I). Ces caractéristiques sont déterminées par l'utilisation de système d'information géographique (SIG). En effet, les transferts de MOT vers un lac dépendent à la fois de facteurs biologiques, chimiques et physiques du bassin versant (Dillon et Molot 1997). Une approche par SIG permet d'obtenir rapidement des informations sur les facteurs influençant fortement l'apport de MOT vers le lac comme la superficie du lac et du bassin versant (Rasmussen et al 1989), la pente (D'arcy et Carignan 1997), la superficie de terres humides (Dillon et Molot 1997), les perturbations du bassin versant (Carignan et al 2000), ou le type de végétation (Quideau et al 2001). L'objectif est de mettre en évidence les facteurs dominants des bassins versants qui vont influencer la quantité mais surtout la qualité de la MOT dans les sédiments récents. Les résultats de cette analyse doivent permettre d'apporter des éléments nouveaux pour comprendre le cycle global du carbone dans ces environnements.

Préciser et caractériser les apports de MOT doit ainsi aider à mieux appréhender la question du devenir des contaminants associés (e.g. métaux traces) dans ces écosystèmes (chapitre III). Cela permet également d'apporter des éléments nouveaux sur la question de l'autotrophie et de l'hétérotrophie des lacs boréaux (Rasmussen et al 1989, Cole et al 1994, Algesten et al 2004, Kainz et Lucotte 2006).

Dans le troisième volet de cette étude écosystémique, nous avons donc utilisé le potentiel intégrateur des biomarqueurs de la matière organique terrigène pour déterminer les principales sources terrigènes de mercure dans les sédiments récents des lacs de la forêt boréale.

Les apports de Hg dans les écosystèmes boréaux et particulièrement les lacs ont augmenté de manière significative depuis le début de l'ère industrielle (Lucotte et al 1995, Jackson 1997). Ce Hg anthropique vient s'ajouter au Hg naturellement présent dans ces écosystèmes et va s'accumuler dans les sédiments de lacs. Cette accumulation a été mesurée lors de nombreuses études (Lucotte et al 1995, Rognerud et Fjeld 2001) qui démontrent également une grande variation des taux de contamination. Dans ce chapitre, nous proposons ~~donc d'utiliser l'information~~ obtenue sur la MOT par l'utilisation des biomarqueurs dérivés de la lignine pour comprendre ces variations des teneurs en Hg. Notre objectif est de comparer le type de MO (source et qualité) associée aux différentes teneurs en Hg dans les sédiments lacustres récents prélevés dans la zone pélagique du lac (zone focale). Cette analyse au niveau sédimentaire permet une intégration spatiale et temporelle de la dynamique de la MOT et du Hg (Håkanson et Jansson 1983). Grâce aux caractéristiques des biomarqueurs de la lignine qui donnent des informations sur la source de la MO (angiospermes vs gymnospermes et boisé vs non-boisé), la contribution des peuplements végétaux du bassin versant aux apports de Hg pourra également être intégrée (chapitre II). L'état de dégradation de la MOT devrait également apporter une nouvelle perspective dans la description des apports de Hg des sols vers les lacs.

Finalement, cette analyse du lien entre la MOT et le Hg peut contribuer au développement d'un outil environnemental qui pourrait être utilisé pour comprendre la dynamique du Hg dans des environnement perturbés mais également celle d'autres contaminants (e.g ; métaux traces) associés à la MO.

Dans la dernière partie de cette étude nous proposons ainsi d'étudier la dynamique de la matière organique des sols et du mercure associé suite à la mise en eau du complexe hydroélectrique de Churchill Falls au Labrador. En effet, La création de réservoirs hydroélectriques implique l'inondation de grandes superficies d'écosystèmes terrestres et aquatique, provoquant des changements environnementaux importants. Un de ces changements le plus étudié est la modification du cycle du Hg (Louchouarn et al 1993, Kelly et al 1997, St Louis et al 2000, Hall et al 2005). En effet, les hauts niveaux de Hg et de MeHg dans les réservoirs sont considérés comme un des impacts environnementaux majeurs associés à leur création, notamment pour les populations locales dont la subsistance dépend en partie des ressources halieutiques (Lucotte et al 1999). Dans les réservoirs, le Hg présent dans les sols inondés représente une source potentielle de contamination non-négligeable. Ainsi de nombreuses études ont attribué les niveaux en Hg observés dans les réservoirs au transfert du Hg depuis les sols inondés jusqu'à la colonne d'eau et les sédiments (Grondin et al 1995, Thérien et Morrison 1999)

Dans le cadre de ce projet, nous avons donc décidé de comparer l'origine du Hg et de la MO retrouvés dans les sédiments de deux lacs inondés faisant partie intégrante du réservoir et d'un lac non perturbé. Les deux lacs inondés sont inclus dans le complexe hydroélectrique de Churchill Falls au Labrador, qui a été créé en 1974. Le lac non-perturbé est situé à proximité et en amont du complexe. À partir des résultats obtenus au chapitre III sur le lien existant entre la MOT et le Hg, les biomarqueurs de la lignine ont été utilisés pour déterminer la source et la composition de la MO sédimentaire avant et après inondation. Cette analyse doit permettre d'obtenir un enregistrement précis des changements de concentration en Hg et de la dynamique de la MO à la suite de l'inondation d'un écosystème boréal.

Contribution

Les quatre articles présentés dans cette thèse sont tous des travaux originaux. J'ai mené ce projet depuis sa conception jusqu'à la rédaction de la thèse. Durant les quatre années de mon doctorat, j'ai donc participé à l'échantillonnage, réalisé la majeure partie des analyses en laboratoire, traité les données générées et j'ai finalement interprété l'ensemble des résultats obtenus. Toutefois, mon travail a évidemment bénéficié des apports de plusieurs membres de l'équipe de mon directeur de recherche, Marc Lucotte, dont les noms apparaissent comme co-auteurs dans chacun des chapitres de cette thèse.

Chapitre I :

Characterization of boreal soil organic matter through lignin biomarkers analysis

Roman Teisserenc, Stéphane Houel, Marc Lucotte, Caroline Dufour

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1.1 Résumé

Les biomarqueurs de la lignine obtenus par oxydation à l'oxyde de cuivre sont souvent utilisés pour décrire les sources et l'état de dégradation de la matière organique terrestre (MOT). Par l'analyse de ces produits d'oxydation, nous avons caractérisé la matière organique des sols de quatre peuplements végétaux différents (pessière, érablière, betulaies blanche et jaune) et de tourbières du moyen nord québécois. D'après les rapports C/V (Cinnamyles/Vanillyles) et S/V (Syringyles/Vanillyles), la pédogenèse réduit la variation des signatures des végétaux de référence de ces biomarqueurs. La matière organique des sols des trois grands écosystèmes terrestres du paysage boréal (tourbières et les peuplements dominés par les gymnospermes ou par les angiospermes) est caractérisée par des signatures de biomarqueurs distinctes. Les rapports P/(V+S) (P : Para-hydroxy phénols) augmentent significativement vers les horizons profonds de sols quel que soit le type de sol. Ce résultat confirme leur utilisation comme indicateur du degré de dégradation de la MOT. Indépendamment du type de couvert végétal, les rapports 3,5Bd/V (3,5Bd : acide 3,5-dihydroxybenzoique) augmentent significativement des horizons organiques vers les horizons minéraux, ce qui confirme leur utilisation potentielle comme indicateur de l'humification de la matière organique des sols. Les résultats de cette étude suggèrent que les rapports 3,5Bd/V peuvent être utilisés comme indicateurs intégrés du transfert de la matière organique des sols vers les milieux aquatiques.

Mot clés : Matière organique des sols, Biomarqueurs de la lignine, Forêt boréale, Oxydation CuO

1.2 Abstract

Lignin phenols obtained after a cupric oxidation extraction are commonly used to describe both the sources and the degradation state of terrestrial organic matter. Through an analysis of lignin oxidation products, we characterized soil organic matter (SOM) from four different forest stands (spruce, maple, yellow and white birch dominated stands) and peatlands from mid-northern Quebec. According to C/V (Cinnamyls to Vanillyls) and S/V (Syringyls to Vanillyls) ratios, pedogenesis occurring in soils reduced the range of reference plant signatures for these biomarkers. SOM of three dominant ecosystems of the boreal landscape (i.e. peatlands, gymnosperm and angiosperm stands) were characterized by distinct lignin signatures. P/(V+S) (P: para-hydroxyphenols) ratios increase significantly with soil depth in all soil types sampled in this study, confirming their use as indicators of the degree of organic matter degradation. Regardless of the vegetation cover, 3,5Bd/V (3,5Bd: 3,5-dihydroxybenzoic acid) ratios increase significantly from organic to mineral soil horizons, which supports their use as biomarkers of SOM degradation. The results of this study suggest that 3,5Bd/V ratios may be used as integrated tracers of transfers of organic matter between soil horizons and aquatic ecosystems.

Keywords: Soil organic matter, Biomarkers, Lignin phenols, Boreal forest, CuO oxidation

1.3 Introduction

The fate of terrestrial organic matter (TOM) in aquatic ecosystems is currently a crucial research aspect of the terrestrial carbon cycle. For decades researchers have used a large spectrum of methods to qualify and quantify carbon transfers between the two ecosystems (carbon to nitrogen atomic ratios (C/N), nitrogen and carbon stable isotopes, lipids, pollens, pigments and lignin phenols);(Cifuentes 1991, Meyers and Ishiwatari 1993, Meyers 1997, Hedges et al 1997, Meyers and Lallier-Vergès 1999, Goñi et al 2005). Hedges and Mann (1979) described lignin compounds and associated phenolic substances derived from vascular plants as unambiguous markers of plant classes and tissue types. Lignin phenols extracted after CuO oxidation are commonly used to describe both the sources and the state of degradation of TOM in surrounding environments and have been used in many environments since the initial work of John Hedges (Meyers 1997 and references therein). The most common markers use the combination of three major compound families: cinnamyls (C), syringyls (S) and vanillyls (V). C/V ratios are used to distinguish between woody and non-woody part of plants, and S/V ratios are used to distinguish between angiosperm and gymnosperm plants. These ratios are variable both among different plant tissues (e.g. bark vs. wood) and the lifetime of the plants (e.g. fresh vs. senescent);(Goñi and Hedges 1992, Opsahl and Benner 1995). Further changes in these ratios are caused by bacterial, fungal, physical and chemical degradation processes of vascular plant debris occurring in soil litter and deeper soil horizons (Ertel and Hedges 1985, Hedges et al 1986, Cifuentes 1991, Hedges 1992).

Once plant lignin is altered and degraded in soils, further degradation in aquatic sediments is usually quite limited (Opsahl and Benner 1995). Consequently, soil alkaline CuO product signatures should represent better proxies than pure plant material for characterizing the composition of TOM (Opsahl and Benner 1995, Miltner and Emeis 2000, Houel et al 2006). In that sense, Opsahl and Benner (1995) proposed that appropriate ligneous end-members for aquatic sediments should be

SOM rather than pure plant tissues. Some recent studies have also tried to link watershed characteristics (vegetation, land use) with lignin signatures found in particulate organic matter and sediments of nearby aquatic ecosystems (Onstad et al 2000, Dalzell et al 2005). They demonstrated that the organic matter signatures in these aquatic environments are within the range of lignin soils signatures rather than those of pure plants.

Beyond the classical C, V and S families obtained by CuO oxidation, *p*-hydroxyphenols (P) and 3,5-dihydroxybenzoic acid (3,5Bd) were mentioned as compounds of interest, particularly in soils studies (Houel et al 2006 and references therein). P/(V+S) ratios are used as indicators of the degree of degradation of terrigenous organic matter (Dittmar and Lara 2001). 3,5Bd/V ratios are used to trace organic matter degradation and consequently to distinguish SOM in organic vs. mineral horizons (Houel et al 2006). Furthermore, using these two ratios, Houel et al (2006) showed that SOM signatures in mineral horizons could be used as model end-members for dissolved TOM encountered in aquatic systems.

In this paper, we reassess the power of lignin-derived phenols to characterize soil organic matter (SOM) of the boreal ecozone. We further propose a revised set of molecular signatures of typical boreal soils and peatlands rather than that of pure plant end-members using the CuO extraction method. Within the broader scope of terrigenous organic matter being transferred to aquatic systems in the boreal ecozone, we propose to establish a synthetic database of the lignin derived phenols found in SOM from mid-northern Quebec, both in the organic and mineral horizons and under different plant species covers. This revised database of molecular compounds will be most useful in biogeochemical studies using CuO oxidation products as tools for paleoreconstruction (sediments, speleothemes), limnological (dissolved organic carbon, particulate organic carbon) and environmental studies. We present results both for classical lignin S/V and C/V ratios and ratios that seem particularly relevant for TOM studies such as P/(V+S) and 3,5Bd/V ratios (Houel et al 2006).

1.4 Materials and Methods

1.4.1 Site description

We sampled 28 cores of soil and peat across the boreal forest domain of Québec (from 46°N to 48.5°N) including deciduous, mixed and coniferous stands (figure 1.1). We distinguished five soil categories representing the most common vegetation covers in mid-northern Quebec (Richard 1987). Four different soil categories were identified by the name of the dominant tree species of the stand: spruce, maple, yellow birch and white birch. The fifth category included the peatlands. We selected our soil samples based on the dominant vegetation species coverage rather than on the geographic or pedological characteristics as lignin biomarkers studies always refer to plant classes (Miltner and Emeis 2000). The sampling sites were chosen with 1/20000 ecoforestry map in well-established forest stands (figure 1.1).

The cores representing the spruce stands were collected in the James Bay region nearby the La Grande hydroelectric complex (5 cores) and in the Abitibi region (2 cores). Spruce stands are covering the main part of Northern Quebec. In the James Bay region, the spruce forest is dominated by black spruce (*Picea mariana*), associated with grey pine (*Pinus banksiana*). The floor is covered with caribou moss (*Cladina* spp.) and sphagnum (*Sphagnum* spp. and *Pleurozium* spp.). In the Abitibi region, the cores were taken in a mature spruce forest also dominated by black spruce. In the southern part of its area of distribution, black spruce is usually associated with balsam fir (*Abies balsamea*). Ericaceous species may cover up to 40 % of the ground (e.g. *Vaccinium angustifolium*, *Kalmia angustifolia*), but the major characteristic of the Abitibian forest is the presence of hypnaceae mosses (e.g. *Pleurozium schreberi*, *Ptilium crista-castrensis*) rather than caribou moss (Grondin 1996). The soil cores were sampled in soils pedologically identified as podzols (Duchaufour 1995).

Soil cores for the angiosperm stand were taken in the mature mixed wood boreal forest between 46° and 47.5° N. For the yellow birch stands, six cores were collected. These yellow birch (*Betula alleghaniensis*) stands are associated with balsam fir (*Abies balsamea*). Sugar maple (*Acer saccharum*) is also often present. The soils observed below are humo-ferric podzols with moder type of humus (Grondin 1996, Soil Classification Working Group 2002). Soils under white birch (*Betula papyrifera*) stands were also identified as humo-ferric podzols. Six cores were collected. The vegetation was primarily composed of white birch and balsam fir. The stands often include trembling aspen (*Populus tremuloides*), as well as white and black spruces. Numerous non-woody species are present on the forest floor, one of the most abundant being the blue-bead lily (*Clintonia borealis*). Four cores were used to characterize the maple stands. In maple stands the vegetation was mainly composed of sugar (*Acer saccharum*) and red maples (*Acer rubrum*). These stands are also mixed with some Eastern hemlock (*Tsuga canadensis*), balsam fir, grey birch (*Betula populifolia*) and white birch, trembling aspen and red spruce (*Picea rubens*). The non-woody plants diversity is composed of about 1500 species (Grondin 1996).
Peatlands cores were taken in the same region as the angiosperm stands. Peatlands of this region are ombrotrophic peat bogs (Payette and Rochefort 2001). Five cores were collected. Sphagnum mosses are the typical species in this habitat. As vascular plant, we observed ericaceous shrubs and dwarf black spruce.

1.4.2 Sampling and chemical analysis

Cores were sampled with a 30 cm long polyvinyl chloride hollow cylinder (15 cm in diameter). The central part of the cores was subsampled at each cm, while peat cores were sampled every 5 cm. Soil samples were kept frozen until laboratory analysis. Prior to analysis, samples were freeze-dried and ground into a fine powder. The samples were ground wholly and no sieving was done since we were interested in getting the bulk soil signatures.

Total carbon and nitrogen contents were determined with a Carlo Erba (NA-1500) elemental analyzer. Two soil horizons were distinguished according to the organic carbon (OC) content of the samples: the organic horizon (≥25% OC) and the mineral horizon (≤8% OC). For the peat cores, a surface layer (0-10 cm) and a deep layer (10-30 cm) were sampled. For the molecular biomarkers, we analyzed one to five subsamples in each organic horizon (surface layer of peatlands) and one to five subsamples in each mineral horizon (deep layer of peatlands) of each core. The number of lignin analyses by stand is presented in table 1.1

Molecular biomarker analyses were performed according to the CuO oxidation method developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). This new method replaces the combustion oven with microwave digestion and uses ethyl acetate instead of ether in the liquid-liquid extraction procedure. Briefly, sediment samples were weighed to include 2–5 mg of organic carbon in the Teflon-lined vessels of an analytical microwave oven (CEM MDS 200). Samples were digested with CuO in presparged 2 mol L 1 NaOH and in the absence of O_2 at 150 °C for 90 min. Extracted reaction products were converted to trimethylsilyl derivatives and were analyzed on a GC/MS system (Varian 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1ms 60 m, 0.32 mm). We analyzed and quantified 12 compounds in our soils samples, which are classified into 5 groups: 1) Cinnamyls (C) (coumaric acid (p-Cd) and ferulic acid (Fd)), 2) Syringyls (S) (syringin (Sl), acetosyrigone (Sn) and syringic acid (Sd)), 3) Vanillyls (V) (vanillin (Vl), acetovanillone (Vn) and vanillic acid (Vd)), 4) Para-hydroxyphenols (P) (*p*-hydroxybenzaldehyde (Pl), *p*-hydroxyacetophenone (Pn) and *p*-hydroxybenzoic acid (Pd)) and 5) 3,5-dihydroxybenzoic acid (3,5Bd).

1.4.3 Statistical analysis

Each indicator is presented in figures distinguishing between the four soils under the dominant vegetation type (spruce, yellow birch, white birch and maple) and the peatlands. We used a Kruskal-Wallis non-parametric test to look for significant differences among the biomarker distributions within the five studied soil categories. In order to identify significantly different soil types we used Noether multiple non-parametric comparison distribution tests. Non-parametric tests are performed because normality was not present for all the soil categories. Results from chemical analyses are presented for each of the five categories. The mean value is given along with the standard errors. To inidate significant differences between soils, we use letters (a,b,c) for organic horizons (or the peat surface layer) and numbers (1, 2, 3) for mineral horizons (or the peat deep layer). Scatter bars not connected by the same symbol are significantly different. Within each soil types, significant differences between organic and mineral horizons are marked with an asterisk (*).

1.5 Results

Carbon to nitrogen atomic ratios (C/N) range between 27 and 34 in the organic horizons of the angiosperm boreal forest soils (figure 1.2). In spruce stands, C/N ratios are significantly higher in the organic horizon (average 49.6±1.2) than in the corresponding horizon of angiosperm soils. The C/N ratios decrease significantly in the mineral horizon of each soil type (down to 20.8±0.8 and 24.2±2.4 for angiosperm and spruce soils, respectively) and no significant difference is observed among soils under the same dominant vegetation type. In the peatlands, there is no significant difference in C/N ratios between the surface and deep layers. However, these values are highly variable in comparison to forest soils, ranging from 40.9±7.5 to 50.5±12.8. Boreal soil S/V ratios vary with respect to vegetation stands (figure 1.3). Low S/V ratios, between 0.20±0.02, and 0.13±0.01, are found in both organic and mineral horizons of spruce soils. In angiosperms soils, S/V ratios are higher with values ranging from 0.24±0.03 to 0.45±0.11. There is no significant difference in these values between the organic and mineral horizons except in yellow birch stands, where a decrease in S/V ratios is noted. In yellow birch and maple stands, S/V ratios are high in the organic horizon and differ significantly from those of spruce soils (gymnosperms). For birch soils, we observe higher S/V ratios in the organic horizon of yellow birch (0.43±0.05) than in the organic horizon of white birch (0.27±0.06). We also observe a high variability in the S/V ratios for the mineral horizon of the angiosperm soils. Peatlands have the highest S/V ratios, with values reaching 0.73±0.18 and 0.54±0.09 in surface and deep layers, respectively.

Contrary to S/V ratios, C/V ratios in spruce soils are high both in the organic (0.42±0.05) and in the mineral horizons (0.62±0.11) (figure 1.4). Moreover, the increase between organic and mineral horizons is significant. In angiosperm stands, C/V ratios are low and range between 0.10±0.02 and 0.19±0.04. In peatlands, C/V ratios are similar in both surface and deep layers, with an average value around 0.4.

P/(V+S) ratios are low (around 0.15) in the organic horizons of all soils (figure 1.5). However, these ratios increase significantly in the mineral horizons, reaching 0.21±0.04 in maple soils and 1.50±0.26 in spruce soils. P/(V+S) ratios are significantly higher in the mineral horizons of spruce soils than in the corresponding horizon of angiosperm stands. The soils under angiosperm stands follow the same general pattern (figure 1.5), with a significant increase of P/(V+S) in mineral horizons (from 0.10 to 0.25). In peatlands, P/(V+S) ratios are high in both surface and deep layers, but these ratios decrease (from 2.07±1.31 to 1.07±0.41) and become increasingly variable in the deep layers.

Excluding peatlands, 3,5Bd/V ratios (figure 1.6) exhibit the same general trend as that observed for the P/(V+S) ratios, with a marked increase of this indicator from the organic to the mineral horizons. This tendency appears stronger for spruce soils. 3,5Bd/V ratios in angiosperm soils (figure 1.6) follow the same increasing trend in the mineral horizon (from 0.05±0.01 to 0.44±0.06). In peatlands, 3,5Bd/V ratios are low (surface: 0.15±0.04; deep: 0.16±0.03) and there is no significant difference between the surface and the deep layers.

Figure 1.7 presents the ratios of vanillic acid over vanillin (Ad/Al)V in soils. In organic horizons, no significant difference is observed among soil samples. (Ad/Al)V ratios for the spruce soils are the lowest in the organic horizons (0.59±0.04). In the organic horizons or surface layers, white birch and maple soils as well as peatlands have similar average ratios, ranging between 0.90 and 1.02. In the yellow birch soils, (Ad/Al)V ratios are higher in the organic (1.40±0.46) and the mineral (3.73±0.78) horizons than in the equivalent horizons of the other four soils, and there is a significant increase between these two horizons. (Ad/Al)V ratios increase significantly between the organic and the mineral horizons in spruce soils. There is no significant variation between horizons in maple and white birch soils as well as between surface and deep layers in peatlands.

1.6 Discussion

1.6.1 C/N ratios

We report here atomic C/N ratios in boreal forest soils that vary between 20 and 50, depending on soil horizons (figure 1.2). These values are commonly found in boreal forest soils and more particularly in podzols (Duchaufour 1995, Aitkenhead and McDowell 2000, Brady and Weil 2002). Our results indicate a significant decrease in C/N ratios from organic to mineral horizons, which may be linked to the mineralization of organic matter with respect to the microbial immobilization of nitrogenous compounds in soils (Sollins et al 1984, Meyers and Ishiwatari 1993). In the organic horizons, we observe higher C/N ratios in spruce soils than in angiosperm soils. This finding is in accordance with previous studies by Finzi et al (1998), who found a dominant tree species effect on nitrogen mineralization in forest soils. Such an effect may account for the significant differences in C/N ratios between soils under gymnosperm and angiosperm stands found both in this study and elsewhere (Côté et al 2000, Smolander et al 2005). In gymnosperm stands, N mineralization is reported to be limited due to soil acidity, allelopathic agents (tannins, flavonoids, phenols, terpenes);(Finzi et al 1998, Paavolainen et al 1998) and by environmental conditions (temperature, soil moisture);(Brady and Weil 2002). Comparable values of C/N ratios (ranging from 19.6 to 76.3) in spruce soils have been observed in Maine (USA) by Dai et al (1996).

In peatlands, C/N ratios are high and relatively constant across layers (figure 1.2). These ratios fall within the range of those measured for peatlands and swamp forests by Aitkenhead and McDowell (2000). In peatlands, C/N ratios are stable due to the fact that they are kept in subaqueous anaerobic conditions thereby limiting oxidative mineralization (Meyers 1997). In addition, acidic conditions found in peatlands limit N mineralization (Finzi et al 1998, Charman 2002).

1.6.2 S/V and C/V ratios

S/V and C/V ratios have been broadly used to both distinguish between angiosperm and gymnosperm plants and to trace woody and non-woody species or part of plants. Studies commonly compare biomarker analyses in waters or sediments with pure source end-members. However, biomarker signatures derived from pure sources (leaves, wood) are highly variable and can cover a wide range of values. In figure 1.8a, we compiled pure plant signatures (means with their 95% confidence intervals) from a series of studies on fresh plant samples from temperate North American ecosystems (Hedges and Parker 1976, Hedges and Mann 1979, Ertel and Hedges 1985, Wilson et al 1985, Hedges and Weliky 1989, Goñi and Hedges 1992). This compilation includes eleven species of angiosperm tissues and ten species of gymnosperm tissues. Angiosperm tissues (woody and non-woody) can be differentiated from gymnosperm tissues by their higher S/V ratios (0.6 - 3.5). Non-woody and woody parts of gymnosperms and angiosperms are distinguishable by their C/V ratios, which range between 0 and 0.07 for woody tissues and between 0.2 to 0.83 for non-woody tissues (figure 1.8a). The high variability of the biomarker signatures of pure sources compiled here may stems in part from the number of plant species considered in this figure and may hence also represent the diversity of plant species and their biomarker signatures found in terrestrial ecosystems. The use of these biomarkers in aquatic or sedimentary systems then necessarily represents a composite of the various signatures. Aside from the dominant tree species cover, a typical watershed of an Eastern Canada boreal forest will support from 8 to 23 different tree species and hundreds of non-woody plant species (Grondin 1996). Using soil as a first integrator of this diversity may therefore constitute a better tool for the historical reconstruction of the terrigenous inputs to aquatic systems (chapter II).

Maximum C/V ratios in pure plants and SOM reach 0.83 (figure 1.8 a and b). S/V ratio values range from 0 to 3.45 in pure plants compared to 0.1 to 0.45 (0.78 considering peatlands) in SOM (figure 1.8 a and b). Hence in soils we observe a narrower range. C/V and S/V ratios appear to be better integrators of all local TOM sources and their fate in soils. They represent the combined contribution of all above ground plants, and the distinction between woody, non-woody, angiosperms and gymnosperms is less striking than in pure plant signatures. Because soil values are different, it should be used to interpret aquatic and sedimentary systems. Identification of SOM biomarkers rather than solely those of pure plants should lead to better interpretations of the meaning of C/V and S/V ratios in these systems.

The combination of S/V and C/V ratios in peatlands gives a specific range of signatures different from that of the soils (figure 1.8b). This new information should be taken into account in lignin biomarker studies in freshwater ecosystems where high C/V and S/V ratios have often been attributed to non-woody angiosperm sources (Hedges and Mann 1979, Meyers and Ishiwatari 1993).

The S/V ratios that we measured are very low in spruce soils, wherever the locations the samples were taken (500 km between Abitibi and James Bay sampling sites) (figure 1.3), which is in accordance with the fact that spruce tissues, and more generally gymnosperm tissues, do not produce any syringyls (Hedges and Parker 1976, Hedges and Mann 1979, Goñi and Hedges 1992). In soils, S/V ratios greater than zero show a presence of angiosperm organic matter (Opsahl and Benner 1995), which is confirmed by the abundance of ericaceae in the undergrowth of spruce forest

(Grondin 1996). S/V ratios are higher in the three other soil types (figure 1.3). However, S/V ratios for white birch soils did not differ significantly from those of spruce soils, and their values are low when compared to pure angiosperms values found in the literature (S/V in wood: 2.6±0.8 in leaf: 1.2±0.6) (Hedges and Parker 1976, Hedges and Mann 1979, Ertel and Hedges 1985, Wilson et al 1985, Goñi and Hedges 1992). The relatively low values of S/V ratios could be explained by the association between white birch (*B. papyrifera*) and balsam fir (*A. balsamea*) in the boreal forest ecosystem (Grondin 1996). As balsam fir does not produce any syringyls, its presence increases the total vanillyls relative concentrations and thus lead to lower S/V ratios. The values of S/V ratios for the organic horizons of maple and yellow birch soils are significantly higher than those for spruce soils (figure 1.3). This is explained by the dominance of an angiosperm cover in these environments (Grondin 1996). Similarities between these two types of soils show that S/V ratios in soils, just as for pure angiosperms signatures, cannot be used to distinguish different stands of angiosperms. This is reinforced by the fact that maples and birches are often associated in the Laurentian boreal forest (Grondin 1996).

A significant decrease in S/V ratios in yellow birch soils is observed between organic and mineral horizons. This is probably due to a decrease in the identification of syringyls compounds with depth. This observation is consistent with other studies showing a higher degradation of syringyls than vanillyls in soils (Kögel 1986, Opsahl and Benner 1995, Amelung et al 1999, Houel et al 2006). In a controlled laboratory study, Hedges et al (1988) showed that white-rot fungal degradation of birch wood tends to decrease the yield of total syringyls phenols much faster than total vanillyl phenols. This decrease in S/V ratios may range from 20 to 50 %. This result is often linked to higher (Ad/Al/)V ratios, which is caused by the oxidative degradation of lignin side chains by white rot fungi (Hedges et al 1988). We observe such an increase in the (Ad/Al/)V ratios of the mineral horizon of yellow birch soils (figure 1.7), but not in the other angiosperms soils. In the latter case, a lower activity of white rot fungi in maple and white birch soils may explain why no significant differences in

S/V signatures are found between horizons. In spruce soils, S/V ratios decrease between horizons but not significantly. This observation may be linked to the fact that brown rot fungi are the main agent for wood decay in coniferous forests (Rayner and Boddy 1988, Filley et al 2002) and that they do not influence S/V ratios in soils (Hedges et al 1988). In peatlands, S/V ratios are higher than in all other soils. This is probably indicative of the presence of Ericaceae (S/V = 3.3±0.4) (Houel 2003), which is the most common family of higher plants in peatlands of northern Quebec.

C/V ratios are commonly used as pure plant source indicators, because non-woody plants and leaves produce much more cinnamyl compounds (ferulic acid and *p*-coumaric acid) than the woody part of plants (Hedges and Mann 1979). C/V ratios are significantly higher in spruce soils (in both organic and mineral horizons) (figure 1.4) and peatlands than in maple, yellow and white birch soils. This result appears to be in contradiction with published values of C/V ratios, which showed higher mean C/V ratios in non-woody tissues of angiosperms than in the same tissues of gymnosperms (figure 1.8a) (Hedges and Parker 1976, Hedges and Mann 1979, Wilson et al 1985, Hedges and Weliky 1989, Goñi and Hedges 1992). According to our data, C/V ratios in soils seem to vary much more between angiosperms and gymnosperms than between the woody or non-woody cover of the soils. This result is corroborated by the fact that we found higher C/V ratios in spruce soils than in any angiosperm soils. These findings are consistent with previous research where spruce and pine humus horizons showed higher concentrations of *p*-coumaric and ferulic acids than the birch organic horizon (Suominen et al 2003, Smolander et al 2005). Furthermore, angiosperm sub cover (maple, birch) in the boreal region includes a greater abundance of non-woody species than spruce sub cover where lower densities of non-woody plants are observed (Grondin 1996). C/V ratios in soils thus appear to follow a trend that seems more related to pedogenesis than to the dominant plant covers.

Spruce tree barks contain high levels of ferulic acids (Goñi and Hedges 1992), which may contribute to the observed elevated concentrations of cinnamyl compounds in spruce soils. These compounds may also be incorporated into spruce soils by root exudates as allopathic agent (Rice 1984, Munzenberger et al 1990). It seems that *p*-coumaric acid is a particularly important allopathic agent released by roots (Blum 2004). Although ligneous compounds concentrations in roots may reach twice those of shoots (Rasse et al 2005), the biomarker signature between those two plant compartments appear to remain identical, particularly for C/V ratios (Nierop and Filley 2007). From organic to mineral horizons, ferulic acid concentrations decrease rapidly due to the degradation of spruce lignin through the demethylation of methoxy groups attached to the aromatic rings (Vane 2003). Total cinnamyl levels stay high, because *p*-coumaric acid (p-Cd), which has no methoxy group and is therefore not influenced by demethylation, is more abundant in mineral than in organic horizons. A decrease in total vanillyl phenols leads to increases in C/V ratios from organic to mineral horizons in spruce soils. C/V ratios in spruce soils may be used as a pedogenetic indicator where C is mainly composed of p-Cd that is not influenced by demethylation. An alternate explanation for the high relative abundance of p-Cd in the mineral horizon is the direct input of this compound by roots.

In peatlands, C/V ratios are similar to those found in organic horizons of spruce stands. This similarity can be explained by the dominance of ericaceae and gymnosperm higher plant species in northern boreal peatlands. C/V ratios are conserved regardless of the depth, reinforcing the idea that lignin ratios stay stable in subaqueous conditions and that further degradation is limited (Opsahl and Benner 1995).

1.6.3 P/(V+S) and 3,5Bd/V ratios

The P phenols obtained by CuO oxidation are composed of p-hydroxybenzaldehyde (Pl), p-hydroxyacetophenone (Pn) and p-hydroxybenzoic acid (Pd). P/(V+S) ratios are used as indicators of the state of degradation of terrigenous organic matter (Dittmar and Lara 2001). In fact, demethylation leads to a selective loss of methoxylated phenol groups of vanillyl and syringyl phenols. *p*-hydroxy phenols are not affected by demethylation and P/(V+S) ratios thus increase with higher states of degradation (Dittmar and Lara 2001). P/(V+S) ratios increase significantly with soil depth (figure 1.5), which is an overall tendency for all soils under the dominant vegetation type sampled in this study. These results confirm that P/(V+S) ratios may constitute appropriate indicators of organic matter degradation (Dittmar and Lara 2001). This degradation trend between organic and mineral horizons appears similar for angiosperm soils. In addition, no significant difference was found among organic horizons and among mineral horizons of the four soils under the dominant vegetation type studied (figure 1.5). For spruce soils, a slight increase (0.3 to 0.49 mg/g OC) of *p*-hydroxyphenol is observed from organic to mineral horizons. This increase appears to be linked to a decrease in identifiable lignin due to the degradation of vanillyl and syringyl monomers, which leads to the higher P/(V+S) ratios found in the mineral horizons of spruce soils. These P/(V+S) ratios are higher in spruce soils than in the other soils and reflect a higher degree of organic matter degradation in spruce soils. In the top fraction of the peatland core, P/(V+S) ratios are significantly higher than in the other soil types. This observation is mostly due to higher concentrations of *p*-hydroxy compounds in peatlands ($\sum P = 2.2 \pm 0.9$ mg/g OC) rather than to a more advanced degree of degradation of identifiable lignin compounds. However, the P/(V+S) ratios that we measured are highly variable. Northern *Sphagnum* peat has been reported to produce mainly *p*-hydroxyl phenolic monomers (Rasmussen et al 1995, Williams et al 1998) with less lignin-derived vascular phenols (Williams et al 1998).

3,5Bd is a common CuO oxidation product found in natural samples from sediment and soils (Ugolini et al 1981, Prahl et al 1994, Louchouarn et al 1999, Farella et al 2001, Houel 2003) but not from fresh vascular plant tissues (Ugolini et al 1981). It is suggested that this compound is a product of soil processes and could be directly linked to lignin degradation (Prahl et al 1994). In terrestrial and freshwater ecosystems, 3,5Bd has been proposed as an indicator of SOM origin (Prahl et al

1994). The likely precursors of this phenolic product are tannins and other flavonoids with hydroxy groups present in alternate positions on the aromatic rings (Goñi and Hedges 1995). Because tannin-like materials tend to accumulate within decaying cells (de Leeuw and Largeau 1993), the relative increase of this compound in the mineral horizons of soils may be related to the extent of degradation and humification of fresh vascular plant tissues (Houel et al 2006). 3,5Bd is produced by humification of organic matter in soils and its concentration should therefore increase from fresh organic horizons to more degraded mineral horizons. 3,5Bd/V ratios are used to trace mature SOM (Louchouarn et al 1999). Furthermore, in the absence of brown macroalgae (Goñi and Hedges 1995), this ratio could be used as an indicator of the quality of terrestrial organic matter in aquatic environments and sediments. Our results confirm the link between 3,5Bd/V ratios and lignin degradation within soil profiles. In addition, we found that this ratio increases significantly from organic to mineral horizons of soils regardless of the vegetation cover (figure 1.6), which supports its use as a biomarker of SOM pedogenesis. This transformation follows a gradient in soils and higher values of 3,5Bd/V ratios are always found in the mineral horizons of soils. This observation, coupled with the fact that further lignin degradation is limited under subaqueous conditions (Opsahl and Benner 1995), supports the use of 3,5Bd/V ratios as tracers of organic matter sources between soil horizons in freshwater ecosystems.

In the mineral horizon of gymnosperm soils, 3,5Bd/V ratios are particularly high, suggesting a significant production of the 3,5Bd compound (figure 1.6). 3,5Bd/V ratios in peatlands do not increase with depth. This seems to reinforce the fact that the production of the 3,5Bd compound is mostly due to pedogenesis, which is limited or inexistent in subaqueous conditions. 3,5Bd/V ratios in peatlands are close to the signature found in organic horizons of spruce stands soils. These observations suggest that nearby forest soils may significantly contribute to the carbon pool found in peatlands in addition to local plant debris, which do not produce any 3,5Bd compounds.

1.7 Conclusion

C/V and S/V ratios measured in SOM are significantly distinct from ratios measured in pure plants. These major changes in the range of reference signature for lignin biomarkers are attributable to pedogenesis. In soils, ligneous compounds signatures represent the combined contribution of all above ground plants. The distinction between woody *vs.* non-woody and angiosperms *vs.* gymnosperms is thus less striking than in pure plant signatures. The combination of S/V and C/V ratios in peatlands give a specific range of signatures different from that of the other soils under the dominant vegetation type. We observe that, in terms of lignin signatures, peatlands, gymnosperm and angiosperm stands represent three distinguishable components of the landscape of boreal watersheds. Along with this study, we initiated a database of SOM signatures using biomarkers derived from the cupric oxidation method (Hedges and Ertel 1982, Goñi and Montgomery 2000). This database is a much-needed tool to precisely describe the SOM mixtures present in the boreal watershed and also the TOM entering aquatic ecosystems. P/(V+S) ratios, which increase significantly with soil depth in all soil categories sampled in this study, can also describe SOM. These results confirm P/(V+S) ratios as indicators of pedogenetic degradation of SOM. 3,5Bd/V ratios increase significantly from organic to mineral horizons of soils regardless of the vegetation cover, which supports their use as biomarkers of SOM degradation. This transformation follows a gradient in soils and higher values of 3,5Bd/V ratios are always found in the mineral horizons of soils, which supports their use as tracers of organic matter sources between soil horizons in freshwater ecosystems. This study brings a new perspective in the field of characterization SOM of boreal forest and allows for distinguishing large forest biomes. The characterization of SOM is quite different from pure plant signatures and act as an integrator of above plant diversity and pedogenesis. In order to work at the landscape level, SOM biomarkers signatures appear to be better proxies to trace TOM sources and fate than pure source signature of plant species and components.

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1.10 Table and figures

Table 1.1
Cupric oxidation analysis in organic and mineral horizons of soils and surface and deep horizons of peatlands.

	Organic / Surface (n)	**Mineral / Deep (n)**
Spruce	35	34
Yellow birch	8	24
White birch	8	9
Maple	6	7
Peatlands	6	10

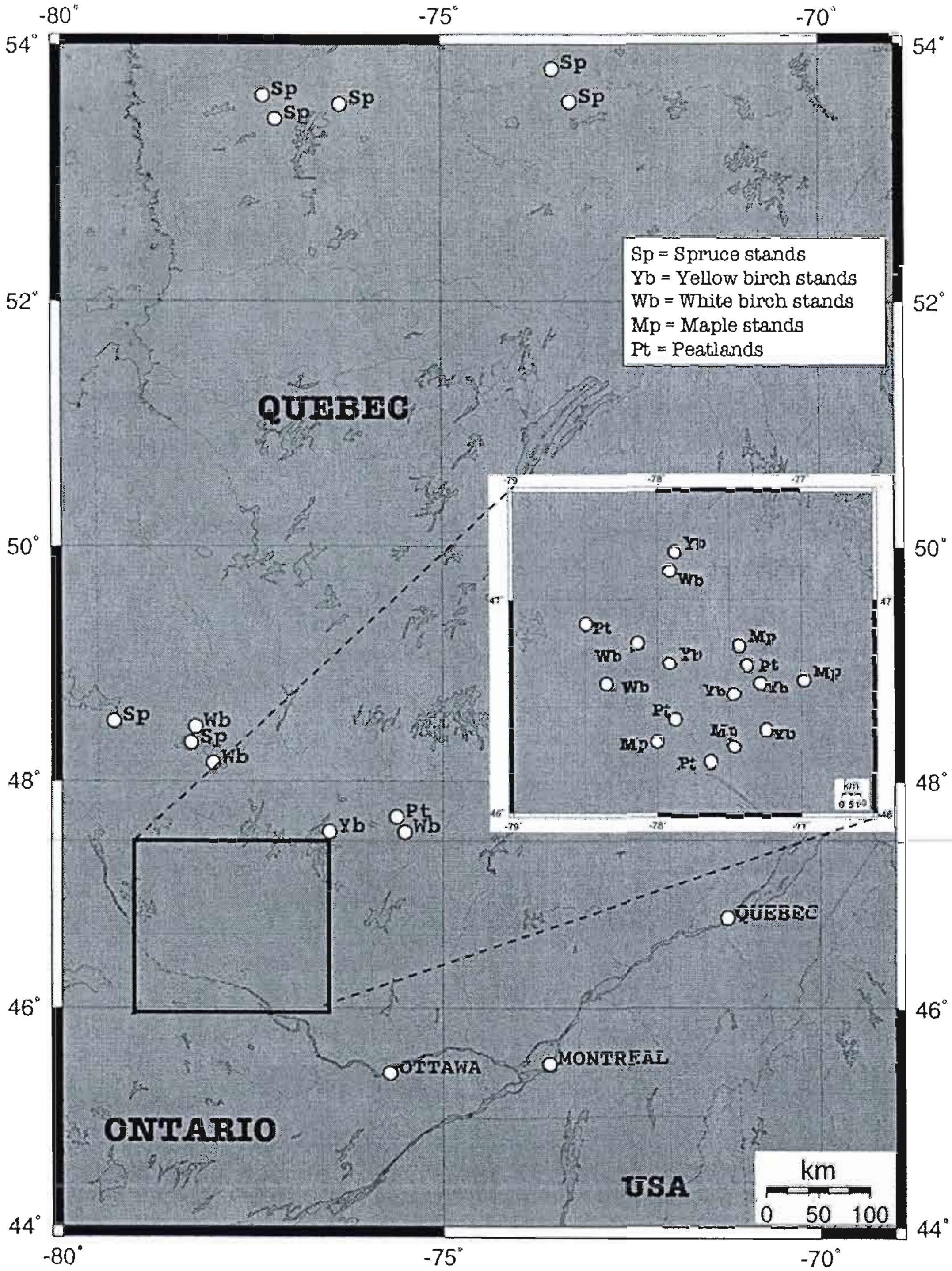

Figure 1.1 Map of Quebec (Canada) with sampling locations.

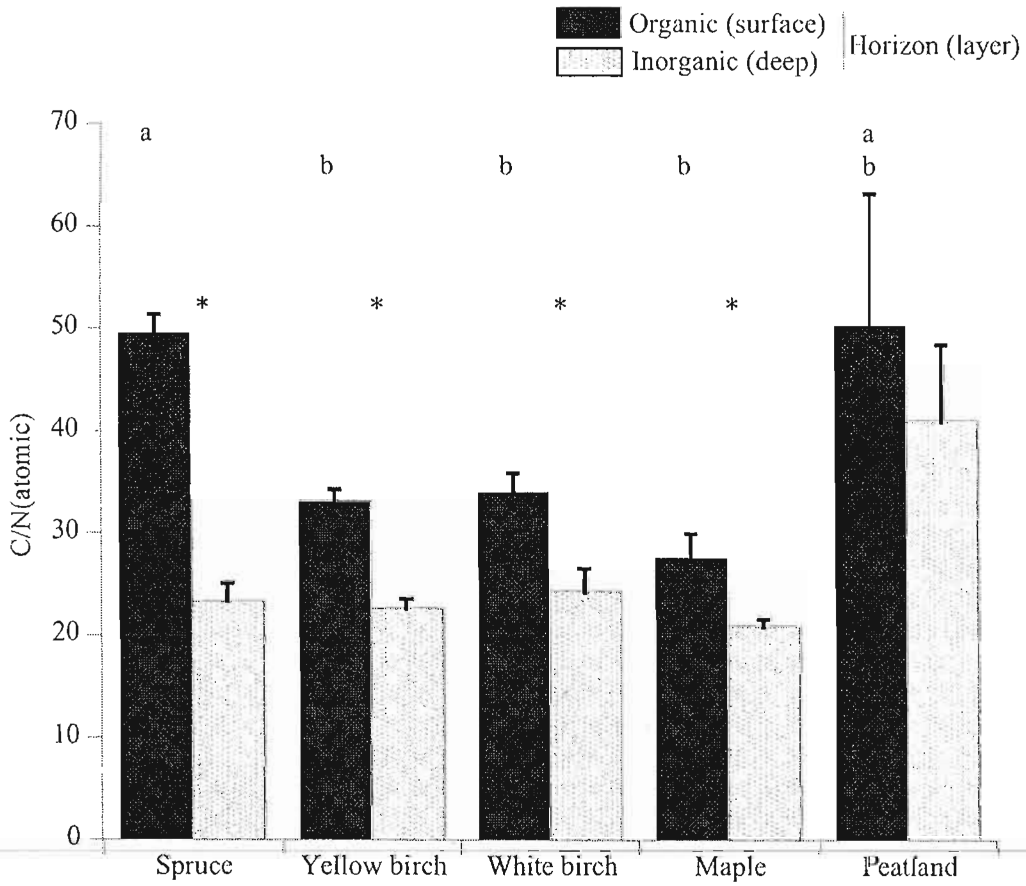

Figure 1.2 C/N ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec. (*: significant differences between horizons, scatter bar not connected by same symbol are significantly different).

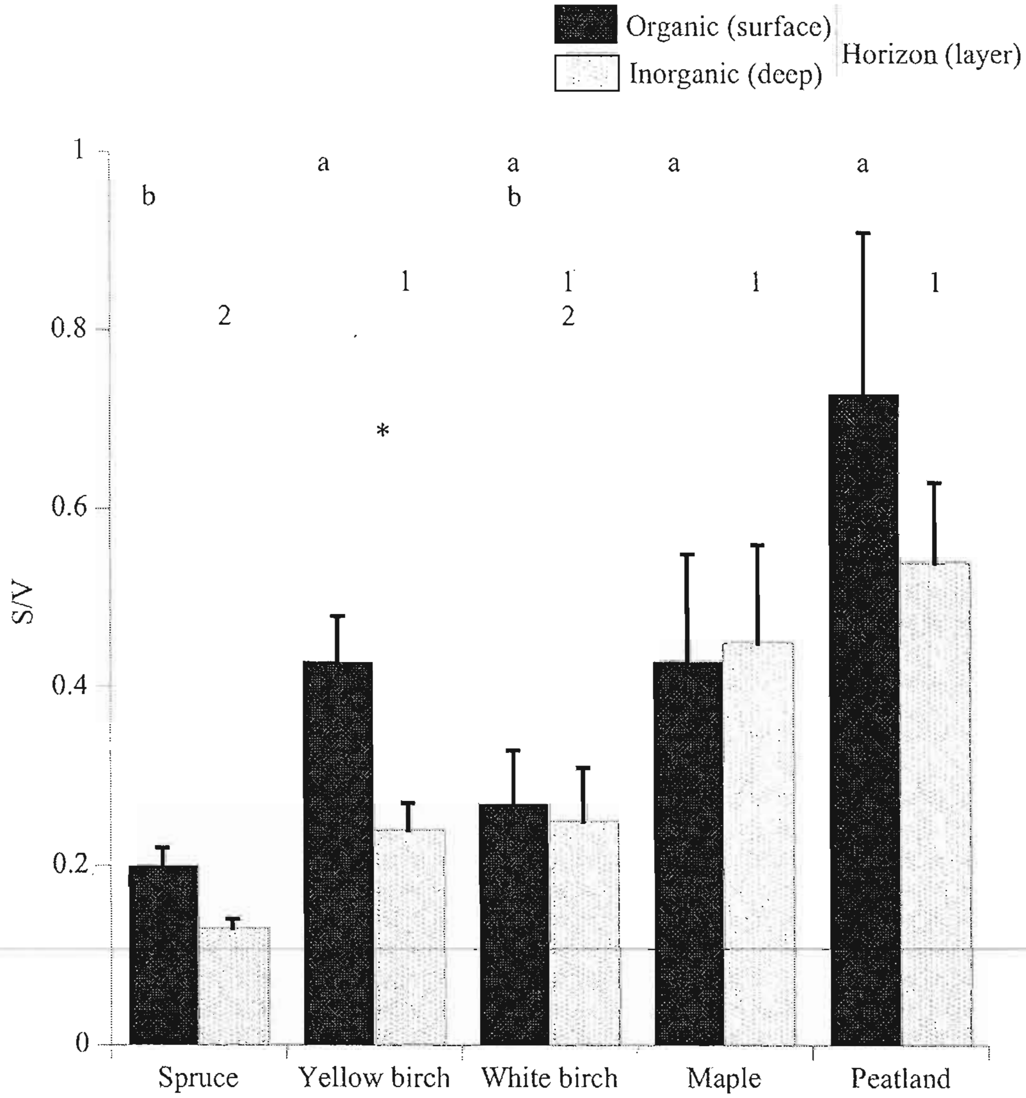

Figure 1.3 S/V ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec.

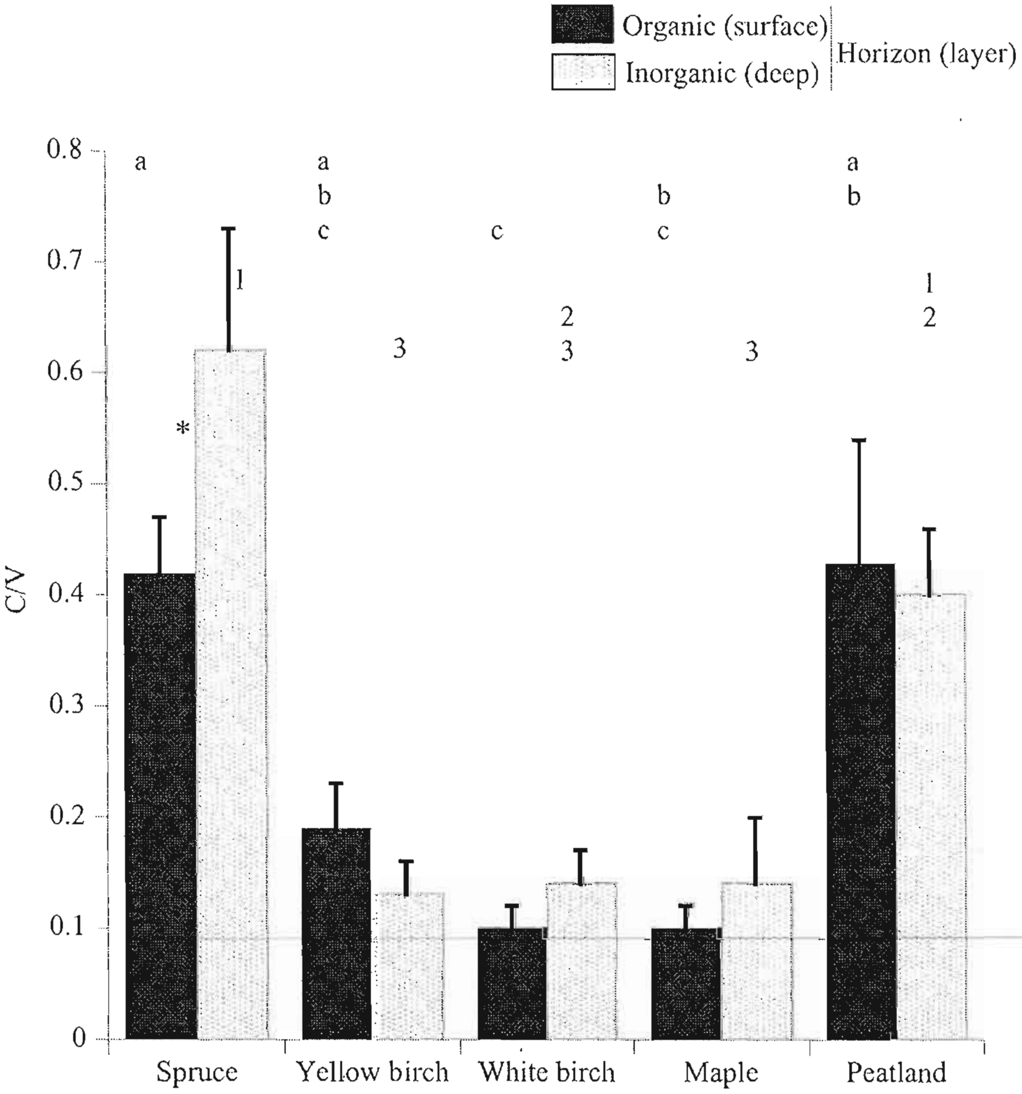

Figure 1.4 C/V ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec.

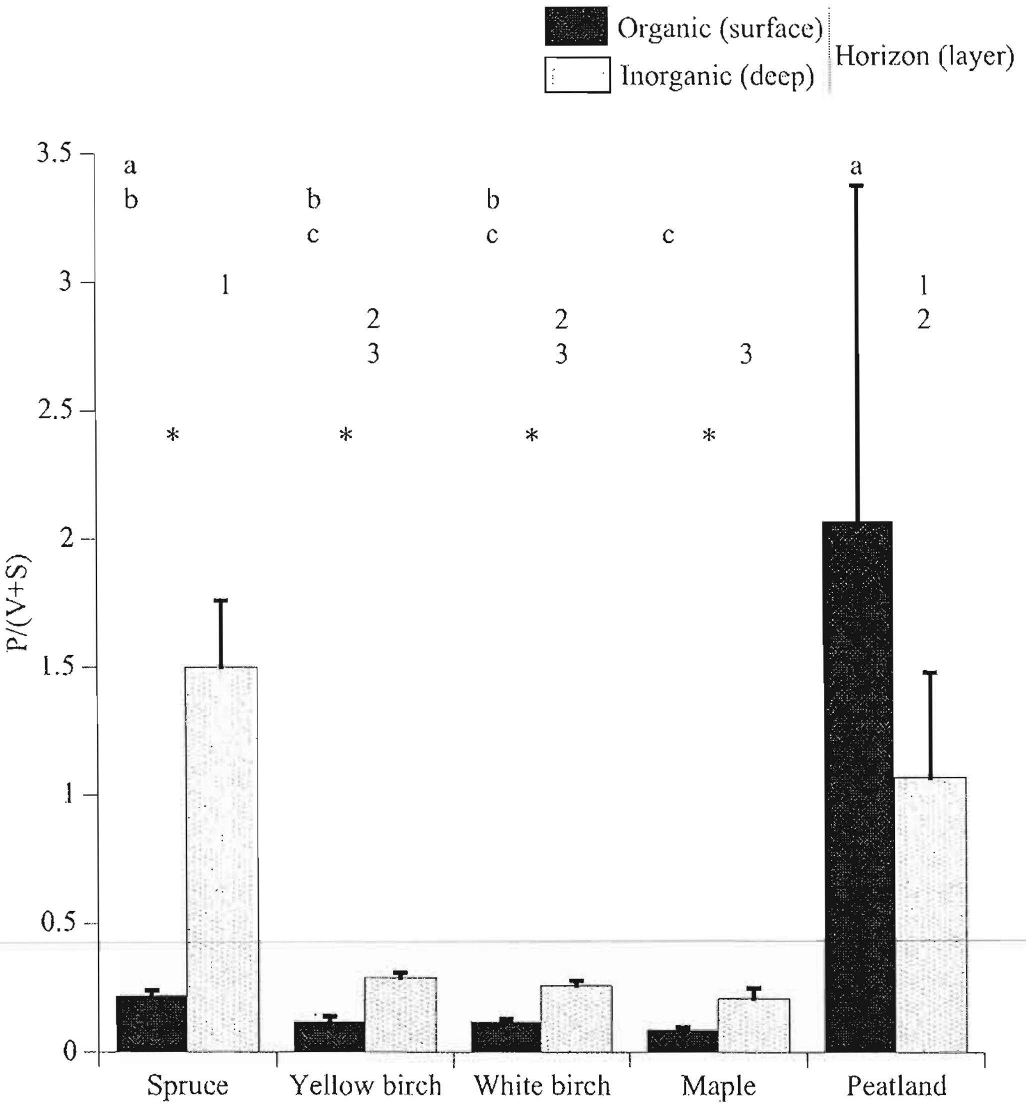

Figure 1.5 P/(V+S) ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec.

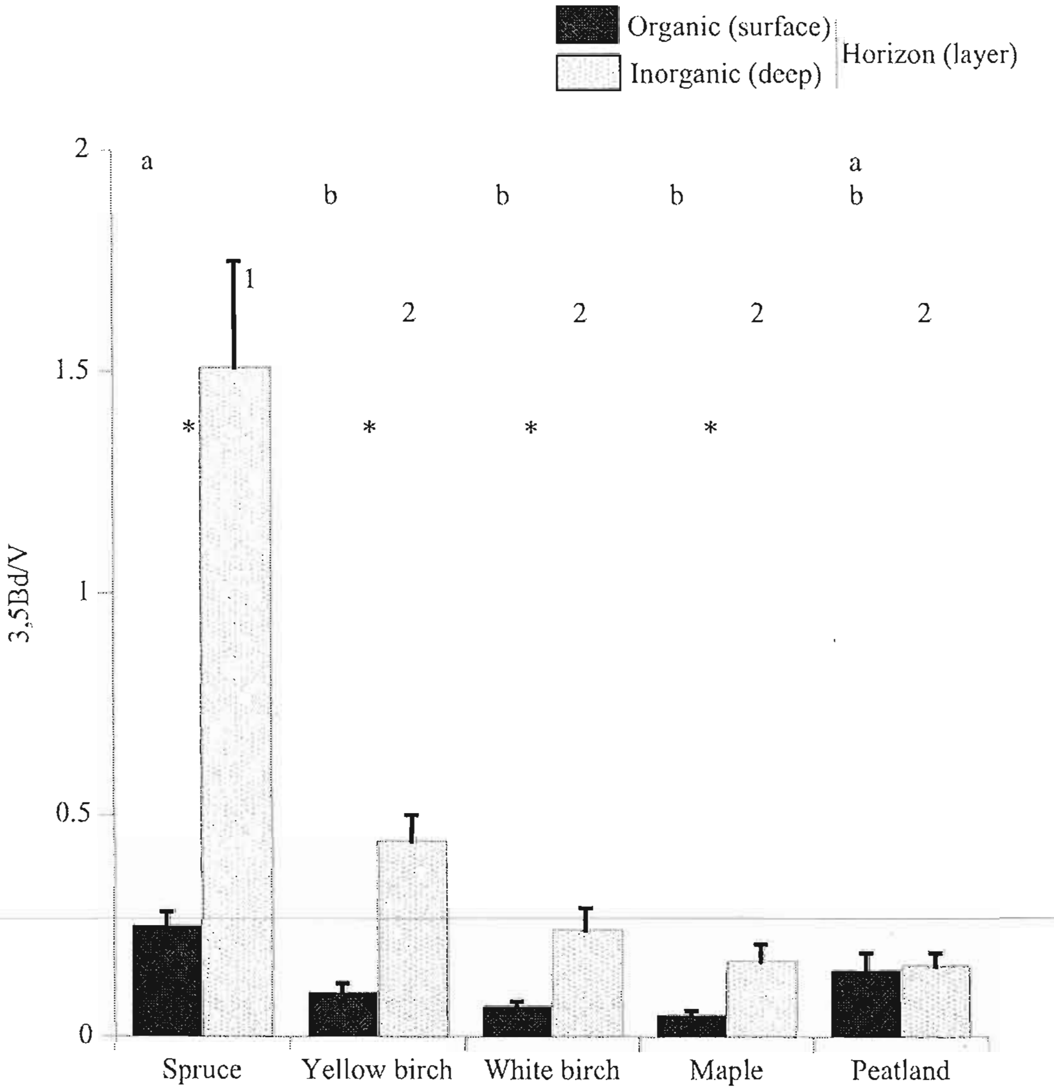

Figure 1.6 3,5Bd/V ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec.

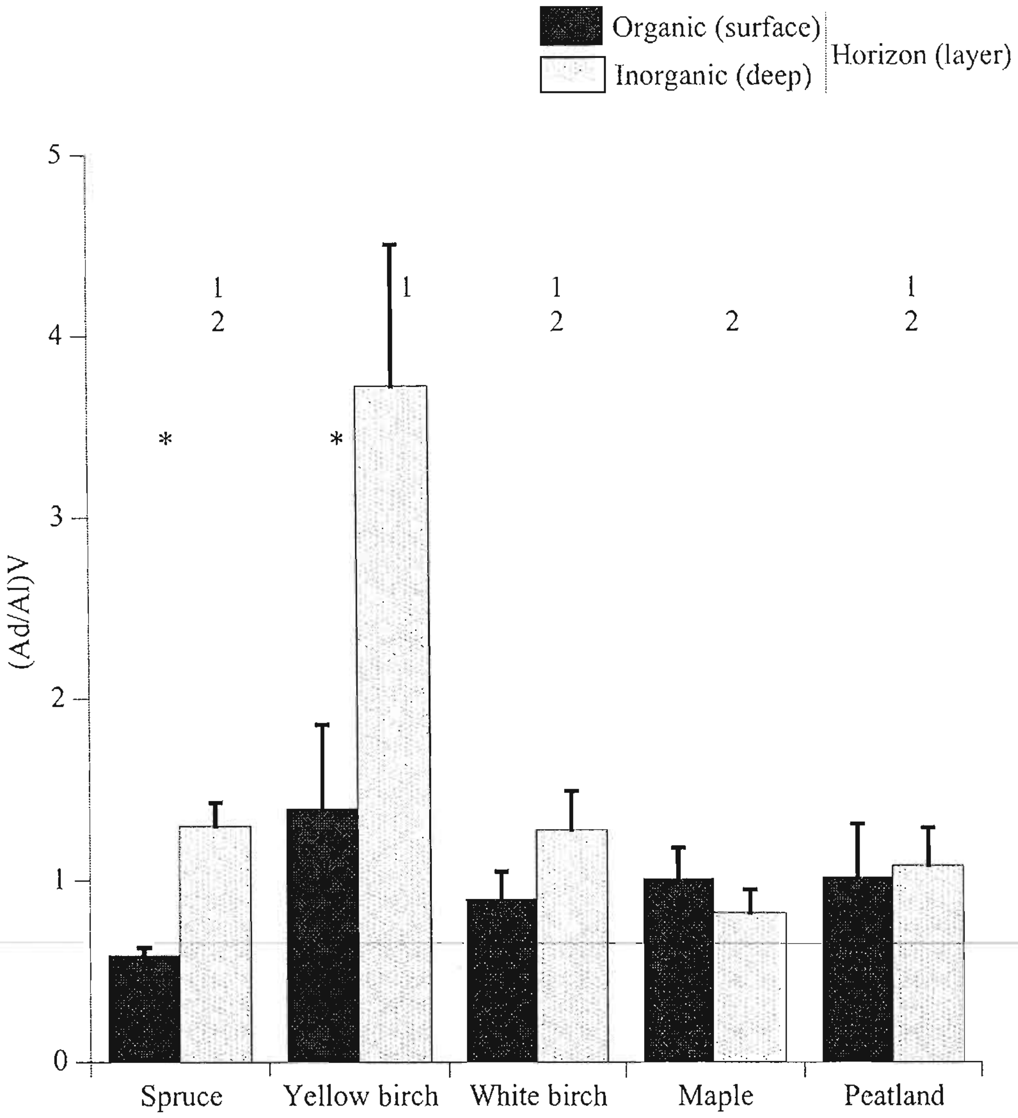

Figure 1.7 (Ad/Al)V ratios in spruce, yellow birch, white birch, and maple stands in the organic and mineral horizons of soils, as well as in the surface and deep layers of peatlands from mid-northern Quebec.

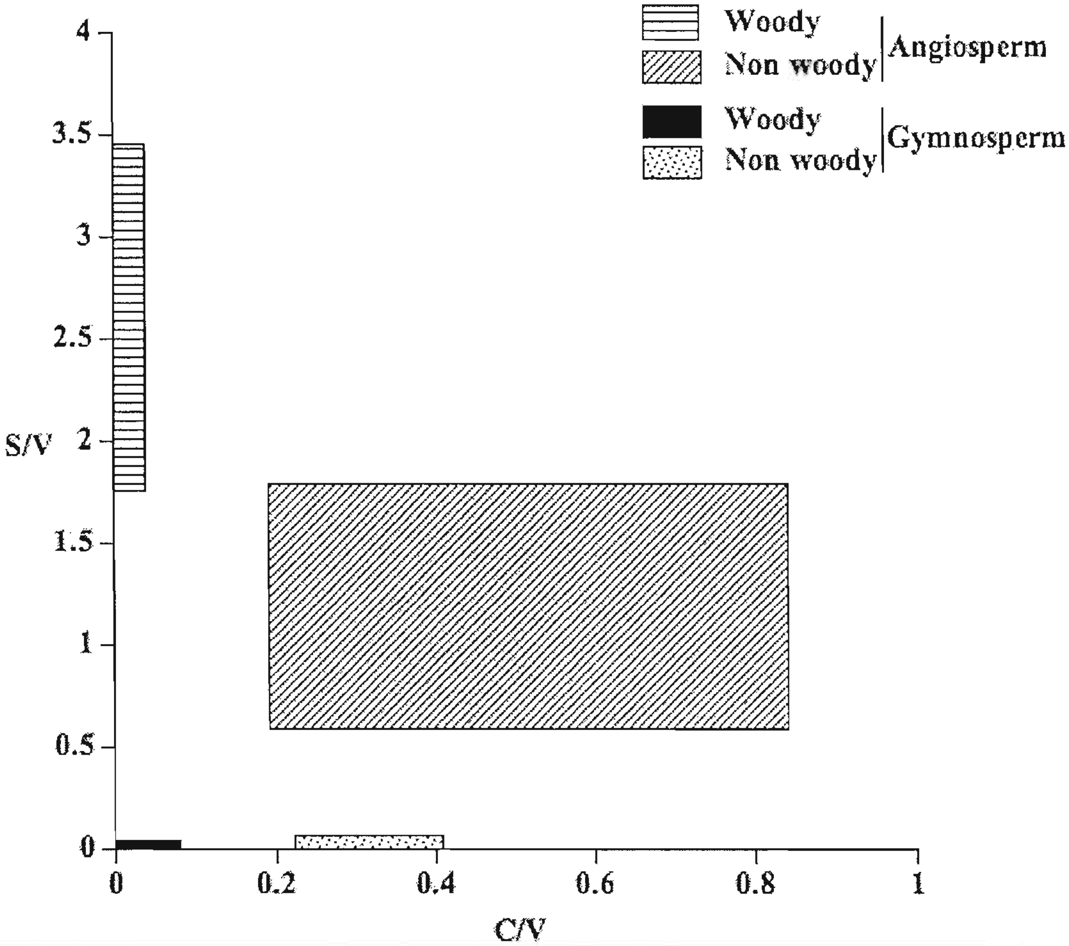

Figure 1.8 **a:** Pure source values of lignin biomarkers for angiosperm tissues (compiled from Hedges and Mann 1979, Hedges and Parker 1976, Ertel and Hedges 1985, Wilson et al 1985, Goñi and Hedges 1992), and for gymnosperm tissues (compiled from Hedges and Mann 1979, Wilson et al 1985, Hedges and Weliky 1989, Goñi and Hedges 1992). Boxes represent mean and 95% confidence interval.

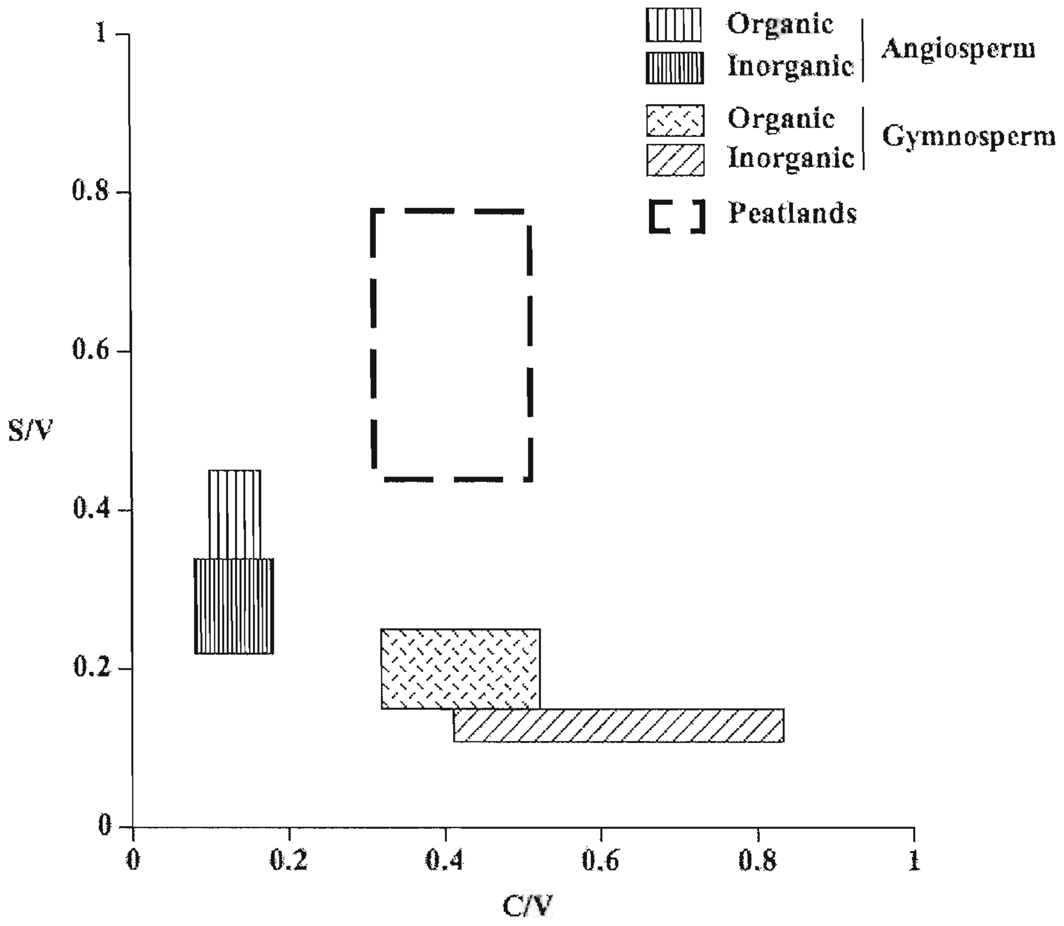

Figure 1.8 **b:** Mean C/V and S/V ratios in angiosperm, gymnosperm soils and peatlands. Boxes represent mean and 95% confidence interval.

Chapitre II :

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

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À soumettre pour publication dans Geochimica et Cosmochimica Acta

2.1 Résumé

Dans cette étude, nous mettons en relation les caractéristiques physiographiques et de végétation d'un bassin versant avec la nature de la matière organique terrigène (MOT) accumulée dans les sédiments d'un lac. Nous caractérisons la MOT à l'aide des biomarqueurs de la lignine en tant qu'indicateurs des sources et de l'état de dégradation de la MOT. Les systèmes d'information géographiques permettent également d'intégrer et de décrire les caractéristiques morpho édaphiques des bassins versants. En combinant ces deux approches, nous avons observé une relation positive et significative entre la pente moyenne du bassin versant et les apports de MOT estimé par λ8 dans les sédiments récents (R^2=0.65). La pente moyenne est également corrélée avec la composition de la MOT. En effet, les rapports P/(V+S) et 3,5Bd/V diminuent significativement avec l'augmentation de la pente moyenne (R^2=0.57 et R^2=0.71 respectivement). Plus précisément, les zones de pente modérée (entre 4 et 10 degrés) ont une influence majeure sur les apports de MOT dans les lacs. La composition de la végétation influence également la composition des sédiments des lacs étudiés. L'augmentation de la présence d'angiospermes dans le bassin versant favorise l'apport de MOT dans les sédiments de lacs tel qu'estimé par λ8 (R^2=0.44). Une relation similaire est observée avec le rapport S/V, indicateur de ce type de source. Finalement, la présence d'angiospermes dans le bassin versant influence l'état de dégradation de la MOT. Dans cette étude, nous avons donc pu déterminer : que les zones de très faibles pentes (0-2 degrés) jouent le rôle de zones tampons pour les apports de lignine et donc par extension sur les apports de MOT vers les sédiments et que la contribution relative de la MOT des horizons organiques de sols augmente dans les bassins versant plus escarpés. Les transferts de MOT d'un bassin versant vers un lac jouent un rôle prépondérant dans les apports de contaminants et dans la production de gaz à effet de serre dans ces systèmes aquatiques. Cette étude a donc des implications significatives pour la compréhension du devenir de la MOT dans les écosystèmes lacustres.

Mots clés : Biomarqueurs de la lignine, Sédiment, Système d'information géographique, Bassin versant, Lac, Matière organique, cycle du carbone

2.2 Abstract

In this study, we linked physiographic and vegetation characteristics of a watershed with the nature of TOM deposited in lake sediments. TOM was characterized using lignin biomarkers as indicators of TOM sources and its state of degradation. Geographical information system (GIS) allowed us to integrate and describe the landscape morpho-edaphic characteristics of a defined drainage basin. By combining these tools we found a significant and positive relationship (R^2=0.65) between mean slope of the watershed and the terrigenous inputs 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=0.43 and R^2=0.55 respectively). Specifically, areas with slopes comprised between 4 and 10 degrees have a major influence on TOM inputs to lakes. The vegetation composition of each watershed influenced the TOM 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). A similar relationship was also observed with the S/V ratio, 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 to 2 degrees) act as buffer zones for lignin inputs and by extension for TOM loading to lake sediments. The relative contribution of TOM from the soil organic horizons also increased in steeper watersheds. Terrigenous organic matter (TOM) transfer from a watershed to a lake plays a key role in contaminant fate and transport and other processes such as greenhouse gas emission in these aquatic ecosystems. This study has significant implications in our understanding of the fate and transport of TOM from terrestrial to lacustrine ecosystems.

Keywords: Lignin biomarkers, Sediment, Geographical Information System, Watershed, Lake, Organic Matter, Carbon cycle

2.3 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 matter (OM) dynamics within lake ecosystems. Two major environmental issues drive this scientific interest: the fate of contaminants and climate change. First, the role of OM, particularly terrestrial organic matter (TOM), is crucial to the contribution of contaminants such as mercury to lakes (Lindqvist 1991, Coquery and Welbourn 1995, Grigal 2002, Ouellet et al 2009). Second, OM dynamics is a central factor controlling carbon dioxide (CO_2) and methane (CH_4) production in these inland aquatic ecosystems. Since Cole et al (1994)'s 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 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 (both quantity and quality) to lakes. The mean slope declination, the drainage area, the lake surface area, the type of soil, and the vegetation type appear to be dominant variables for TOM transport to lakes (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 particular organic carbon (DOC and POC), however few studies have used sediment records to address this question (Müller et al 1998). Compared to the water column, sediment records have the potential to integrate time variability and sediments sampled in the maximal depositional zone (i.e. focal zone) also integrate spatial variation of overall lake–watershed OM dynamics (Håkanson et Jansson 1983). Furthermore, organic matter buried in lake sediments represents a carbon sink that remains stable for millennia (Cole et al 2007). We thus 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 a novel approach by coupling these TOM biomarkers with geographical information systems (GIS). TOM biomarkers yielded by mild cupric oxide (CuO) oxidation, 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. Lignin derived phenols have been both used in soils (Otto and Simpson 2006, Nierop and Filley 2007) and 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, Hernes et al 2007, Duan et al 2007). Within the daunting task of characterizing a given drainage basin, the analysis of lignin biomarkers in sediments is an advantageous tool for evaluating basin scale processes (Houel et al 2006). GIS is a powerful tool for mapping and analysing geo-reference data, which permits spatial integration 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 specifically assess which parts of a watershed might contribute to TOM transfers in both quantity and quality to recent lacustrine sediments.

2.4 Materials and Methods.

2.4.1 Sampling sites

The twelve lakes sampled in this study are spread out over 51 000 km^2 within the Canadian Shield boreal forest ecosystem. 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 km^2 respectively. They are located in the Lowland of the Abitibi, which belongs to the Superior geological province. The bedrock is composed of igneous and metamorphic rocks. Their watersheds sustains agriculture, mining and small-scale urban areas on Quaternary deposits of sand and clay. The ten 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 lie on till or sand. Lake Desjardins East and Desjardins West (10.26 and 8.88 km^2 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. Lake Desjardins East flows into Lake Desjardins West. The last eight lakes are located in the Outaouais region. The region is characterised 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 km^2. 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.

2.4.2 Sampling

Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth 1958) at the deepest point of the lake. The technique consists of slowly inserting a 1.5 m long Plexiglas tube (10 cm diameter) in the sediment using compressed air. This corer offers the advantage of avoiding perturbing the water-sediment interface. Each core was sub-sampled at every centimeter. To avoid cross contamination between samples, the contour in contact with the corer was discarded. The samples were then freeze-dried prior to analysis. For the purpose of our study we considered only the first five-centimeters of the core in order to describe more recent OM dynamics.

2.4.3 Chemical analysis

Sediment samples were homogenized with a glass rod before total carbon and nitrogen analysis. This was done using a Carlo Erba (NA-1500) elemental analyzer with a reproducibility of 5%. Analysis of molecular biomarkers was performed according to 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 GC/MS system (VARIAN 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1ms 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 phenol families: Vanillyls (V: ubiquitous in all terrestrial plants), Cinnamyls (C: produced by non-woody tissues) and Syringyls (S: specific of angiosperm plants) (Hedges and Mann 1979). These three families are used to determine sources of TOM along with their relative abundance ($\lambda 8$: sum of V, C and S). P-hydroxyl phenols 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).

2.4.4 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: 1/50000), extracted from the hypsographic and hydrographic elements of the National Topographic Data Base (NTDB, http://geobase.ca/). We delineated each watershed using GRASS and the watershed analysis tool. Watershed delineation 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 different categories of slopes. 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 (satellite image taken between 1999 and 2002). From these seven classes, we reclassified the data from on-site validation and ecoforestry maps in four classes (evergreen, deciduous, wetlands and others) (scale: 1/20 000 - Quebec forestry ministry).

2.4.5 Principal component analysis

We run a Principal component analysis (PCA) using JMP^{tm} software on both lignin and GIS variables for the twelve lakes. This test was performed as an exploratory tool in order to highlight relationships between the two datasets.

2.5 Results

2.5.1 Lakes and watershed

Results of the spatial analysis of lakes and watersheds are presented in table 2.1. Ratios between drainage area and lake area (DA/LA) vary between 3.70 and 13.93. Lake 53699 and Lake 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 Témiscamingue 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.

2.5.2 Early diagenesis

In order to integrate OM dynamics between a lake and its surrounding watershed, we chose to analyze the first five centimeters of each sediment core. The first five centimeters 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 centimeter 2 to 5 (Annexe B). For each indicator, the relationships are linear with regression coefficients varying between 0.75 and 0.96 and slopes close to 1 (1.00-1.24). The C/V, S/V and 3,5Bd/V ratios seem less affected by early diagenesis than the λ8 and P/(V+S) 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 30 years (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). No change in Lake Vera recent sediments was observed following wood harversting because sampling occurred just one year after disturbance and limit the record of this disturbance in first millimeters of the core.

2.5.3 Lignin biomarkers composition of sediments

Lignin biomarker measurements are presented in figure 2.1. Figure 2.1a presents the relationship between λ and C/N ratios in sediments. C/N ratios in sediments are between 13 and 16. Like C/N, λ8 is an indicator of terrigenous inputs of OM. However, we did not observe any significant correlation between the two variables. The λ8 values differ greatly between lakes (from 0.81 to 2.27). Figure 2.1b presents C/V ratios and S/V ratios observed in sediments. The C/V ratios range from 0.19 to 0.63, while S/V ratios vary between 0.05 and 0.4, with increasing S/V values corresponding to decreasing C/V ratios. The 3,5Bd/V and P/(V+S) ratios are presented in figure 2c. These two indicators are positively correlated to each other with values of P/(V+S) between 0.31 and 0.87, and 3,5Bd/V values between 0.02 and 0.7.

2.5.4 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 4.23 and 2.07, respectively, and accounted for 70% of the variance (figure 2.2). Thus, the PCA highlights two major axes. The first axis (X) (47% of the variance) is explained by the variation of the slope, the angiosperm ratio, $\lambda8$, P/(V+S) and 3,5Bd/V. The second axis (Y) (23% of the variance) is explained by the variation of the DA/LA, C/N 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 Eygliers 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 has a specific location on the Y-axis, with high C/N ratio and a high influence of DA/LA.

2.5.5 Watershed characteristics and TOM composition in lakes

Following the PCA, we tested all the potential relationships between sediment biomarker records and watershed characteristics. Figures 2.3 to 2.5 present significant linear or polynomial relationships between molecular biomarkers and GIS-derived watershed characteristics. Figure 2.3a shows a significant and positive relationship (R^2=0.65) between $\lambda8$ in recent sediments and the mean slope of the watershed. The mean slope also correlates with the composition of TOM in recent sediments as P/(V+S) and 3,5Bd/V ratios significantly decrease with the steepness of the watersheds (R^2=0.43 and R^2=0.55 respectively) (figure 2.4a). The ratio between DA/LA is often used to estimate terrigenous inputs to lakes. However, when plotted against $\lambda8$, we did not observe significant relationships in sediments.

The GIS analysis allowed us to determine more precisely which parts of the watershed are important contributors of TOM exports to lakes. In fact, the increasing proportion of areas with slopes between 0 and 2 degrees in a given watershed lowers the terrigenous inputs estimated by λ8 (figure 2.3b; R^2=0.69), and these inputs are more degraded (higher P/(V+S) and 3,5Bd/V ratios) in sediments (figure 2.4b). Similarly, we observed an inverse relationships with the increasing presence of areas with slopes comprised between 4 and 10 degrees and the increasing presence of wetlands in the watershed (figure 2.3c and 2.5b).

The vegetation composition of each watershed influences the composition of recent sediments of the sampled lakes (figure 2.5). The increasing presence of angiosperm trees in the watershed influences the export of TOM to the lake as λ increase significantly with the presence of this type of vegetation (R^2=0.44) (figure 2.5a). A similar relationship is also observed with the S/V ratio (R^2=0.51 for the twelve lakes and R^2=0.77 when Lake Malartic is removed from the data set) (figure 2.5c). The type of vegetation also greatly influences the degradation state of OM. The increasing presence of angiosperm trees in the watershed brings less degraded OM to lake sediments.

2.6 Discussion

C/N ratios are commonly used in lakes to estimate allochthonous versus autochthonous inputs of OM. TOM usually has C/N ratios greater than 20 and aquatic non-vascular plants have C/N ratios between 4 and 10 (Meyers and Ishiwatari 1993). There is little variation of the C/N signals between lakes. An average C/N value of 15 indicates that the OM found in sediments is composed of a mixture of allochthonous and autochthonous OM. With a C/N value of 15, the overall algal productivity is considered moderate (Routh et al 2007), which is in accordance with the oligotrophic status of these lakes, as reported by Dufour (2005). These values are similar to previous observations in boreal lake sediments (Ertel and Hedges 1985, Meyers and Ishiwatari 1993, Meyers 2003, Kainz and Lucotte 2006). The λ8 indicator is also used as a proxy for the relative contribution of allochthonous OM in sediments, because lignin-derived biomarkers are specific to terrestrial plants (Hedges and Mann 1979). Surprisingly, however, we could not observe any correlation between C/N ratios and λ8. Possible reasons could be that variations of the C/N ratios are induced by shifts in the balance between in situ production and terrigenous inputs, while λ8 values are influenced by vegetation types and soil processes (Houel 2003). Another reason includes that these two indicators also range in two different scales and it maybe that the range of lakes studied here is not sufficient to yield high C/N variations. This result shows that λ8 may be a more sensitive tool to assess TOM inputs in lake sediments because λ8 shows significant variation of λ8 values among lakes while C/N ratios show a very narrow range. For example, λ8 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 λ8 values in lake sediments has been reported, which is remarkable for lakes that are all situated within a radius of 100 km and such a wide range of λ8 values was previously only reported for time series variations in sedimentary records (Hu et al 1999, Houel et al 2006). λ8 values are lower than those found in lake Washington by Goñi and Montgomery (2000), but similar to values found by Houel et al (2006) in the same region. Values for the S/V and C/V ratios are also very variable in the studied lakes, suggesting that changes in the types of vegetation influence TOM inputs. There is no concomitant variation between these two variables. The range of values presented in figure 2.1b fits well with values measured in soils from watersheds in this region (chapter I), suggesting that soils, rather than pure end-members, are the main source of TOM inputs.

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-hydroxy phenols are not affected by demethylation and P/(V+S) ratios increase with higher states of degradation (Dittmar and Lara 2001). The sources of p-hydroxy phenols are terrestrial plants and phytoplankton (Hedges et al 1988). However, in oligotrophic lakes, the influence of autochthonous OM production on p-hydroxy phenols is limited (Houel et al 2006). Furthermore, *p*-hydroxyacetophenone (Pn) is unequivocally derived from terrestrial plant and a constant Pn/P ratio; which was the case with our dataset, enables one to confirm the terrestrial origin of P phenols (Hedges et al 1988). The evolution of the maturation degree of TOM is also recorded in 3,5Bd/V ratios. This indicator is now 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 figure 2.1c show that the states of degradation of TOM found in lake sediments vary greatly between the studied lakes.

As previously mentioned, PCA was used as an exploratory tool to highlight the link between the two matrixes of data generated within this study: the watershed morphoedaphic data and the sediment CuO derived biomarkers. This analysis enables 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 regulate soil moisture conditions (Ogawa et al 2006). In steep slopes, runoff will occur mostly on the topsoil, within soil organic horizons where the lignin content is high (chapter I). When the slope decreases, water percolates more efficiently and reaches deeper soil horizons where lignin content is lower (chapter I, Houel et al 2006, Hernes et al 2007). The use of GIS allows determining the range of slopes that drive TOM transfer processes. By compiling slope data at 2-degree intervals, we were able to show that low slope areas (0 to 2 degrees) act as buffer zones for lignin inputs and consequently 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 wetland, as proposed by Xenopoulos et al (2003) as well as Dillon and Molot (1997), the $\lambda 8$ values suggest that wetlands act as retention zones for TOM (Stallard 1998). In fact, we observed that the increasing presence of peatlands in the watershed lowers terrestrial OM inputs in lake sediments (figure 2.5b). The compilation of slopes between 4 to 10 degrees (figure 2.3) suggests that these moderate slopes sustain more efficient TOM transfers to the lake.

Beyond these slope-related changes in λ8 values, the watershed slope also influences the P/(V+S) and 3,5Bd/V ratios 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 sediments.

With the increasing presence of angiosperm stands in the watershed, we observed an increase of TOM in sediments (figure 2.5a). 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. The second factor is that the flux of DOC is higher in deciduous forest than coniferous ones (Michalzik et al 2001). Hence, lignin compositions of lake sediments are also useful for providing information regarding vegetation composition and contribution of respective classes to the watershed ~~with increasing S/V ratios pointing~~ towards an increasing presence and contribution of TOM to watersheds by angiosperms. Miltner and Emeis (2000) have already hypothesized this link in large-scale environment but without precisely describing the vegetation occupying the watersheds. This study is the first to show the direct link between TOM and drainage area composition.

2.7 Conclusion

This study has significant implications in our understandings of TOM fate in lacustrine ecosystems. First lignin biomarkers analyzed in sediments represent a good integration of watershed-scale processes of TOM. Specifically, they stress the role of both topographic and edaphic properties of the drainage basin to TOM inputs in boreal lakes. Secondly, the combined use of GIS and lignin biomarkers is a promising tool as it allows highlighting the role and contribution of specific areas of the watershed (low-slope areas) or vegetation (angiosperms) for TOM lake loadings. Further, the use of specific lignin biomarkers in continental aquatic ecosystems allows to describe the source (e.g. gymnosperms vs. angiosperms) and state of degradation of TOM, which helps to improve our understanding of organic matter cycling and contaminant fate within these ecosystems.

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2.9 References

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2.10 Table and figures

Table 2.1

Watershed geographic and topographic properties of the 12 study lakes. 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°.

Lakes	Localisation 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 East	46.63°, -78.27°	319	10.26	38.84	3.79	2.99	0.46	0.21	0.31	0.46	0.07
Desjardins West	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

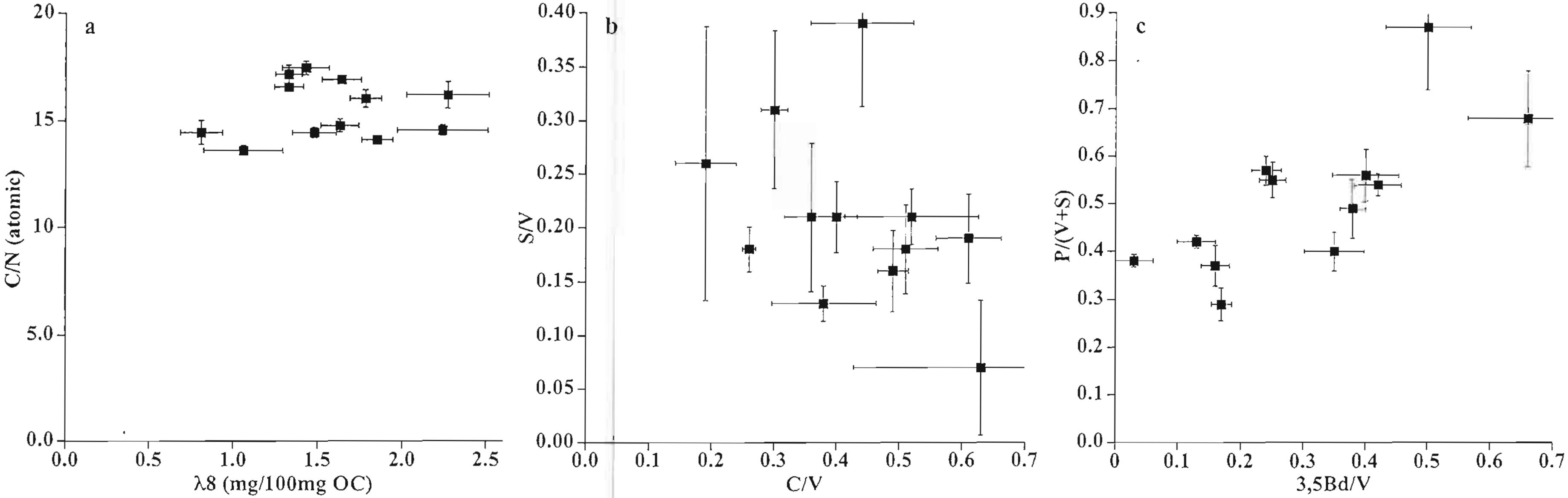

Figure 2.1 TOM indicators measured in recent sediments of the twelve lakes. **a:** C/N ratios vs. λ8 (mg/100mg OC), **b:** S/V vs. C/V, **c:** P/(V+S) vs. (3,5Bd/V)

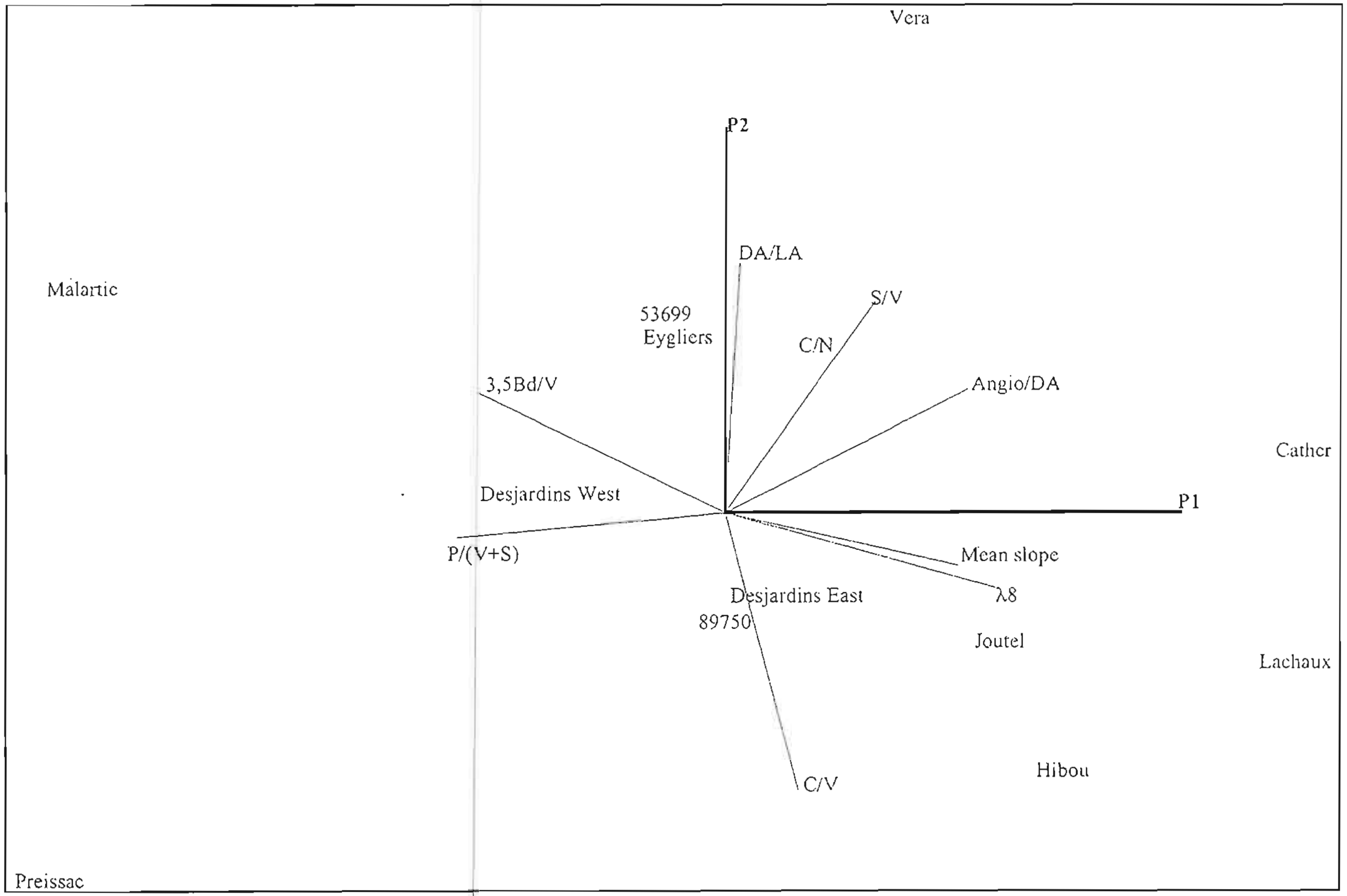

Figure 2.2 Plot of the principal component analysis performed on CuO derived biomarkers measured in recent sediments and watershed morpho-edaphic characteristics

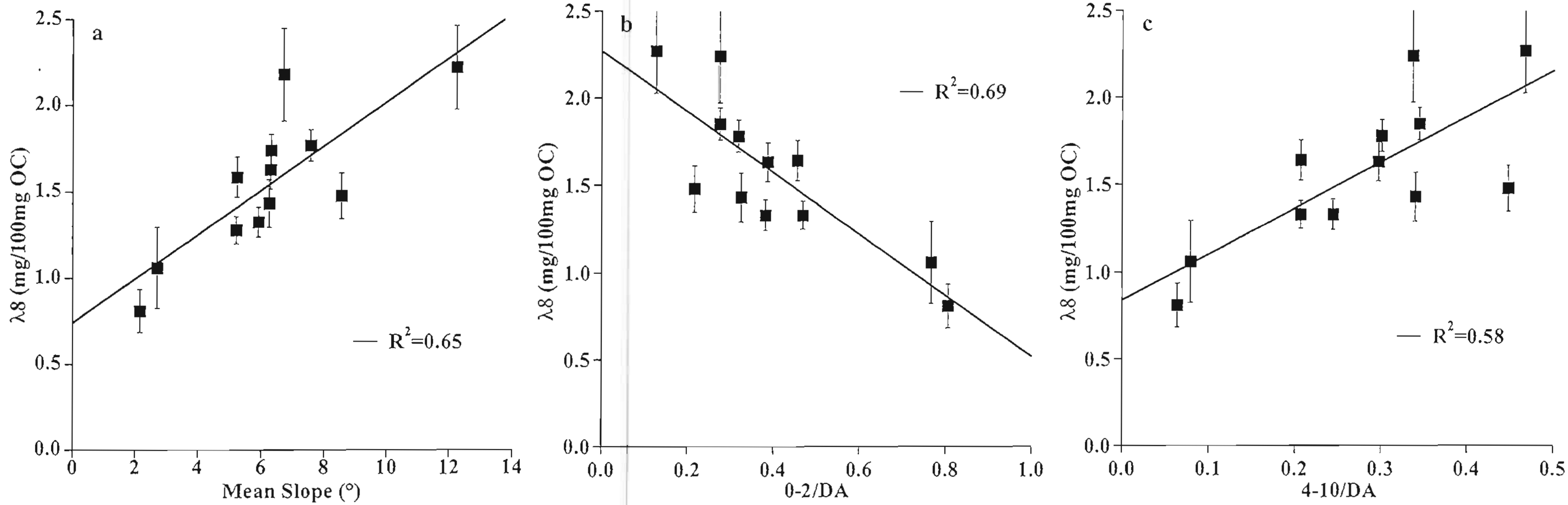

Figure 2.3 Influence of watershed slope on TOM inputs estimated with λ8 (mg/100mg OC). **a:** λ8 vs. mean slope of drainage area in degree; **b:** λ8 vs. ratio of drainage area with 0 to 2° slope (0-2) to drainage area (DA); **c:** λ8 vs. ratio of drainage area with 4 to 10° slope (4-10) to DA.

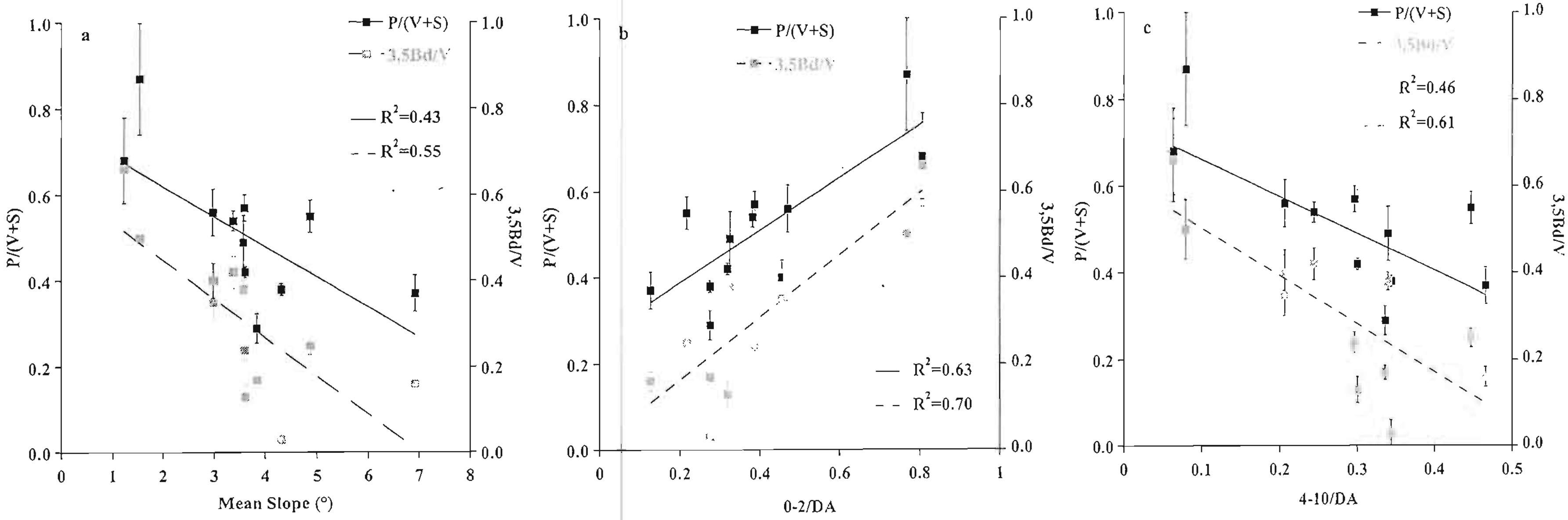

Figure 2.4 Influence of watershed slope on TOM composition estimated with P/(V+S) and 3,5Bd/V ratios. **a:** P/(V+S) and 3,5Bd/V vs. mean slope of drainage area in degree; **b:** P/(V+S) and 3,5Bd/V vs. ratio of drainage area with 0 to 2° slope (0-2) to DA; **c:** P/(V+S) and 3,5Bd/V vs. ratio of drainage area with 4 to 10° slope (4-10) to DA.

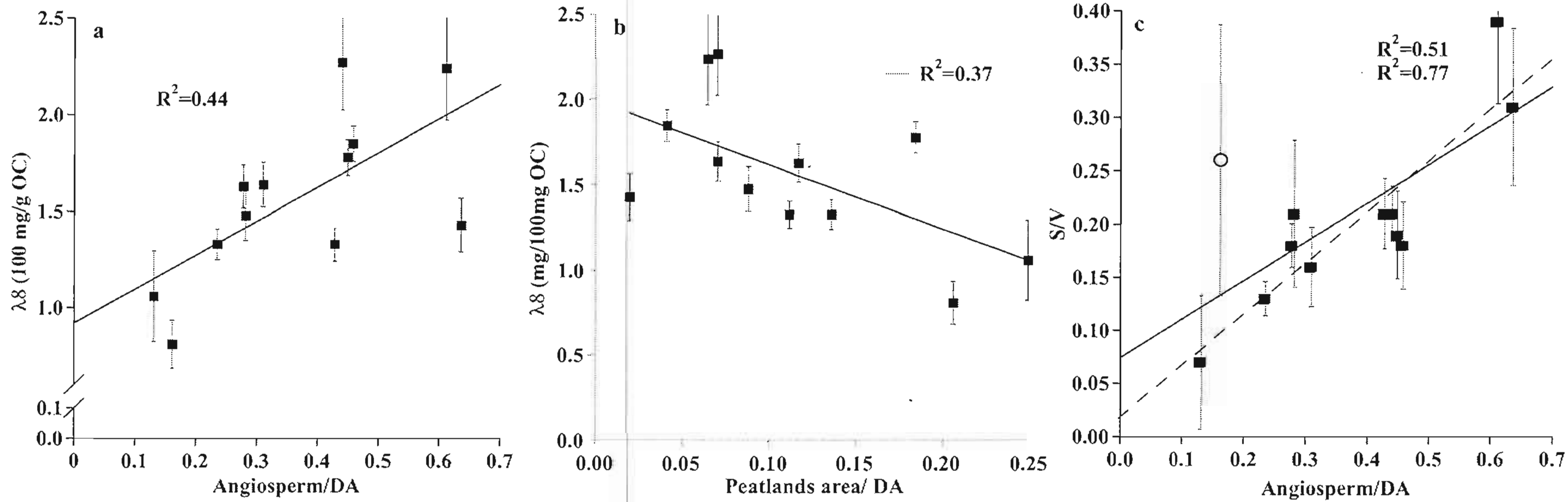

Figure 2.5 Role of the type of vegetation cover on the drainage basin (angiosperms and peatlands) in TOM inputs to lake sediments. **a:** λ8 vs. ratio of angiosperm dominant cover (Angiosperm) to DA (Angiosperm/DA); **b:** λ8 vs. ratio of peatlands area to DA (Peatlands area/DA); **c:** S/V vs. Angiosperm/DA (white circle : Lake Malartic).

Chapitre III :
TOM biomarkers as tracers of Hg sources in recent lake sediments of the Boreal forest

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À soumettre pour publication dans Biogeochemistry

3.1 Résumé

Pour pallier à la difficulté de mesurer et d'intégrer à l'échelle de tout un bassin versant les différents apports de matière organique terrigène (MOT) et le mercure (Hg) qui y est associé vers un lac, nous préconisons l'analyse de biomarqueurs de composés ligneux dans les sédiments lacustres. Quinze lacs ont été échantillonnés au Québec et au Labrador. Dans chaque lac, une carotte de sédiments a été prélevée dans la zone la plus profonde du lac. Les cinq premiers centimètres de chaque carotte ont ensuite été analysés en laboratoire pour déterminer la concentration en Hg total et des différents biomarqueurs terrigènes. Nos résultats mettent en évidence trois régions distinctes déterminées par des apports de MOT et de Hg différents. L'Outaouais et le Témiscamingue (région A : 10 lacs) sont caractérisés par des concentrations en Hg très variables (entre 120 et 390 ppb) et des teneurs élevées en MOT ($\Sigma 8$ entre 24.5 et 43.1 mg/10g d'échantillon). L'Abitibi (région B : 2 lacs) est caractérisée par des taux de Hg intermédiaires (95.5 et 150 ppb) et des teneurs de MOT très faibles ($\Sigma 8$ moyen = 2 mg/10g d'échantillon). Le Labrador (région C : 3 lacs) est caractérisé par des niveaux de Hg très faibles ([T-Hg] moyen = 23 ppb) et des teneurs de MOT également très faibles ($\Sigma 8$ moyen = 1.9 mg/10g d'échantillon). Dans les lacs de la région A, la variation des teneurs en Hg est bien expliquée par l'augmentation du rapport 3,5Bd/V ($R^2=0.84$; $p<0.0002$) et la diminution du rapport C/V ($R^2=0.5$; $p<0.0227$). Dans la région B, les sédiments sont enrichis en Hg lorsque comparés aux apports de MOT ([T-Hg]/$\Sigma 8$=63.5). Une contamination locale due à l'activité minière explique cet enrichissement relatif. Finalement au Labrador, la dynamique de la MOT est dominée par les gymnospermes et la végétation arbustive ou rase (C/V moyen = 0.8). Cette spécificité entraîne un apport très faible de Hg des bassins versants vers les lacs. Notre étude montre donc que la source ~~et la qualité de la MOT~~ sont déterminantes pour comprendre les variations d'apports en Hg dans les sédiments récents. Plus précisément, l'augmentation des apports de MOT dérivés des horizons humifiés des sols explique une grande part des apports de Hg dans les sédiments.

Mots clés : Mercure, Biomarqueurs de la lignine, Lacs de la forêt boréale, Matière organique terrigène

3.2 Abstract

Terrestrial organic matter (TOM) plays a key role in mercury (Hg) dynamics between watersheds and lakes. Integrating the watershed complexity is a daunting task. Within the scope of this project, we characterized organic matter at a molecular level in order to determine Hg transfer conditions to the sediments. We sampled 15 lakes in the Quebec and Labrador boreal forest. In each lake, we sampled a sediment core at the deepest point in addition to analyze total Hg and a set of terrigenous biomarkers in recent sediments (5 cm). Our results allow determination of three regions characterized by specific TOM and Hg inputs. The Outaouais and Temiscamingue regions (region A: 10 lakes) are characterized by highly variable Hg concentrations from 120 to 390 ppb and high TOM inputs ($\Sigma8$ ranges from 24.5 to 43.1 mg/10g of sample). The Abitibi region (region B: 2 lakes) is characterized by median Hg level (95.5 and 150 ppb) and low TOM inputs (mean $\Sigma8 = 2$ mg/10g of sample). In region A, total Hg variation is well explained by an increase of 3,5Bd/V ratios ($R^2=0.84$; $p<0.0002$) and a decrease of C/V ratios ($R^2=0.5$; $p<0.0227$). In the two other regions, the number of lake sampled limits the interpretation of the results. However in region B, we observe that sediments are enriched in Hg when normalized by TOM contents ($[T\text{-}Hg]/\Sigma8=63.5$). Local point source of Hg explains this relative enrichment. In Labrador, TOM dynamics is dominated by gymnosperm stands and non-woody plants (mean C/V=0.8). Their watersheds are characterized by low primary production. These two parameters lead to very low [T-Hg] in recent sediments. Beyond the particular case of Abitibi and Labrador, our study shows that TOM sources and quality are determinant for Hg loadings in lake sediments. More precisely, increasing TOM derived from humified soil horizons explains most of Hg level variations within sediments.

Keywords: Mercury, Lignin biomarker, Boreal forest lakes, Terrigenous organic matter, Sediment

3.3 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 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 such as in northern boreal areas, high Hg levels are observed. Indeed, Hg (anthropogenic and 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 total Hg (T-Hg) are well recorded (Lucotte et al 1995, Rognerud and Fjeld 2001). Previous studies measuring T-Hg concentrations 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 terrestrial organic matter (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). However, some studies raised the issue that TOM quality (both source and composition), rather than the sole quantity of OM 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 type, density and hight (Schroeder and Munthe 1998, Demers et al 2007). Furthermore, the hydrologic regime of forested watersheds is modified by its vegetation composition, leading to differential Hg and

OM leaching into lakes.

Lignin phenol derivatives, obtained after a mild cupric oxidation (CuO), yield interesting information on TOM source and composition. For example, in several environments, they have been broadly used to describe the OM composition of sediments from various watersheds in addition to reconstruct 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 and more precisely Hg (Louchouarn and Lucotte 1998, Caron et al 2008, Ouellet et al 2009). Earlier studies validated the use of CuO derived biomarkers to describe OM composition variations due to watershed characteristics (chapter II). Here, we propose to test 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 originating from deciduous and coniferous species as well as describing its state of degradation, we aim at better 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.

3.4 Materials and Methods.

3.4.1 Sampling sites

Fifteen oligotrophic lakes situated in the boreal forest were sampled. These lakes are located in four distinct administrative regions of North-eastern Canada: Outaouais, Abitibi, Temiscamingue (Québec) and Labrador (Figure 3.1; Table 3.1). All lakes studied are part of the boreal forest ecosystem dominated by black spruce (*Picea mariana*), balsam fir (*Abies balsamea*), and grey pine (*Pinus divaricata*) for gymnosperm species and by white and yellow birch (*Betula papyrifera* and *Betula alleghaniensis*), maple (*Acer spp.*) and aspen (*Populus sp.*) for angiosperm species. Whereas the watersheds in Labrador are covered by open woodland dominated by black spruce, lichen (*Cladonia spp.*) and moss (*Bryophyta spp.*), the southern watersheds of Quebec are covered by mixed wood forest still dominated by coniferous species in Abitibi and by deciduous species for the ten lakes of the Outaouais and Temiscamingue regions (figure 3.1). Lakes Preissac and Malartic are located in the Lowlands of the Abitibi geological province, which belong to the Superior geological province. The bedrock is composed of igneous and metamorphic rocks. Their watershed sustains agriculture, mining and urban development on a Quaternary deposit of sand and clay. Lakes from the Outaouais and Temiscamingue regions are located on the Grenville geological province. These lakes lie on gneiss bedrock covered by thin glacial deposits. The soils are mainly podzolic, and overly till or sand deposits. The three Labrador lakes are also located on the Grenville geological province. Gneiss and granite from the Precambrian Canadian Shield dominate the bedrock geology in this region.

3.4.2 Sampling

Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth 1958) at maximum depth of each lake. The technique consists of inserting a 1.5 m long Plexiglas tube (10 cm diameter) in the sediment using compressed air. This corer offers the advantage of producing very few perturbations at the water–sediment interface. The top five centimeters were subsampled at each centimeter in order to study the recent OM 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.

3.4.3 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 GC/MS system (VARIAN 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1ms 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 ($\Sigma 8$ normalized according to 10g of sample: sum of V, C and S). p-Hydroxyl phenols and a 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, chapter I).

Analyses of total Hg (T-Hg) concentrations were performed by cold vapour atomic fluorescence spectrometry detection (CVA-FS) following the protocol developed by Bloom end Fitzgerald (1988) and adapted by Pichet et al (1999). Briefly, a combination of acid HNO_3 (16N) : HCl (6N) (10:1 mL) is added to approximately 250 mg of freeze dried, ground sediment and then heated to 120°C for 6 hours. The solution is brought back to a volume of 30 ml with NANOpure® water and analyzed with cold vapor fluorescence atomic spectrometry (CVFAS) with a detection limit of 1 ng/g. The sole difference with Bloom and Fitzgerald method was that Hg is not pre-concentrated in a gold column but injected directly.

3.5 Results

In the following section we present the average values and standard deviation for the top five centimeters of each sediment core. Figure 3.2 presents sedimentary T-Hg concentrations plotted against $\Sigma 8$, which is used to estimate lignin concentrations in sediments for 10 grams of sample (Hedges et Parker 1976, Hedges et Ertel 1982, Onstad et al 2000). In this figure, we can separate the lakes into three distinct groups (identified as A, B and C). The first set of lakes (A) represents the eight lakes from the Outaouais region and two lakes from the Temiscamingue region. Their sediments are characterized by high level of T-Hg (from 120 to 390 ppb) and the highest Σ8 values (from 24.5 to 43.1 mg/ 10g of dw). The second set of lake (B) represents two lakes from the Abitibi region (Preissac and Malartic). They have moderate level of T-Hg compared to other lakes (95 and 150 ppb for Malartic and Preissac respectively) and very low values of Σ8 (1.6 and 2.4 mg/10g dw respectively). Finally, group C is composed by the three Labrador lakes (Panch, Grand and Seal). Their sediment records exhibit both very low T-Hg (from 10 to 33 ppb) and very low Σ8 (from 1 to 2.5 mg/10 g dw). Detailed results of chemical lignins analysis are shown in figures 3.3 to 3.6 and are presented for each group of lakes A, B and C identified on figure 3.2. In these figures, T-Hg values are normalized to Σ8. This normalization is justified by the fact that previous studies have shown a strong relationship between sedimentary [T-Hg] and TOM inputs into a lake (Swain et al 1992, Lucotte et al 1995, Kainz and Lucotte 2006). Hence this representation allows to limit the effect of variable sedimentation rates on [T-Hg] among lakes within a given region, thus allowing to better characterize the role of specific terrigenous compounds on Hg inputs into a lake.

Figure 3.3 presents the relationship of [T-Hg]/Σ8 to 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, chapter I). Firstly, we observe that [T-Hg]/Σ8 ratios vary between 3 and 12 in the Outaouais and Temiscamingue region lakes (region A). In Labrador, the same order of magnitude is observed with [T-Hg]/Σ8 ratios between 10 and 15 (region C). In the Abitibi, these ratios are about one order of magnitude higher (between 60 and 70)(region B). On the other hand, S/V ratios are similar in the three regions considered ranging between 0.05 to 0.40. We do not observe any relationship between [T-Hg]/Σ8 and S/V ratios in the three regions considered.

The variation of C/V ratios is much higher than that of S/V ratios among the three regions (figure 3.4). In region A, C/V ratios vary between 0.25 to 0.65. This variation of non-woody and coniferous derived lignin in sediments (Hedges et Mann 1979, Hu et al 1999) explains up to 50% of the observed variation of [T-Hg]/Σ8. In region B, Lakes Malartic and Preissac exhibit two distinct signals of C/V ratios with values of 0.2 and 0.63 respectively. Finally in Labrador (region C), we observe the highest range of C/V ratios from 0.14 to 1.45 while no tendency is observed with [T-Hg]/Σ8 variation.

Figure 3.5 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). In the region A, 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 this region. In region B (Abitibi), P/(V+S) ratios are higher with higher degree of TOM degradation observed in Lake Preissac (0.63 and 0.87). Finally, Seal and Panch lakes have the highest P/(V+S) ratios (1.16 and 1.2 respectively), Grand Lake presenting fresher TOM inputs to sediments (P/(V+S)=0.42).

Finally, figure 3.6 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 from region A ($R^2=0.84$; $p<0.0002$). In region B, 3,5Bd/V ratios are higher than in region A and quite similar for the two lakes (0.5 and 0.68 for lakes Preissac and Malartic respectively). In region C, a wide range of 3,5Bd/V is observed from 0.26 in Grand Lake to 1.11 in Seal Lake.

3.6 Discussion

3.6.1 Hg and TOM in recent sediments

TOM loadings from watershed to lakes was estimated using Σ8 measurement in recent sediments. This indicator plotted against [T-Hg] allowed highlighting three regions. The first region regroups the eight lakes from Outaouais and the two from Temiscamingue. In this group of lake (region A), we observe a high variation of [T-Hg] in lake sediments. However TOM inputs, estimated by Σ8, are rather similar (figure 3.2). In these small headwater lakes, estimation of TOM inputs is not sufficient to understand the [T-Hg] variation in sediments. Indeed, in these pristine or slightly perturbed watersheds (Roué-Legall et al 2005, chapter II), absence of OM dynamics modification does not explain the observed variation in [T-Hg]. This results may be surprising as 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). However, as suggested in previous studies, the quality and particularly the source of TOM should provide more precise information on Hg dynamics (Kainz and Lucotte 2006) than bulk estimation of TOM inputs (Sanei and Goodarzi 2006, Ouellet et al 2009). These lakes constitute a particularly interesting case study as variations of sedimentary [T-Hg] among lakes cannot be related to TOM inputs variation nor anthropogenic activities.

In the two other regions under study, the small number of sampled lakes limits the interpretation of the results. However, we observe that recent sediments from Preissac and Malartic lakes (region B) are much enriched in Hg according to TOM levels (mean [T-Hg]/Σ8=63.5 in Abitibi lakes compared to 12.5 and 8 in Labrador and Outaouais respectively). These two lakes lie on the Abitibi clay belt and a previous study has shown that this parameter was determinant for Hg level in lakes (Beaulne et al 2009). Indeed, sorption of Hg on clay minerals is a well known phenomenon that enhances Hg accumulation and mobilization in sediments (Farrah and Pickering 1978, Dmytriw et al 1995). The relative enrichment in Hg compared with TOM inputs may also be explained by local point sources of Hg. The Horne smelter in Rouyn-Noranda has increased atmospheric pollutants in the region, recorded in lakes sediments (Dixit et al 2007) and several mine tailing compose the landscape of this region (Benzaazoua et al 2008). Moreover, agriculture and wood harvesting are present in the watershed and may also influence both cycle of TOM and Hg. Indeed, both deforestation and forest fire have been shown to modify export of TOM and most particularly lignin (Farella et al 2001, Kalbitz et al 2004, Duan et al 2007) and T-Hg from soils to aquatic ecosystems (Caldwell et al 2000, Garcia and Carignan 2005).

In Labrador we observe low levels of Hg in sediments (figure 3.2). These values are similar to those measured during a survey of several contaminants in nearby Labrador lake sediments (Natural Resources Canada 2008). Compared to the two other regions, TOM inputs, as estimated by $\Sigma8$, are low. In Labrador, upland vegetation is mainly composed of open woodland of black spruce, moss and lichen along with large patches of barren rock. The thinness of the organic soil horizon and the low terrestrial primary production explain the limited export of OM to lakes (Engstrom 1987, Roberts et al 2006). Finally, open areas limit atmospheric Hg accumulation in soil, as Hg scavenging from atmosphere is limited (Sheehan et al 2006).

3.6.2 Hg and TOM sources

Lignin derived biomarkers hold valuable 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, chapter I and II). 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, chapter I). Our results in region A 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. However the increasing presence of a non-woody or coniferous source in the watershed seems to lower the inputs of Hg to the lake (figure 3.3 and 3.4). 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 (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 atmospheric Hg retention 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 (chapter II). 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).

For the two other regions under study, we notice that S/V ratios are rather similar with values measured in region A. In Labrador, where the landscape is dominated by gymnosperms and non-woody herbaceous plants, such S/V values indicate significant inputs of angiosperm-derived lignins (chapter II). These angiosperm stands are usually found around lakes and streams (Foster and King 1986, Roberts et al 2006), within a proximal zone of moderate slopes that brings significant amount of TOM (Beaulne et al 2009, chapter II). However, C/V ratios measured in Labrador confirm that coniferous and non-woody areas dominate the composition of TOM entering lake sediments (figure 3.4). [T-Hg] do not vary much with S/V and C/V ratios in Labrador lake sediments.

In the Abitibi lakes, S/V and C/V ratios are very different for nearby lakes, confirming the marked impact of different land use (agriculture, forestry) in their respective watersheds (Farella et al 2001, Caron et al 2008, chapter II). Lake Malartic exhibits the lowest C/V ratio in sediments. This lake is surrounded by grassland devoted to fodder. Thus, each year most of the non-woody species composing these pastures are removed from the watershed and may explain a lower input of cinnamyl phenols leading to a particular sediment record. These land-use differences do not affect Hg level in sediments as no variation in [T-Hg] is observed with C/V ratios variation (figure 3.4). This result seems to support a dominant role of Hg contamination from local point source as explanation for [T-Hg] variation in recent sediments.

3.6.3 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) an indicator of the state of TOM degradation. TOM freshness, estimated trough P/(V+S) ratios, does not influence Hg inputs to sediments of region A (figure 3.5). Yet we were expecting a relationship between this indicator and [T-Hg] as P/(V+S) ratios increased in soils where [T-Hg] are higher (Grondin et al 1995). 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 close relationship between these small lakes and their watershed may limit the variation of this ratio because absence of high variation of P/(V+S) in angiosperm's soils between horizons (chapter I), may explains the absence of relationship with Hg loadings in these southern lakes surrounded by deciduous vegetation (chapter II).

Increase in P/(V+S) ratios in region B and C is accompanied by an increase in Hg level in sediments (figure 3.5). These results indicate that more Hg is associated with TOM that has undergone higher degradation processes in soils. However, these results should be considered with caution for two main reasons: the number of sampled lakes is limited and an ambiguous source of p-hydroxy phenols is observed in Grand, Preissac and Malartic lakes. Indeed, p-hydroxybenzaldehyde (Pl) and p-hydroxyenzoic acid (Pd) may also be produced by plankton (Hedges et al 1988).

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 SOM 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).

Whereas in lake sediments from regions B and C we could not conclude on any tendency between this indicator and T-Hg levels (figure 3.6), the relationship between [T-Hg] and 3,5Bd/V in region A is strong (r^2=0.84). This strong relationship suggests that more Hg is transferred to lake sediments when it is associated with more humified TOM. This observation doesn't fit with results observed in the water column of lakes where anthropogenic activities (agriculture, forestry) drastically disturbed the steady-state equilibrium of soil organic matter with selective erosion of soil humus and litter (Ouellet et al 2009). Thus, in unperturbed watersheds, the leaching of more humified horizons below the surface litter increases the association between Hg and TOM. In a previous study, we observed that the mean slope of the watershed influenced the 3,5Bd/V ratio in sediments (chapter II). Indeed, when the mean slope of the watershed decreases, water percolates more efficiently and accesses deeper soil horizons where 3,5Bd/V ratios are higher and Hg is strongly associated with OM (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 have achieve to assess the role of soils horizon on this dynamics.

3.7 Conclusion

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. Beyond anthropogenic perturbations (region B) or very specific areas such as the Labrador region, 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 processes and coniferous stands in the watershed or open areas on terrestrial Hg transfers to a lake. This study highlights the potential usage of lignin derived biomarkers to better understand the Hg cycle at the ecosystem level. Furthermore, it allows integrating the pathways of Hg from an entire drainage basin and it points out to key areas for Hg leaching and transfer to aquatic systems.

3.8 Acknowledgments

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3.10 Table and figures

Table 3.1
Localization of the 15 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
Preissac	Abitibi	129.2	512.9	3.97
Malartic	Abitibi	122.3	610.9	5.00
Panch	Labrador	17.48	82.3	4.71
Grand	Labrador	322.2	4545.3	14.11
Seal	Labrador	35.97	68.16	1.89

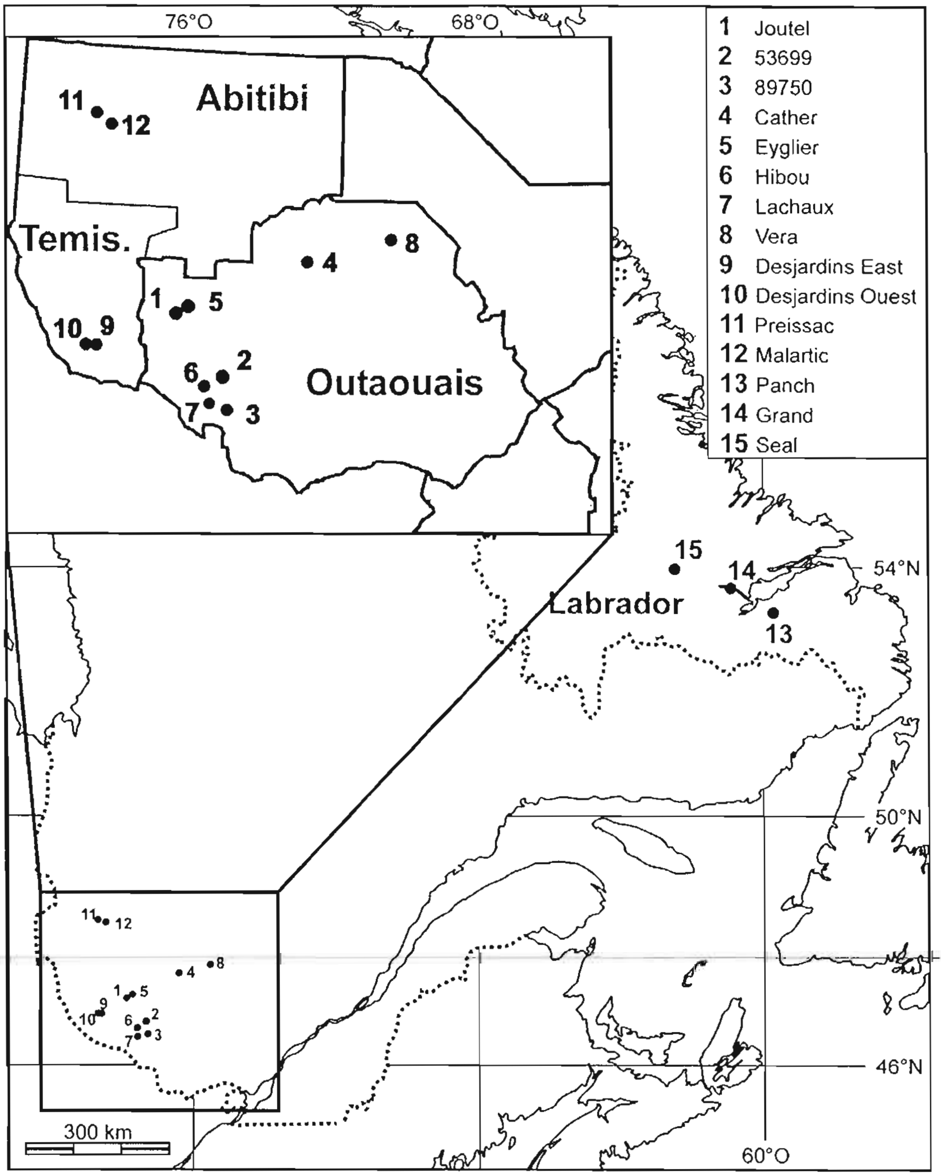

Figure 3.1 Map showing the studied lakes

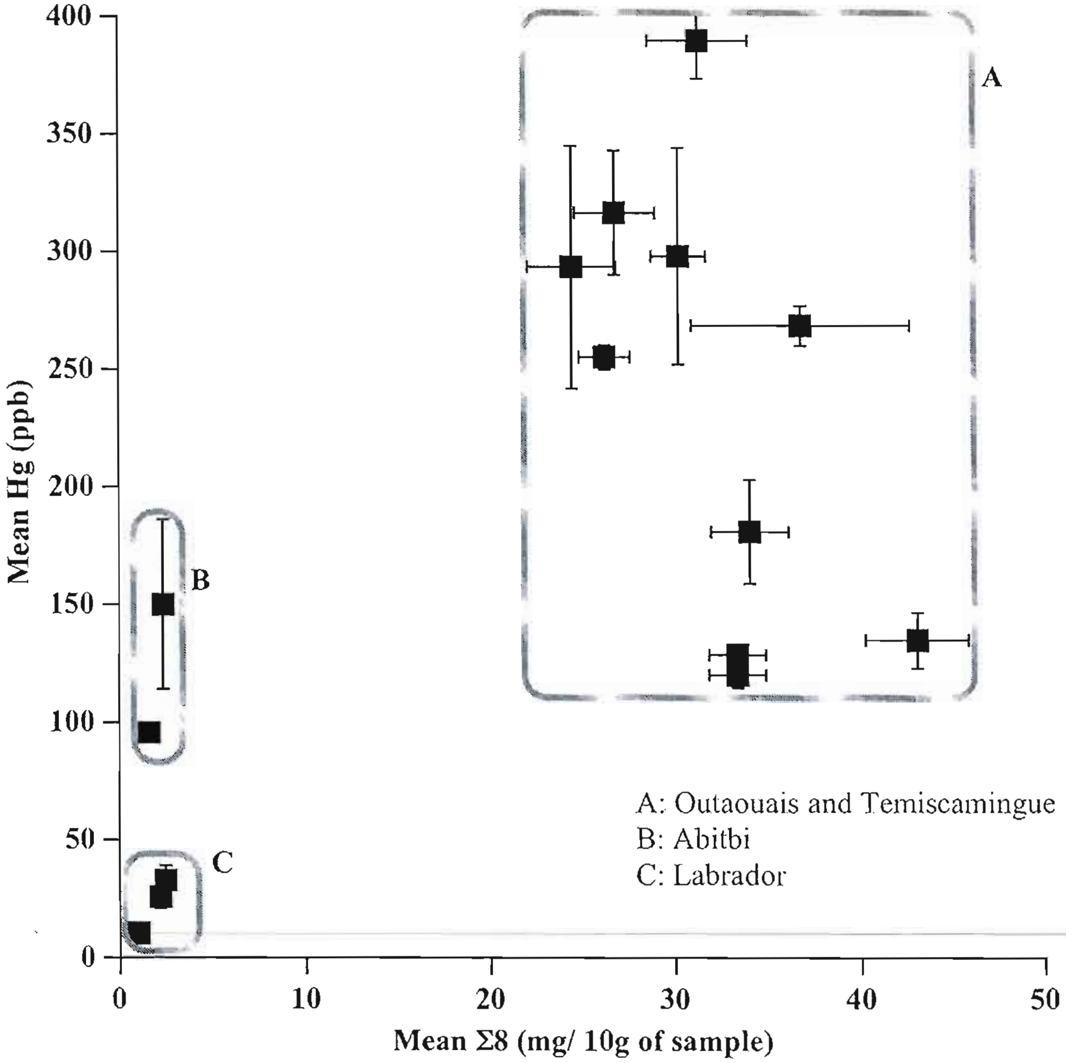

Figure 3.2 Relationship between [T-Hg] and Σ8 in recent lake sediments sampled

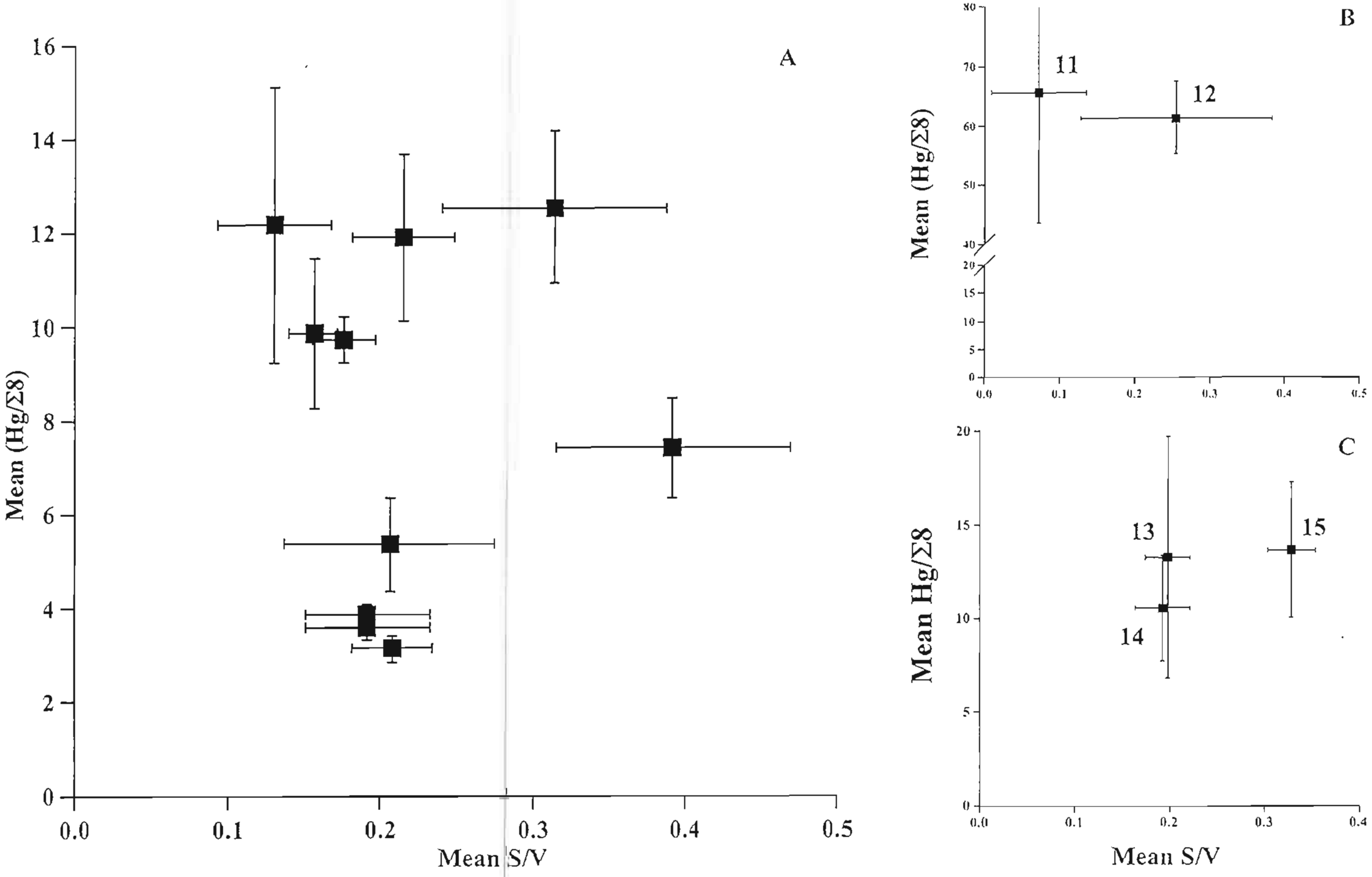

Figure 3.3 Relationship between [T-Hg]/Σ8 and S/V ratios in recent lake sediments regrouped under the three regions: A: Outaouais and Temiscamingue, B: Abitibi and C: Labrador (numbers correspond to lakes identified in fig. 3.1)

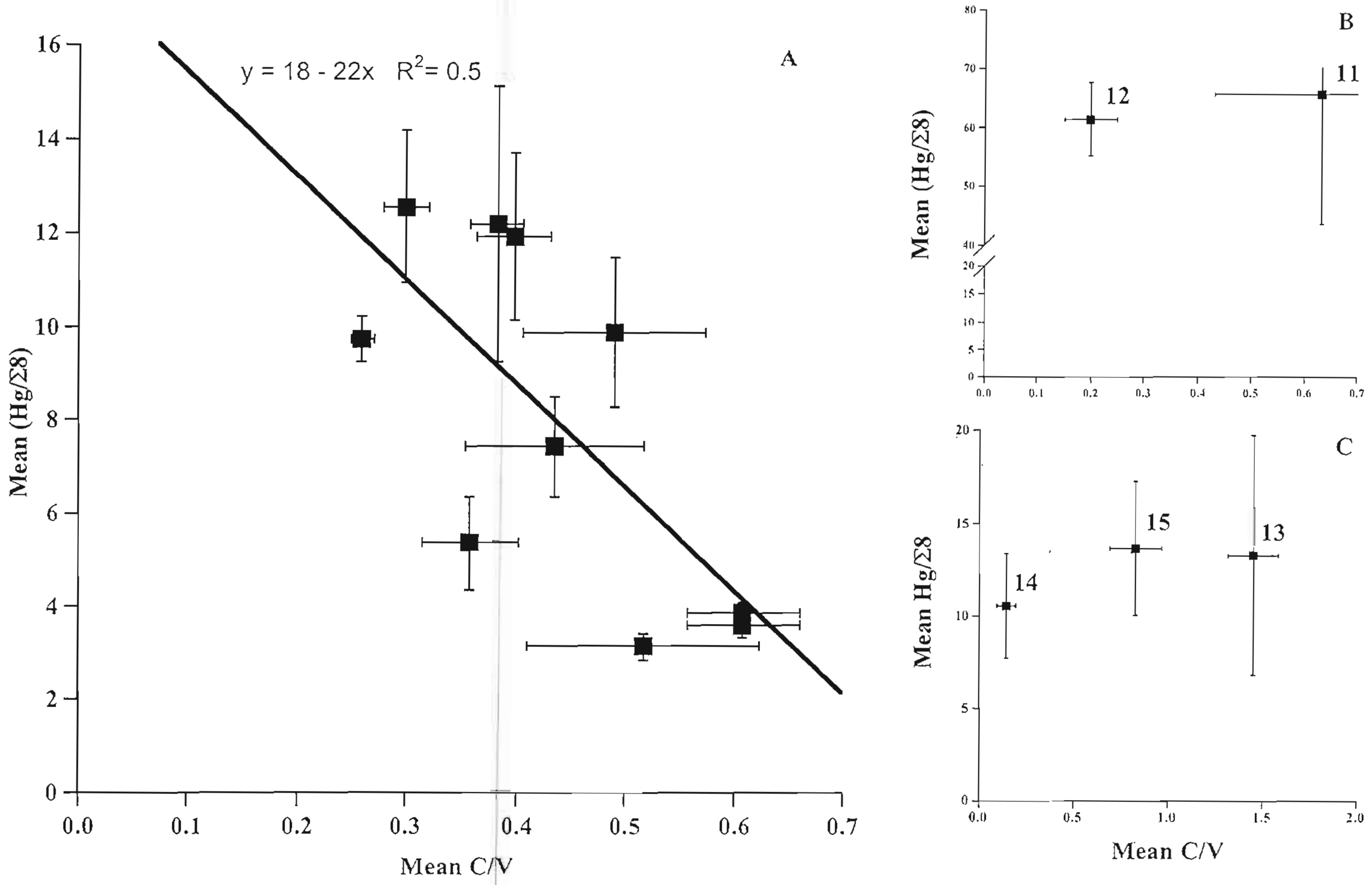

Figure 3.4 Relationship between [T-Hg]/Σ8 and C/V ratios in recent lake sediments regrouped under the three regions: A: Outaouais and Temiscamingue, B: Abitibi and C: Labrador (numbers correspond to lakes identified in fig. 3.1)

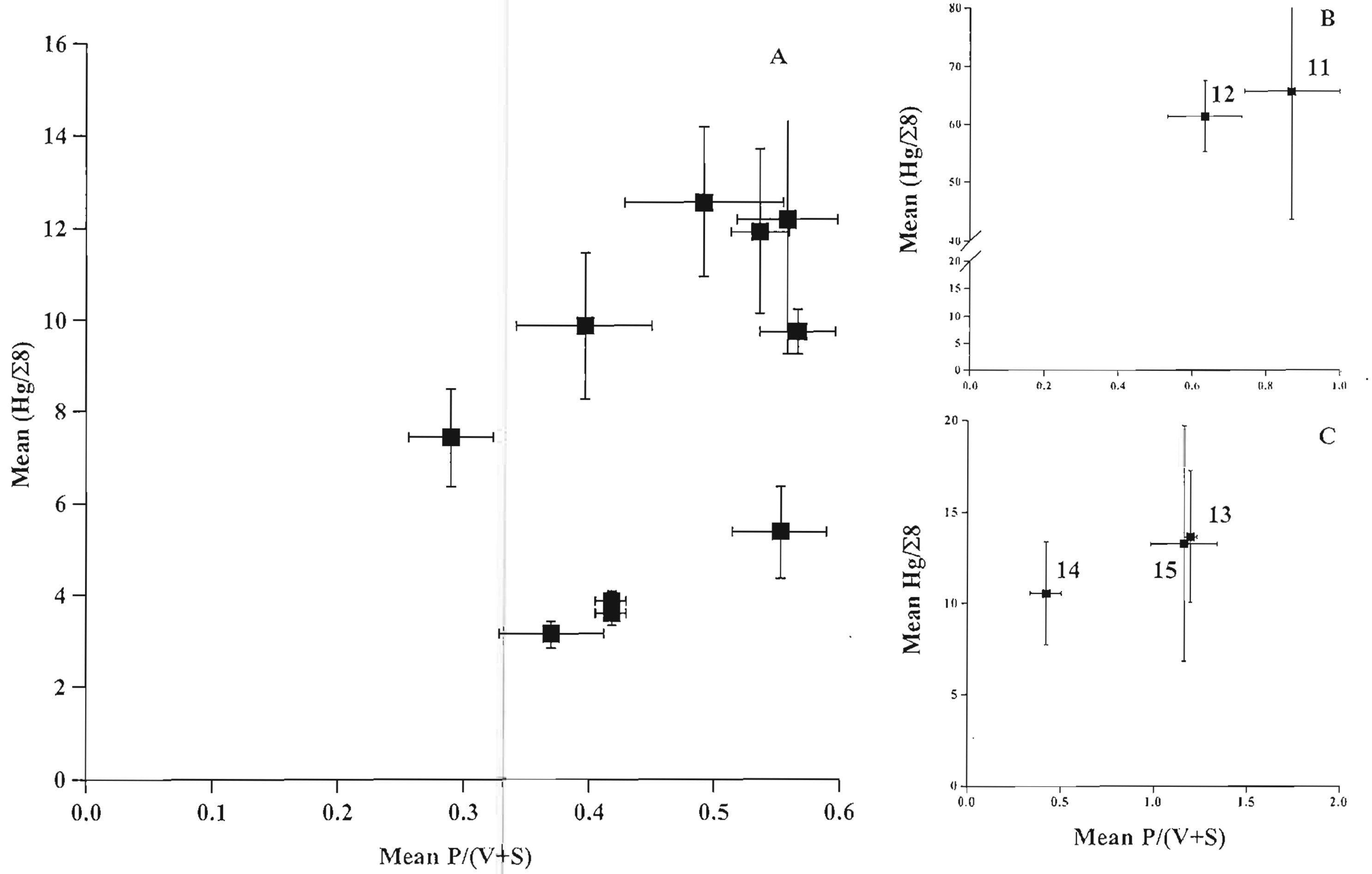

Figure 3.5 Relationship between [T-Hg]/Σ8 and P/(V+S) ratios in recent lake sediments regrouped under the three regions: A: Outaouais and Temiscamingue, B: Abitibi and C: Labrador (numbers correspond to lakes identified in fig. 3.1)

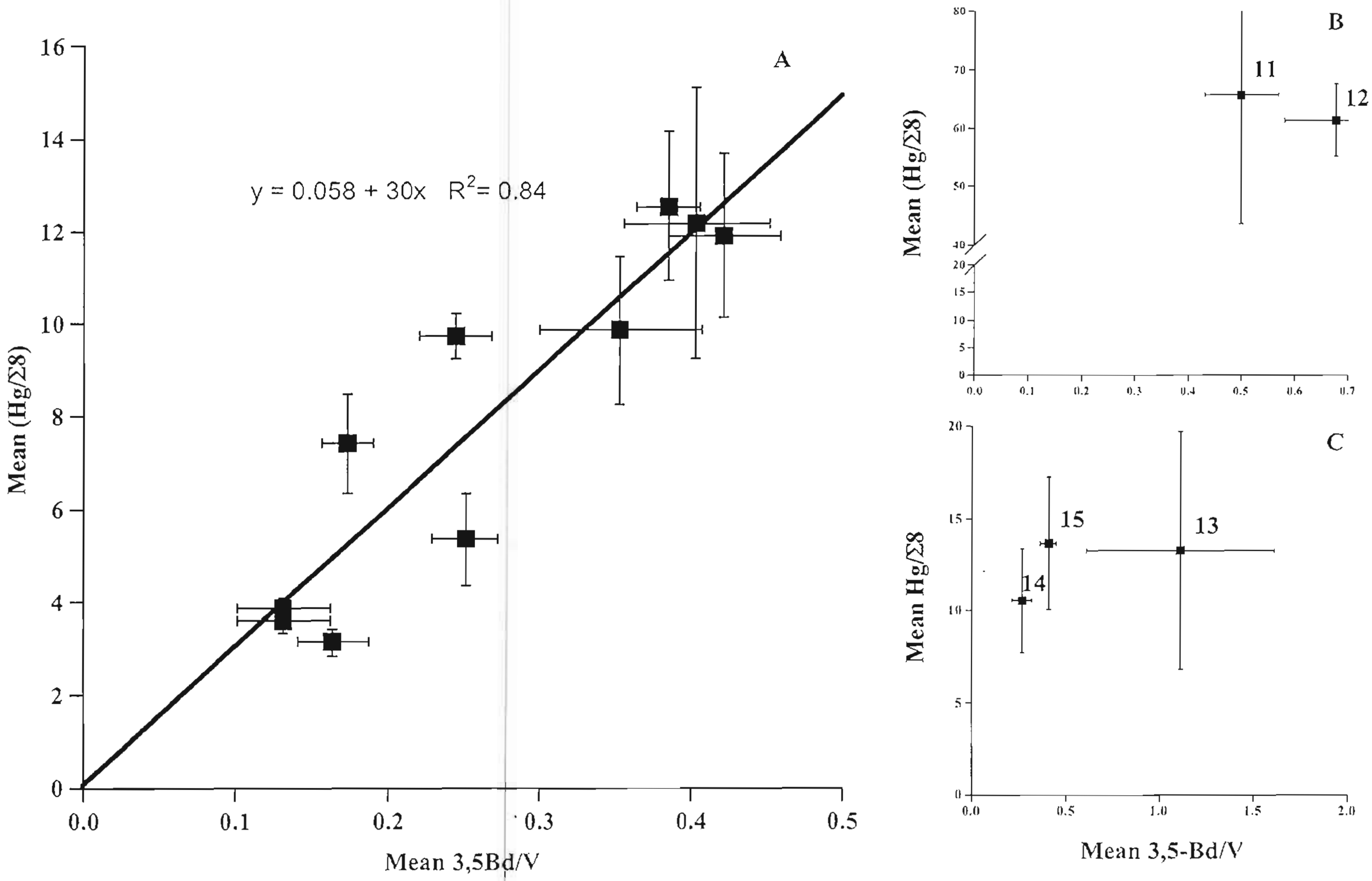

Figure 3.6 Relationship between [T-Hg]/Σ8 and 3,5Bd/V ratios in recent lake sediments regrouped under the three regions: A: Outaouais and Temiscamingue, B: Abitibi and C: Labrador (numbers correspond to lakes identified in fig. 3.1)

Chapitre IV :

Combined dynamics of mercury and terrigenous organic matter following impoundment of Churchill Falls Hydroelectric Reservoir, Labrador.

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À soumettre pour publication dans *Limnology and Oceanography*

4.1 Résumé

Les sédiments des lacs Gabbro et Sandgirt, inondés, et du lac Atikonak ont été échantillonnés pour déterminer les sources du Hg observé dans le complexe hydroélectrique de Chruchill Falls au Labrador. Les biomarqueurs de la lignine, qui sont exclusivement dérivés de la végétation terrestre, ont été utilisés comme indicateurs de source de la matière organique terrigène (TOM). Dans le lac Atikonak, qui n'a pas été modifié par l'inondation, les concentrations de Hg total ([THg]) dans les sédiments ont augmenté progressivement dans le temps. Par opposition, dans les lacs Gabbro et Sandgrit inondés, des augmentations drastiques de [THg] ont été observées après l'inondation. Contrairement au lac Atikonak, ces augmentations de [THg] dans les lacs inondés sont associées à un changement de la nature de la MOT. À la suite de la mise en eau, la proportion de MOT dans les sédiments a augmenté significativement. La composition de la MOT montre qu'elle est également moins dégradée et présente une signature typique des horizons organiques de sols forestiers. Les résultats obtenus dans cette étude démontrent que l'augmentation des niveaux de Hg dans les sédiments de réservoir est causée par l'inondation des sols forestiers et l'érosion de leurs horizons de surface. Il est également important de remarquer que les [THg] restent élevées 38 ans après la mise en eau du réservoir.

Mots clés : Réservoir, Hydroélectricité, Mercure, Biomarqueurs de la lignine

4.2 Abstract

Sediments from Gabbro and Sandgirt flooded lakes as well as Atikonak Lake were sampled to investigate the sources of Hg in the Churchill Falls Hydroelectric complex (Labrador). Lignin biomarkers, exclusively derived from terrestrial vegetation, were used as indicators of terrigenous organic matter (TOM) sources. In Atikonak Lake, which has not been impacted by flooding, total Hg concentrations (T-[Hg]) in sediments gradually increased over the recent years. In Gabbro and Sandgirt flooded lakes however, drastic increases of T-[Hg] have been observed since impoundment. In contrast to Lake Atikonak, T-[Hg] increases in the flooded lakes are associated with a change both in the quantity and the nature of TOM. Following impoundment, TOM in sediments has greatly increased. The nature of this terrigenous organic matter is also less degraded and presents a biomarker signal typical of forest soil organic horizons. The results obtained herein demonstrate that the Hg increase in the sediments of reservoirs is induced by the flooding of forest soils and their subsequent erosion and re-sedimentation. We also observe that high [Hg] are still observed 38 years after reservoir impoundment.

Keywords: Hydroelectricity, Reservoir, Mercury, Lignin Biomarkers

4.3 Introduction

The creation of reservoirs results in flooding large areas of terrestrial and aquatic ecosystems and induces major environmental impacts. Many studies have addressed these impacts, which range from drastic landscape changes to perturbations in elemental biogeochemical cycles (Louchouarn et al 1993, Kelly et al 1997, St Louis et al 2000, Hall et al 2005). One of the most widely documented changes is the alteration of the mercury (Hg) cycle. Indeed, the creation of these artificial water bodies is accompanied by increased levels of both total and methyl mercury in their water column, sediments, and biota (Anderson et al 1995, St Louis et al 2004, Lucotte et al 2005). High Hg concentrations ([Hg]) in fish are of particular concern because they may translate into high Hg exposure for subsistence or sport fishers. Hg is thus considered to represent one of the greatest environmental drawbacks of all the reservoir-induced changes. In Labrador, both the native population and sport fishers used to fish in the Churchill Falls hydroelectric complex. In order to maximise fish consumption while minimizing Hg exposure of local communities, the collaborative mercury research network (COMERN) has undertaken an ecosystem study of the mercury cycle in this reservoir. The specific objective of the current research was to determine the Hg source in the reservoir. It is well known that both anthropogenic and natural Hg can be carried to remote areas far from their point sources by atmospheric transport (Jackson 1997, Fitzgerald et al 1998). Hg is deposited via dry or wet deposition on vegetation and water surfaces. It tends to accumulate on the surface horizons of soils and ultimately leaches into the aquatic systems (Grondin et al 1995, Grigal 2002, Rencz et al 2003). Numerous studies have shown a clear increase of [Hg] in lake sediments related to anthropogenic activities since the beginning of industrial era (Lucotte et al 1995, Rognerud and Fjeld 2001). It has been shown that organic matter (OM) plays a critical role in the transfer of Hg from terrestrial ecosystem to aquatic environments (Kolka et al 1999, Kainz et al 2003, Kainz and Lucotte 2006). In reservoirs, flooded soils also constitutes an important reservoir of Hg which is usually bound to organic matter (Grondin et al 1995, Thérien et Morrison 1999). Following flooding, organic matter dynamics at the new soil-water interface are modified and may greatly influence the levels of Hg releases towards the new aquatic systems. In order to characterize these changes, we studied the evolution of the sediment records of three lakes, Sandgirt and Gabbro lakes - which are now included within the Churchill Falls Hydroelectric complex - and Atikonak Lake, which is located upstream of the reservoir. We used common biomarkers derived from mild cupric oxide (CuO) oxidation to trace organic matter behaviour and deposition. These biomarkers include lignin derived phenols and specific tannins and flavonoid-derived compounds. Formally designated as lignin biomarkers, these compounds are specific markers of terrestrial organic matter (TOM) derived from plants (Hedges and Mann 1979b, Houel et al 2006). They have also been used to trace the terrestrial origins of organic matter in many ecosystems (Hedges et al 1986, Miltner and Emeis 2000, Otto and Simpson 2006, Dalzell et al 2007). Recent studies have shown that the use of lignin biomarkers is useful in describing TOM associated with Hg (Caron et al 2008, chapter III). Our primary hypothesis is that the analysis of sedimentary deposits in a flooded lake can provide a detailed record of the change both in [Hg] and in organic matter dynamics following the impoundment of forest ecosystem.

4.4 Materials and Methods.

4.4.1 Study sites

The Churchill Falls Hydroelectric complex is located in central Labrador, Canada (figure 1). The bedrock geology in this region is dominated by gneiss and granites that belong to the Precambrian Canadian Shield (Greene 1974). Sandgirt and Gabbro lakes, which are now included in the Smallwood Reservoir, are draining the water of the Labrador plateau that lies in the Churchill geological province. Glacial retreat in this central part of Labrador occurred around 6000 years BP. The climate of central

Labrador is continental, with long snowy and severe winter. The annual precipitation is from 900 to 1100 mm and is characterised by heavy snow accumulation (300-400 cm) (Roberts et al 2006). The annual growing season lasts from 100 to 120 days. The main vegetation in this area consists of open woodland dominated by black spruce (Picea mariana) and lichen (*Cladonia rangiferina*). Soil organic horizons are thin and patchy (Engstrom 1987). Atikonak Lake, 150 km to the south of the hydroelectric complex, is located in the eastern part of the Grenville geological province (Engstrom and Hansen 1985). Its watershed is located at the northern limit of the boreal forest. Black spruce and lichen still dominate the landscape. However, the tree density is higher and organic horizons of soils are thicker. Peatlands also dominate the landscape in both areas along with small and shallow lakes.

Built between 1966 and 1974, the Churchill Fall Hydroelectric Complex constitutes the second largest series of reservoirs in the world, with a surface area of 6650 km^2. Created by damming the Churchill river and the derivation of the Naskapi river, the reservoir is composed of 88 dikes and is divided into three water bodies regulated by three control structures: the Forebay reservoir, the Smallwood reservoir and the Ossokmanuan reservoir. Lake Sandgirt is included within Smallwood reservoir and Lake Gabbro within Ossokmanuan reservoir. A proportion of 40% and 25% respectively of the flooded surface of the Smallwood and Ossokmanuan reservoirs are composed of flooded land, which were once forest, muskeg and barrens (Duthie and Ostrofsky 1974). The drainage area of the complex is now 69000 km^2 including diversions.

4.4.2 Sampling

Sediment cores were sampled using a pneumatic Mackereth corer (Mackereth 1958) at the focal point of each three lakes. The technique consists of inserting a 1-meter long Plexiglas tube (diameter 10 cm) into the sediment using compressed air. This corer offers the advantage of producing very few perturbations at the water-sediment interface. Sediment cores were then sub-sampled in 20 mL glass vials (pre-combusted at 500°C for 3 hours and capped with Teflon® liners) every centimeter with a Teflon® spatula. To avoid cross contamination between samples, the sediment contour in contact with the corer was removed. The samples were then freeze-dried prior to analysis. The core lengths were 25 cm, 45 cm and 50 cm in Sandgirt, Atikonak and Gabbro lakes respectively.

4.4.3 Chemical analysis

Sediment samples were homogenized manually with an agate mortar grinder before total carbon and nitrogen analysis using a Carlo Erba (NA-1500) elemental analyzer. The analyses carried out in duplicate show a reproducibility of ±5%. Molecular biomarker analyses were performed according to the copper oxidation (CuO) method initially developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). Briefly, sediment samples are weighed to include 3 to 10 mg of organic carbon in reaction vessels, 3.2 mL stainless steel pressure minibombs from Prime Focus®. Samples are oxidized with CuO in a 2 mol L^{-1} NaOH solution and in the absence of O_2 at 150°C for 150 min in a modified GC oven. Once the mini-bombs are opened, known amounts of ethyl vanillin are added to the solution as internal standards. The aqueous solutions are then acidifed to pH 1 with concentrated HCl and extracted with ethyl acetate. After evaporation in centrivap coldtrap, reaction products are dissolved in pyridine and derivatized with BSTFA/TMCS to form trimethylsilyl derivatives. Extraction products are then analyzed on a GC/MS system (VARIAN 3800/Saturn 2000) fitted with a fused capillary column (Varian FactorFour VF-1ms 60 m, 0.32 mm). We analyzed and quantified 12 compounds which are classified in 5 groups: 1) Cinnamyls (C) (coumaric acid, (p-Cd) and ferulic acid (Fd)), 2) Syringyls (S) (syringin (Sl), acetosyrigon (Sn) and syringic acid (Sd)), 3) Vanillyls (V) (vanillin (Vl), acetovanillon (Vn) and vanillic acid (Vd)), 4) Para-hydroxyphenols (P) (p-hydroxybenzaldehyde (Pl), p-hydroxyacetophenon (Pn) and p-hydroxybenzoic acid (Pd)) and 5) 3,5-dihydroxybenzoic acid (3,5Bd).

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

4.4.4 Statistical Analysis

Statistical tests were applied to compare sediment profiles between recent sediments parameter values and baseline values. When normality was respected, we used student t test. If not, a non-parametric Wilcoxon test was applied. Level of confidence was set at 0.05.

4.5 Results

4.5.1 Mercury

Sedimentary profiles of Hg for the three lakes are presented in figure 4.2. In Atikonak Lake, a gradual increase in [Hg] is observed. The [Hg] baseline of the sediment core ranges from 80 to 100 ppb. [Hg] increase gradually to reach 220 ppb in recent sediments. The inflexion of [Hg] arises at a depth of 20 cm. The two flooded lakes show the same profile pattern with a sharp and sudden increase in [Hg] in recent sediments (last 6-7centimetres). Sandgirt and Gabbro lakes show a [Hg] baseline around 20 ppb and 90 ppb respectively, while the recent mean [Hg] increase by a factor of 7.4 and 1.6 respectively. We also observe a noticeable increase of [Hg] at centimetre 18 in Gabbro Lake, that returned smoothly to baseline concentrations in the following overlying centimeters.

4.5.2 Terrestrial organic matter

Terrestrial organic matter inputs in sediments is estimated with lambda (λ8) which is the carbon-normalized total yield of the eight lignin derived phenols - vanillin, acetovanillone, vanillic acid, syringealdehyde, acetosyringone, syringic acid, p-coumaric and ferulic acids (in mg/100mg OC) - and Σ8, expressed as a yield normalized to total dry mass of the sample (mg/10g dry weight). These two variables are used to estimate the relative amounts of total lignin in sedimentary organic matter and by extension the relative importance of terrestrially-derived organic matter in samples (Hedges and Mann 1979b, Hedges and Prahl 1993, Houel et al 2006). In Atikonak Lake, both λ8 and Σ8 are stable along the core, indicating no change in terrestrial organic matter inputs in sediments over time (figures 4.3 and 4.4). The range of λ8 variation, between 0.5 and 1 mg/100mg OC, is similar to the ones observed in previous studies of lake sediments at similar latitudes (Hedges et al 1982, Hu et al 1999, Pempkoviak et al 2006, Houel et al 2006). The Σ8 values are around 5 mg/10g dw sample on the average, which is low compared to values found by Pempkowiak et al (2006) but lies within the range of data reported by Houel et al (2006).

λ8 and Σ8 follow the same trend at the two flooded sites; with a sharp and significant increase of the two indicators in recently deposited sediments (figures 4.3 and 4.4). The increase of lignin content in sediments is more drastic in Sandgirt Lake, with baseline values of λ8 and Σ8 around 0.1 mg/100mg OC and 0.02 mg/10g dw sample respectively and with recent values up to 2 mg/100mg OC and 30 mg/10g dw sample ($p<0.0001$ and $p<0.0005$ respectively). In Gabbro Lake, the values significantly shift from 0.5 to 2.5 mg/100mg OC for λ8 ($p<0.0001$) and from 2 to 20 mg/10 dw sample for Σ8 ($p<0.0003$). In Gabbro Lake, we also observed an increase of λ8 and Σ8 centered around centimeter 18.

4.5.3 Terrestrial organic matter composition

As for $\lambda 8$ and $\Sigma 8$, the S/V and C/V ratios in the sediments of Lake Atikonak remain stable along the core (figures 4.5 and 4.6). The S/V (in turn of 0.4) and C/V (between 1 and 1.5) ratios are within the range of values found in northern ecosystems (Hu et al 1999, Houel et al 2006, chapter II). In Lake Gabbro, the S/V and C/V ratios are variable but show a decreasing trend from values of about 0.5 and 2.5 respectively in the bottom of the core to 0.2 and 0.2 respectively on the top of the core (figures 4.5 and 4.6). These variations are mainly explained by changes in the concentration of vanillyl phenols (ΣV) (figure 4.7). The ΣV follows the same trend as $\lambda 8$ and $\Sigma 8$, and is the main driver of this pattern, with a significant increase in recent sediments ($p<0.0001$). We also observed a significant increase of the syringyl phenols (ΣS) ($p<0.0005$), but not for the cinnamyl phenols (ΣC) ($p<0.86$). For Sandgirt Lake, the C/V ratios decrease significantly ($p<0.0001$), but this decrease is related to an increase of total vanillyl phenols that is proportionnaly higher than the one of cinnamyl phenols (figures 4.5, 4.6 and 4.7). In fact both of these phenol families increase significantly after flooding (figure 4.7). On the other hand, S/V ratios increase significantly. Total syringyl phenols (ΣS) are not identified at the bottom of the core and the S/V ratio is null.

In the sediments of Atikonak Lake, the P/(V+S) ratios are stable along the core, with average value of 1.28±0.06 (figure 4.8). The 3,5Bd/V ratios are also quite stable over time with a value near 1. However, between depths 28 and 31 cm, the average value for this ratio increases by around 0.50 to reach 1.50 (figure 4.9).

In the two flooded lakes, we observed the same pattern for the P/(V+S) and 3,5Bd/V ratios. The P/(V+S) and 3,5Bd/V ratios are quite variable at the bottom of the cores and are very stable above centimeter 10 and centimeter 5 in Gabbro and Sandgirt lakes, respectively (figures 4.8 and 4.9). Even if high variations in these ratios can be observed below these depths, the trend of both indicators in these lakes is to stabilize at a lower level in top cores. Again, the total vanillyl phenol content of the samples is the main force driving these variations.

4.6 Discussion

4.6.1 Identification of the flooding event in sediment record

Sedimentary record of a flooded lake holds information on both pre and post flooding event. Usually this event modifies OM dynamics in sediment and sharp increases of TOM inputs are recorded (Jackson 1988, Louchouarn et al 1993, Houel 2003). In this study, we observed such a change in organic matter dynamics (according to $\lambda 8$ and $\Sigma 8$) at centimeter 8 and centimeter 6 in Gabbro and Sandgirt lakes respectively. Indeed at these depths $\lambda 8$ increase by a factor of 2.6 in Gabbro Lake and by a factor of 17.4 in Sandgirt Lake. We then set the flooding event at these depths in the following interpretation of the results.

4.6.2 Total lignin derived phenols and mercury concentrations

The [Hg] in recent sediments of the three lakes under study are much higher than baseline levels observed in the deep sediments. Increases of [Hg] in boreal lake sediments may be explained by three principal factors. Mercury remobilisation from bottom sediments has been proposed by Rasmussen (1994) to explain part of this increase but Fitzgerald et al (1998) demonstrated that this phenomenon is very limited and cannot explain Hg enrichments observed in lake sediments of the northern hemisphere. Watershed perturbations such as forest fires, landslides, and forest logging, play a key role in the Hg cycle in boreal catchments (Munthe and Hultberg 2004, Garcia and Carignan 2005) and are usually recorded in sedimentary profiles (Caldwell et al 2000). These perturbations may influence local [Hg] in lake sediments. The last explanation for unperturbed watersheds is related to a broad scientific consensus that sedimentary Hg enrichment is mainly of anthropogenic origin (Fitzgerald et al 1998). In fact, long-range atmospheric transport and deposition brings anthropogenic Hg to remote areas far from point sources atmospheric emissions (Fitzgerald et al 1998). This newly deposited mercury is then transferred to lakes by runoff. The sediment profile of [Hg] in Atikonak Lake, which has not been impacted by damming, is a classical profile of anthropogenic Hg enrichment since the beginning of the industrial era (Louchouarn et al 1993, Lucotte et al 1995, Munthe et al 2007). Increases in [Hg] started at centimetre 20. The Hg sediment enrichment factor between recent sediments and the baseline level is 1.5. This value is within the range of values observed by Lucotte et al (1995) in lake sediment from the James Bay area. Results obtained from lignin biomarker profiles confirm that increases of [Hg] cannot be attributed to any watershed perturbation, as the terrestrial organic matter contributions to sediments have remained constant over time. Observed values of λ8 and Σ8 for Atikonak Lake sediments have remained remarkably stable over recent years. This indicates that there has been no major watershed perturbation or change in terrigenous organic matter inputs to the lake over the last decades. The relative amount of terrigenous material in sediments is comparable to the one reported in previous studies of similar ecosystems (Hu et al 1999, Houel et al 2006, chapter II).

As observed in our results, [Hg] in the sediments of Gabbro and Sandgirt lakes increase abruptly from baseline level to recent sediments. Both lakes have a drastic increase of [Hg] at centimetres 8 and 6 respectively. This increase can easily be associated with the flooding event. This conclusion is well supported by the profiles of λ8 and Σ8, which show simultaneous increases. These results denote important inputs of new terrigenous organic matter into the sediments and within the ecosystem. Thus we are able to confirm that terrigenous organic matter plays a key role controlling Hg inputs to the lakes. It also reinforces the link between organic matter and Hg in aquatic and terrestrial ecosystems found in many studies (Meili 1992, Grondin et al 1995, Lucotte et al 1995, Ouellet et al 2009, Obrist et al 2009). Shift of

OM and Hg levels is still observed after almost 40 years (1970 to present), thus registering the implementation of a new status in the two flooded lakes. The baseline values of $\lambda 8$ and $\Sigma 8$ also provide insight on the status of the lakes before flooding. Gabbro Lake had levels of terrestrial organic matter input similar to those of Atikonak Lake. This may be explained by the fact that these two lakes belong to the Atikonak River drainage basin. On the contrary, in Sandgirt Lake, which is mainly drained by the Ashuanipi River, the terrigenous organic matter inputs recorded in sediments before flooding are very low and several lignin-derived phenols have not been identified. This goes along with low levels of [Hg]. The geographical situation of the lake, in the Labrador central plateau, surrounded by small-interconnected lakes and barrens, may explain the very low level of lignin and Hg found in its sediments before flooding. Sandgirt Lake was also a particularly shallow lake before flooding with a Secchi depth of only 6 meters (Duthie and Ostrofsky 1975). The very low value of $\Sigma 8$ observed in baseline sediments of Sandgirt Lake corresponds to the fact that baseline sediments of that core were effectively essentially composed of silt and grey clay.

The increase of TOM inputs upon flooding is much more important in Sandgirt Lake than in Gabbro Lake. This is likely linked to the overall flooded area. Gabbro Lake is now included within the Ossokmanuan reservoir, with an area of 950 km^2 at maximum water level, whereas Sandgirt Lake is now part of the Smallwood Reservoir with an area of 56000 km^2. Furthermore the terrestrial flooded compartment is different in the two lakes, only 25% of the flooded area of Ossokmamuan Reservoir was composed of upland and muskeg, compared with 40% in Smallwood Reservoir (Duthie and Ostrofsky 1974). The profiles of $\lambda 8$ and $\Sigma 8$ for Gabbro Lake also seem to indicate a major perturbation of the watershed several years before flooding. This event modified the ecosystem dynamics for some time before a return to the baseline level, in respect to organic matter inputs. The same perturbation also impacted [Hg] in sediments. These simultaneous increases in TOM and Hg in sediment may be related to a severe forest fire (Nelson et al 2007). Forest fires induce an increase in soil leaching and a release of organic matter and associated contaminants (Caldwell et al 2000). These changes last for several years as the forest regenerates and slowly grows back into a mature forest.

4.6.3 Terrestrial organic matter origin

TOM origin can be determined according to values of S/V and C/V ratios. The ratio of syringyl to vanillyl phenols (S/V) has been broadly used to distinguish between angiosperm and gymnosperm plants, considering that only angiosperm plants produce syringyl phenols (syringealdehyde, acetosyringone, syringic acid)(Hedges and Mann 1979a). The ratio of cinnamyl to vanillyl phenols (C/V) is commonly used as a source indicator, because non-woody plants and leaves produce much more cinnamyl phenols (ferulic acid and p-coumaric acid) than the woody part of plants. Meanwhile, vanillyl phenols are ubiquitous in all terrestrial plants (Hedges and Mann 1979b).

P/(V+S) ratios are used as indicators of the state of degradation of terrigenous organic matter. In fact, diagenetic demethylation leads to a selective loss of methoxylated phenol groups of vanillyl and syringyl phenols. The p-hydroxy phenols yield is not affected by demethylation and the P/(V+S) ratios should increase with higher states of degradation (Dittmar and Lara 2001). The 3,5Bd is a common CuO oxidation product found in natural samples from sediment and soils (Ugolini et al 1981, Prahl et al 1994, Louchouarn et al 1999, Farella et al 2001, Houel et al 2006), but not from fresh vascular plant tissues (Ugolini et al 1981). It has been suggested that this compound is a product of pedogenesis and could be directly linked to lignin degradation. In terrestrial and freshwater ecosystems, the 3,5Bd has been proposed as an indicator of SOM origin (Pralh et al 1994). The likely precursors of this phenolic product are tannins and other flavonoids with hydroxy groups at hand in alternate positions on the aromatic rings (Goñi and Hedges 1995). Because tannin-like materials tend to accumulate within decaying cells (de Leeuw and Largeau 1993), the relative increase of this compound in the mineral horizons of soils may be related to the extent of degradation and humification of fresh vascular plant tissues (Houel et al 2006, chapter I). The TOM quality had remained constant in the sediments of Atikonak Lake. Indeed, S/V and C/V profiles remain stable along the cores. Since this is a descriptor of terrestrial plant composition, we can conclude that no major changes have occurred trough the last decades covered by the sedimentary profile in the watershed of this lake. The value of S/V ratio is relatively high for such a northern ecosystem. Given that only angiosperm plants produce syringyl monomers, we expected to observe lower S/V ratios in sediments. However, in a previous study, we found that spruce forests may produce significant amounts of syringyls monomers (chapter I). Furthermore, leaching and sorption processes occurring in soils may greatly influence S/V and C/V ratios found in the water column and sediments (Hernes et al 2007). The C/V ratios measured in sediments are also higher than values found in boreal forest soils. However, Hu et al (1999) have found similar ratios in lake sediments and were able to link them to pollen produced by Picea mariana (C/V=13.2), the dominant tree species in the studied region. Herbaceous species from peatlands may also contribute to these elevated C/V ratios. The P/(V+S) and 3,5Bd/V ratios in Atikonak Lake sediments indicate that TOM is highly degraded and has undergone major humification processes. Signatures observed in sediments are similar to the ones of inorganic horizons of spruce soils (chapter I). These values are usually associated with low mean slope watersheds (chapter II).

In Gabbro Lake, the S/V and C/V ratios in sediment profiles are driven by the change of vanillyl phenols content. Following impoundment, the total yield of vanillyl phenols increased much more than the C and V phenols families. This leads to a decrease in both S/V and C/V ratios, which remain constant in the new water body sediments. The relative rise of vanillyl phenols compared with cinnamyl and syringyl phenols may be explained by the flooding of vast areas of forest and soil. Indeed, whereas C and S are specific to certain classes of plants; V are ubiquitous to all terrestrial plants (Hedges and Mann 1979a). In Sandgirt Lake, the absence of syringyl phenols before flooding and their presence in recent sediments caused an important increase in this ratio. However, the values observed after flooding remain low and are characteristic of coniferous boreal forest soils. The C/V ratios are lower after flooding; however the C/V values before flooding are not consistent as their variations are only due to the presence or absence of the various lignin phenols analysed.

The P/(V+S) and 3,5Bd/V ratios are also affected by the variable contribution of vanillyl phenols. However, the simultaneous decrease of these two ratios suggests inputs of TOM which is less degraded in sediments following flooding. The remobilisation of organic carbon from surface horizons of soils may explain these low ratios. Indeed we used the mixing model proposed by Houel et al (2006) to test the hypothesis of an increase of the proportion of sedimentary organic matter originating from surface soil horizons. This model is a simple two end-members mixing equation to characterize the change in lignin signature from soil horizons (soil litter vs. mineral soil). We tested this model with λ6 (mass-normalized sum of three vanillyl phenols (V) and three syringyl phenols (S)) and 3,5Bd/V as the fit with this two indicators was better than with the λ6 and P/(V+S) indicators, similarly to observations made by Houel et al (2006). In this mixing model, λ6 is used instead of λ8 because of high variability of cinnamyl phenol pools characteristic of many herbaceous tissues and pollens (Opsahl and Benner 1995, Kuo et al 2008). We used the mass-normalised yield of each indicator measured in surface organic spruce stand soil horizons and in deep mineral soil horizons from James Bay (chapter I). The data are presented in Table 4.1. According to this model, recent sediment in Gabbro and Sandgirt lakes have increased inputs from soil surface horizons (figure 4.10). Whereas deep sediments are mainly composed by degraded constituents characteristic of soil organic matter sorbed on fine particles (>99% in the two lakes) (Louchouarn et al 1999, Houel et al 2006), recent sediment received significant proportion of fresh surface litter (between 5 and 20%). Considering that high concentrations of mercury in boreal forest are observed within organic horizons of soils (Grondin et al 1995), these results confirm the postulate that the whole biogeochemical cycle of Hg is tightly coupled to the cycle of organic matter (Lindqvist et al 1991, Meili 1991).

Finally, the observed profiles, since 1970, of each indicator and [Hg] following the flooding in Gabbro and Sandgirt lakes suggest that flooded soils are still the major reservoir of mercury and organic matter in the sediments of these former lakes. Previous studies have shown that remobilization of flooded soil organic matter and mercury are limited to the first years after perturbation (Louchouarn et al 1993, Grondin et al 1995, Houel et al 2006). This occurs essentially because the remobilization is limited to drawdown zone and areas of low depth where wind and waves impact lake bottom. The Churchill Falls hydroelectric complex is located on the Labrador plateau characterized by low mean slope. Mean depth of the reservoir is low and average drawdown is around 4 m in the Smallwood Reservoir and 3.5 m in the Ossokmanuan Reservoir (Duthie and Ostrofsky 1974). These particular characteristics imply that large areas of soils are potentially remobilised regularly and may explain why flooded soils still bring Hg and SOM almost 40 years after impoundment.

4.7 Conclusion

This study demonstrates, through TOM biomarkers analysis, that the flooding of lakes with reservoir impoundment causes an increase of Hg levels in sediments of flooded lakes. This increase is associated with increasing inputs of TOM. These shifts in OM and Hg levels are still observed after forty years of flooding. We also observed that TOM and Hg inputs were higher in Sandgirt Lake than in Gabbro Lake. These results demonstrate the importance of the overall flooded area on Hg and TOM dynamics. The nature of this terrigenous organic matter is also less degraded and presents a biomarker signal typical of forest soil organic horizons. Finally, in boreal reservoirs, Hg levels in fish are generally high following the impoundments and tend to decrease, to values comparable to adjacent lakes, 10 to 20 years after the reservoir creation (Verdon et al 1991). However in the Smallwood reservoir, Anderson et al (1995) showed that this decrease is not observed for northern pike (*Esox lucius*) and lake trout (*Salvelinus namaycush*) and that Hg levels in flesh stayed high for almost 20 years. We observed in sediments records that level of Hg and freshness of organic matter are lasting for years in the new water bodies. This observation is probably related to the fact that this hydroelectric complex is very wide and composed of vast area of shallow water zones where soil erosion is still occurring after decades of impoundment (Louchouarn et al 1993). This reservoir particularity has potentially long term impact on [Hg] in fish.

4.8 Acknowledgments

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4.10 Figures and table

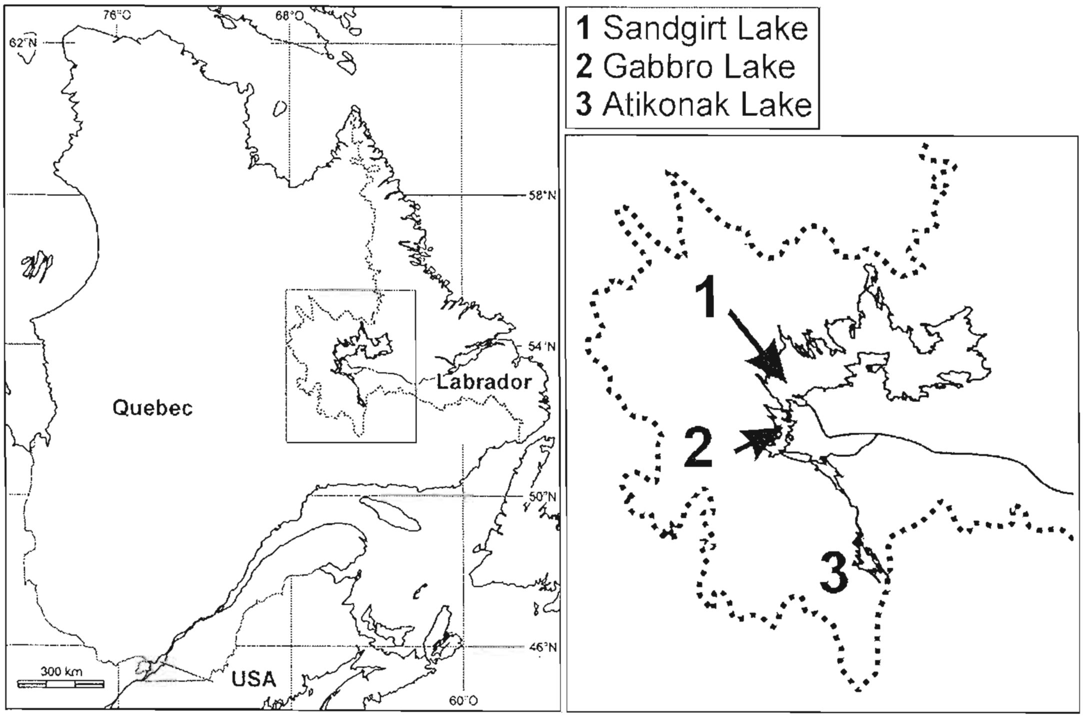

Figure 4.1 Map of sampled sites

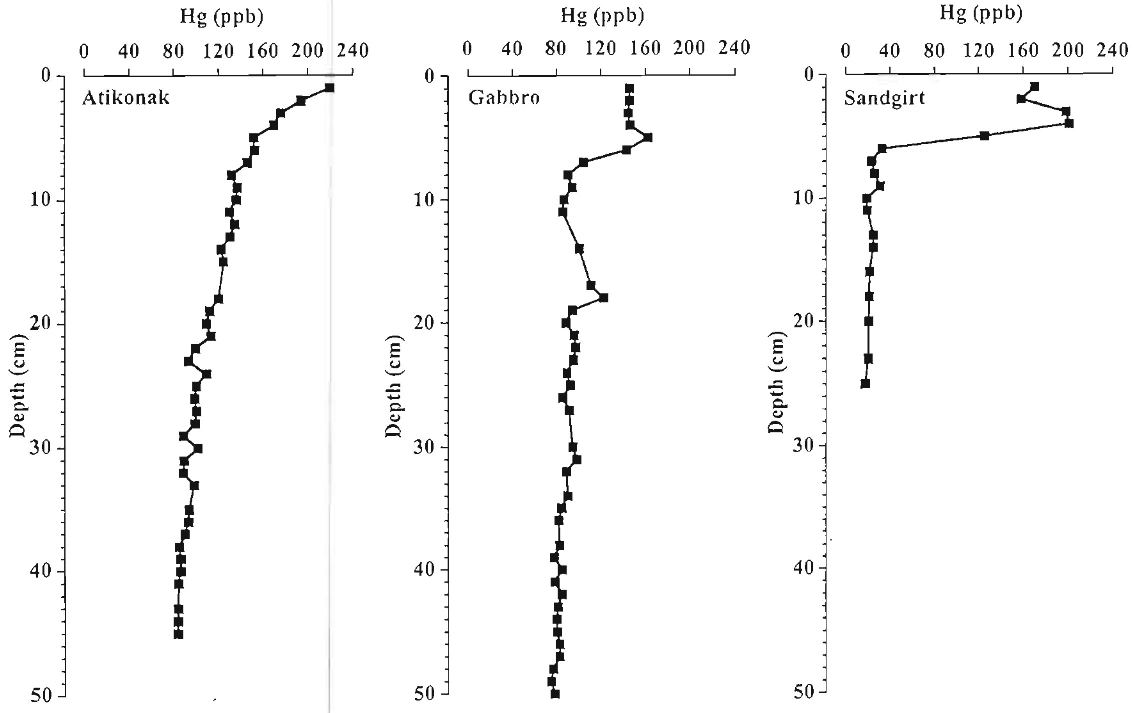

Figure 4.2 Sedimentary profiles of Hg (ppb) in the three lakes.

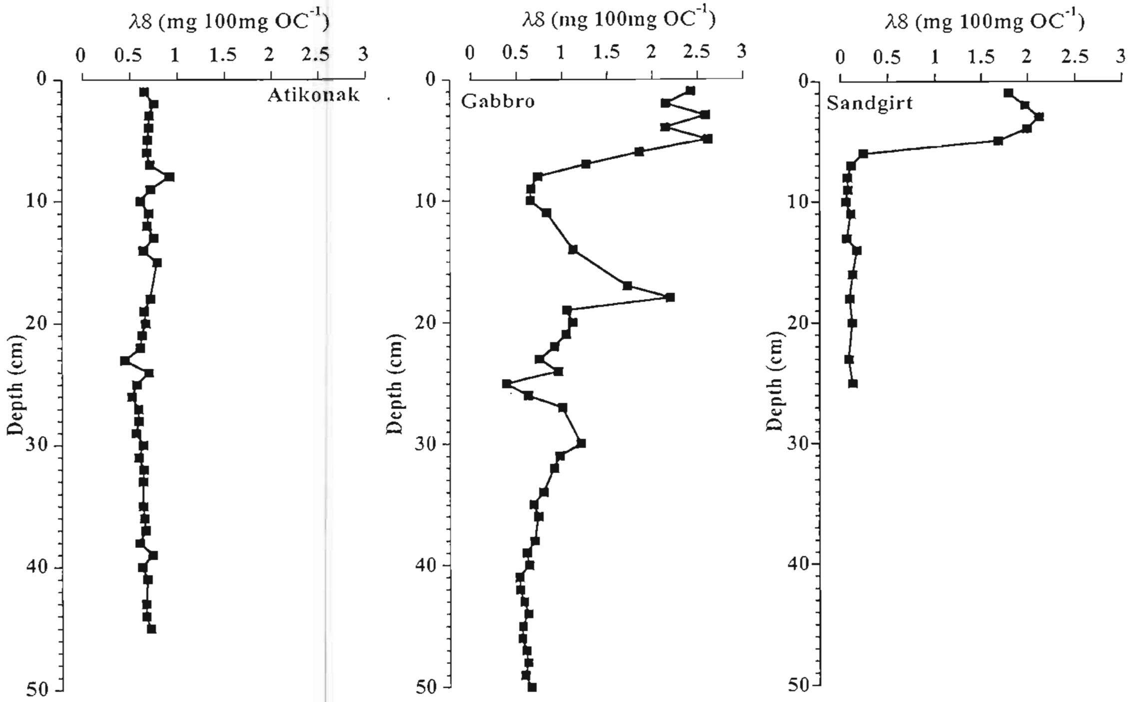

Figure 4.3 Sedimentary profiles of λ8 (mg/100mg OC).

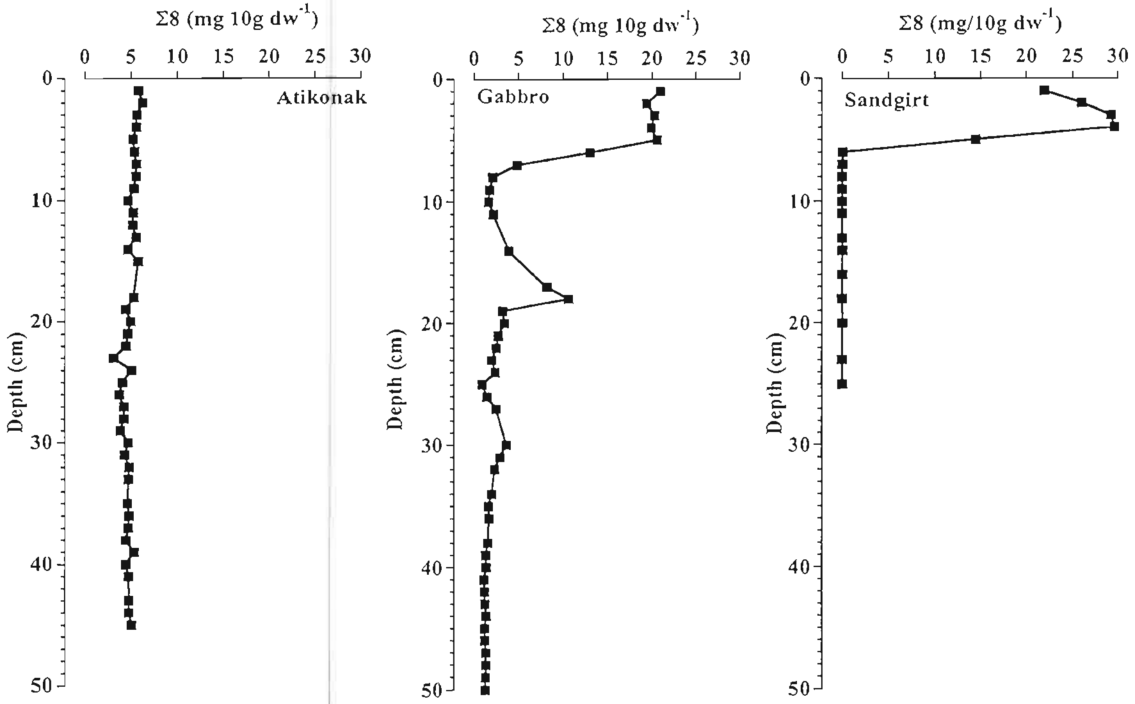

Figure 4.4 Sedimentary profiles of Σ8 ratios (mg/10g dw).

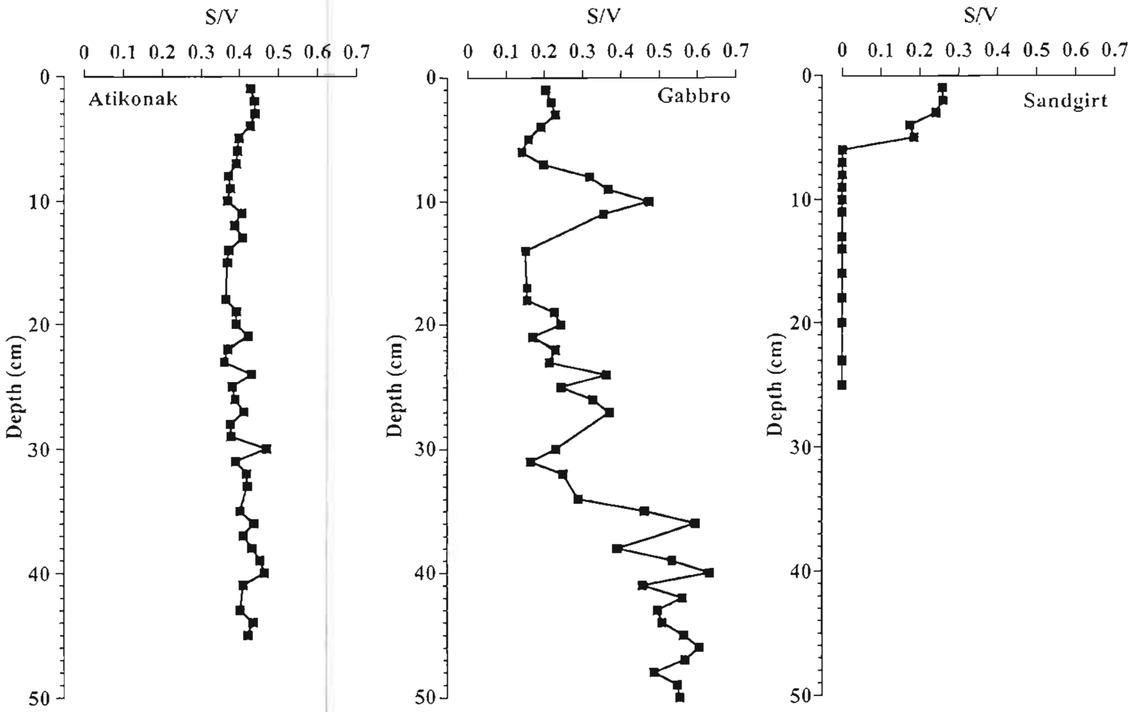

Figure 4.5 Sedimentary profiles of S/V ratios.

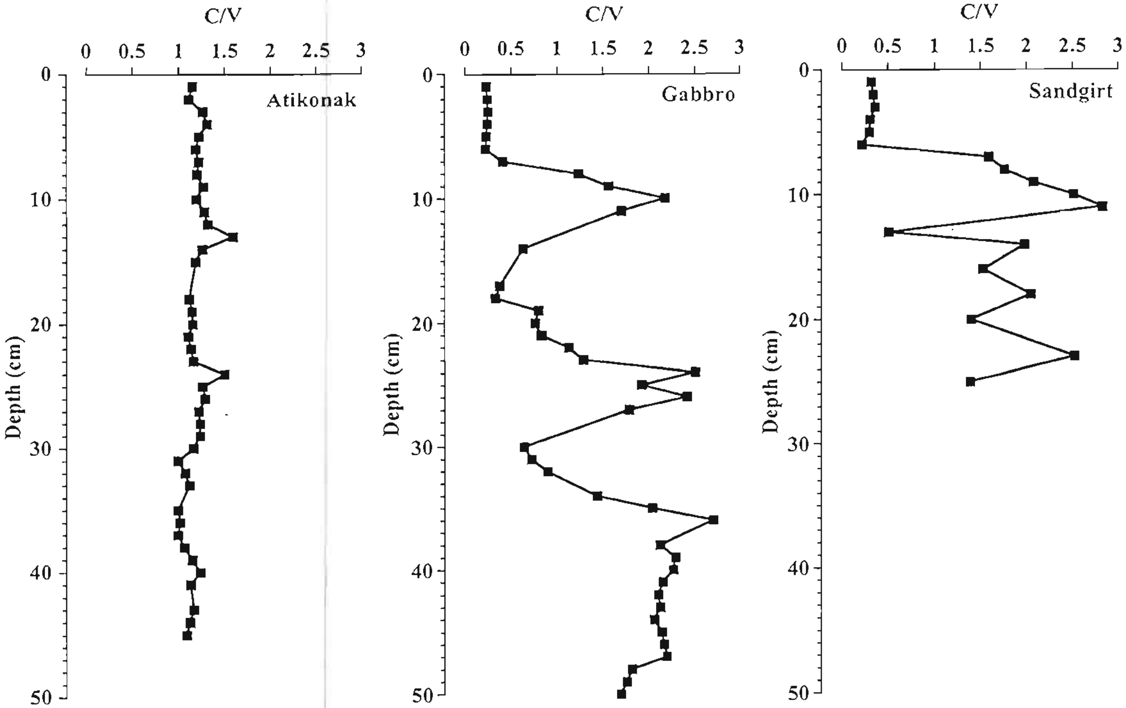

Figure 4.6 Sedimentary profiles of C/V ratios.

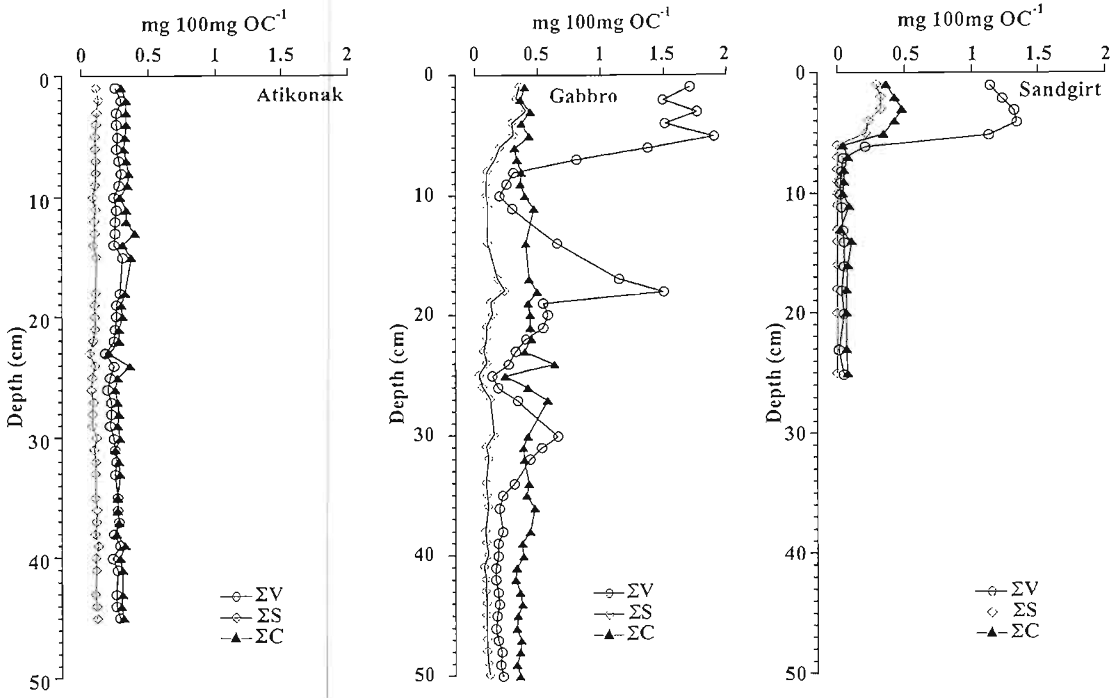

Figure 4.7 Sedimentary profiles of ΣV, ΣS and ΣC (mg/ 100mg OC).

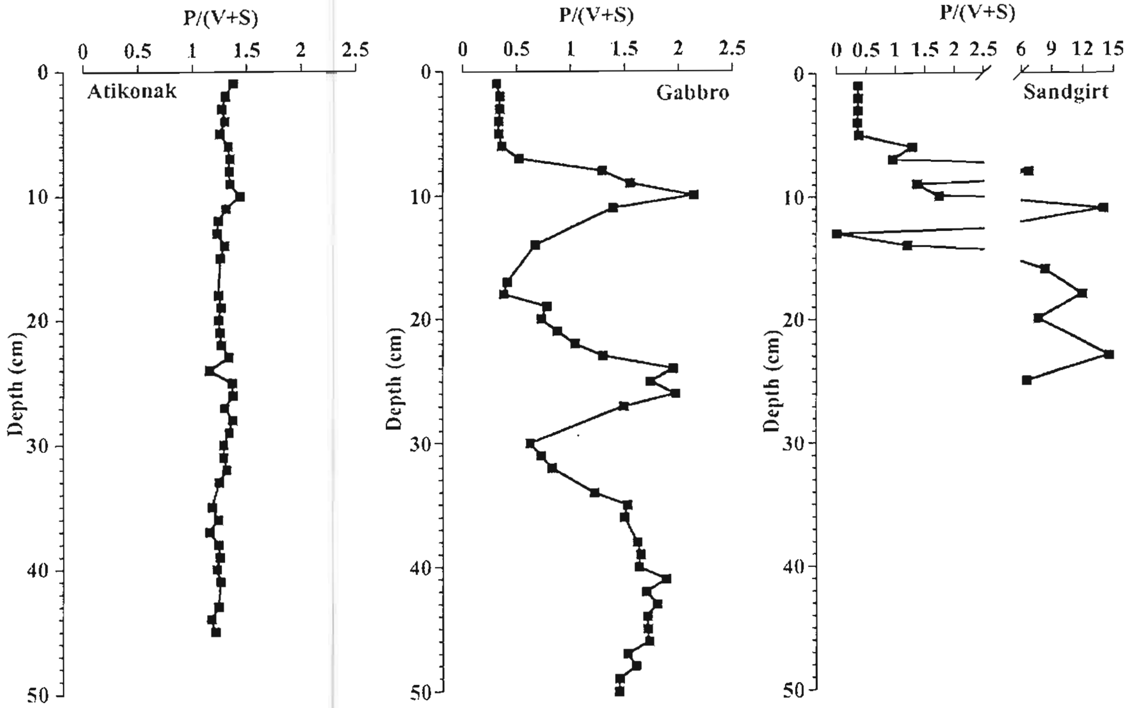

Figure 4.8 Sedimentary profiles of P/(V+S) ratios.

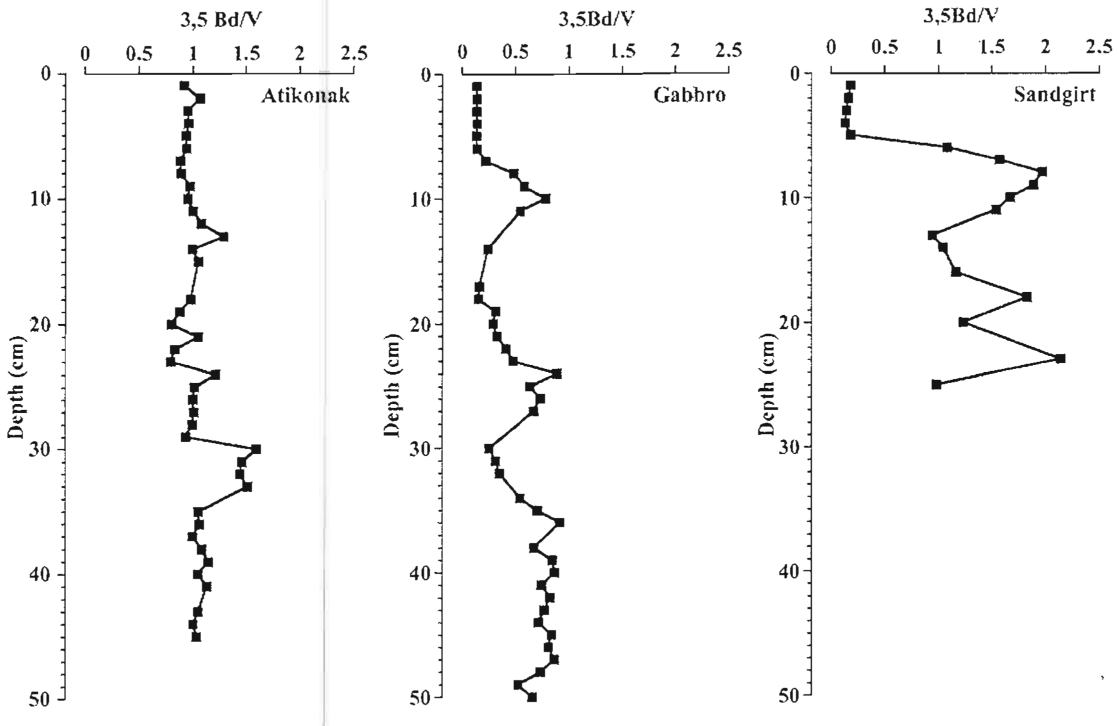

Figure 4.9 Sedimentary profiles of 3,5Bd/V ratios.

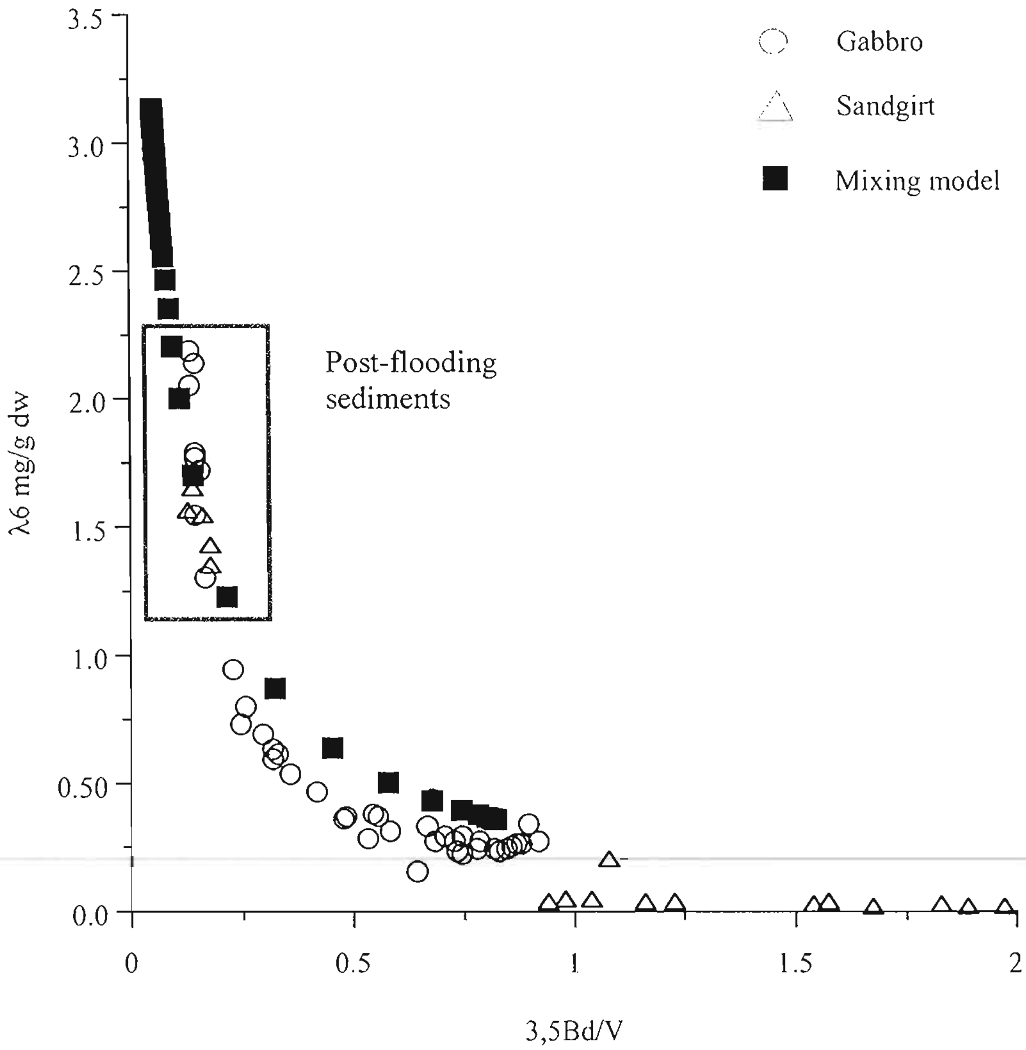

Figure 4.10 Biomarkers signatures in Gabbro and Sandgirt sediments and comparison to theoretical values based on a mixing model between surface litter and deep mineral SOM end-members.

Table 4.1
Mass normalized concentration of biomarkers used as end-member in the mixing-model mg.(g dw)$^{-1}$. Data compiled from previous study (chapter I).

	λ6	ΣV	3,5Bd
Surface organic horizon (n=18)	12.9 ± 3.6	6.5 ± 2.1	1.1 ± 0.4
Deep mineral horizon (n=28)	0.12 ± 0.05	0.11 ± 0.09	0.08 ± 0.05

Conclusion générale

Cette thèse regroupe les résultats et interprétations de quatre études portant sur la dynamique de la matière organique terrigène (MOT) (chapitre I, II, III et IV) et du mercure (Hg) (chapitre III et IV) dans l'environnement boréal. L'objectif général de la thèse était de faire avancer les connaissances sur la contamination des lacs de la forêt boréale par le Hg. L'approche proposée a reposé sur l'analyse au niveau moléculaire de biomarqueurs ligneux spécifiques de la MOT, principal vecteur du Hg dans les environnements lacustres (Kolka et al 1999, Grigal 2003). La première étude a porté sur la définition d'un cadre de référence pour les biomarqueurs de la lignine afin d'optimiser leur utilisation en milieu lacustre. Dans un deuxième temps, la composition en biomarqueurs de la lignine des sédiments récents de lacs a été comparée aux caractéristiques morphoédaphiques du bassin versant. Dans le troisième chapitre, les teneurs en Hg des sédiments récents ont été mises en perspective avec les différentes caractéristiques de la MOT retrouvée dans ces sédiments. Finalement, les biomarqueurs de la lignine ont été utilisés pour déterminer l'origine de la contamination par le Hg d'un réservoir hydroélectrique. Les principales conclusions de chaque chapitre sont résumées ci-dessous.

Les sols ont été choisis comme milieu de référence pour les biomarqueurs de la lignine parce qu'ils jouent un rôle intégrateur et d'interface clé entre la végétation et les milieux aquatiques (Meyers et Ishiwatari 1993, Opsahl et Benner 1995). Dans cette étude, nous démontrons que la définition d'une base de donnée des biomarqueurs dans les sols permet de caractériser précisément l'origine et l'état de dégradation de la MOT. En premier lieu, les rapports S/V et C/V mesurés dans les sols sont très différents des valeurs obtenues à partir des sources pures (Hedges and Parker 1976, Hedges and Mann 1979, Ertel and Hedges 1984). La gamme de valeurs obtenue est plus étroite et est similaire aux valeurs mesurées dans les milieux aquatiques (Louchouarn et Lucotte 1998, Benner et Opsahl 2001, Houel et al 2006). La distinction des trois principaux écosystèmes de la forêt boréale (forêt feuillue, forêt de conifères et tourbières) est plus aisée qu'avec les sources pures. Au-delà des indicateurs classiques, cette étude a démontré l'utilité des rapports P/(V+S) et 3,5Bd/V comme indicateur de l'évolution pédogénétique des composés dérivés de la lignine et par extension de la MOT. En effet grâce aux résultats obtenus, il est dorénavant possible d'identifier l'origine de la MOT selon son état de dégradation (P/(V+S)) et son degré d'humification (3,5Bd/V). De plus, l'évolution de ces indicateurs est similaire dans les différents sols étudiés. L'ensemble des résultats obtenus dans cette étude démontre que les biomarqueurs mesurés dans les sols sont des meilleurs indicateurs pour déterminer la source et le devenir de la MOT à l'échelle d'un écosystème bassin versant - lac. Dans la perspective de recherches futures, il serait intéressant de compléter l'échantillonnage des divers peuplements végétaux par des sources pures fraîches, dégradées et finalement de faire une analyse des lessivats de sols pour avoir le portrait complet des biomarqueurs de la lignine dans un bassin versant.

Le deuxième volet de la thèse a permis d'apporter des éléments nouveaux dans la compréhension du cycle de la MOT dans un système « lac-bassin versant ». Il démontre que les biomarqueurs de la lignine, mesurés dans les sédiments lacustres, représentent une intégration de la dynamique de la MOT provenant des bassins versants. L'utilisation d'une approche combinant les systèmes d'information géographiques et les biomarqueurs de la lignine permet de mettre en évidence des zones clés du bassin versant pour le transfert de la MOT vers les lacs. Ainsi, les zones de pentes modérées (entre 4 et 10°) et couvertes par une forêt de feuillus régulent les apports de MOT dans les sédiments, aussi bien en quantité normalisée pour le carbone organique ($\lambda 8$) qu'en qualité (P/(V+S) et 3,5Bd/V). En limnologie, l'étude de l'influence d'un bassin versant sur un lac est relativement nouvelle. Cet intérêt s'est développé autour de deux problématiques principales : la question de l'autotrophie/hétérotrophie de ces milieux et la question des perturbations anthropiques (fertilisation, contamination,...). Pour étudier les interactions lac-bassin versant, la majorité des études ont utilisé le carbone organique dissous et le carbone organique particulaire dans la colonne d'eau. Les sédiments étant généralement utilisés pour les reconstructions historiques. Nous démontrons ici que l'analyse de biomarqueurs spécifiques dans les sédiments lacustres récents permet de décrire des processus clés de la dynamique bassin versant-lac. Les résultats de cette étude permettent donc de proposer les biomarqueurs de la lignine comme outil privilégié pour appréhender la question du devenir des contaminants associés à la matière organique dans les environnements lacustres.

L'analyse des biomarqueurs de la lignine dans les sédiments lacustres récents a permis d'améliorer notre compréhension du cycle du Hg dans ces environnements. Au-delà des quantités de MOT apportées dans les sédiments, ces biomarqueurs permettent une caractérisation fine des sources et de la qualité de la MOT associée au Hg. Ainsi, la qualité de la matière organique et particulièrement son origine des différents horizons de sols jouent un rôle clé dans le transport du Hg vers les lacs. De plus, cette étude met en évidence l'influence de la composition végétale du bassin versant sur le transfert du Hg du milieu terrestre vers un lac. En utilisant une approche moléculaire, il est donc possible d'intégrer la dynamique complexe du Hg depuis son dépôt atmosphérique sur la végétation jusqu'à son transfert vers un lac. Cette étude permet de mettre en évidence les processus qui entraînent des variations d'apports de Hg entre différents lacs d'une même région. Ces conclusions doivent servir comme élément de réflexion pour améliorer les modèles de prédictions des niveaux de Hg dans la chaîne alimentaire et particulièrement dans les poissons.

L'approche moléculaire a également été retenue pour élucider les sources de Hg dans les sédiments de lacs inondés lors de la formation d'un réservoir hydroélectrique. Cette étude met en évidence une augmentation importante des concentrations en Hg après l'inondation. L'analyse des différents biomarqueurs de la lignine dans cet environnement démontre que ce Hg est associé à la remobilisation de la MOT des sols inondés. Ce résultat confirme que la MOT joue un rôle déterminant dans le devenir du Hg dans les milieux terrestres et aquatiques. Les résultats obtenus montrent également qu'un nouvel équilibre semble s'être établi puisque les accumulations sédimentaires de Hg et de matière organique restent élevés quarante ans après la perturbation. L'analyse de la MOT au niveau moléculaire permet aussi de préciser la source du Hg. Alors que peu de changements des signatures S/V et C/V sont observées, ceci signifie que la composition végétale à l'origine des apports de MOT n'a que peu évolué après la mise en eau. Par contre, les résultats obtenus pour le rapport P/(V+S) et 3,5Bd/V montrent que l'érosion des horizons de surface des sols est responsable de l'augmentation des apports en Hg. Ce résultat est confirmé par l'évolution de la signature sédimentaire des deux lacs inondés comparé à une équation de mélange entre un pôle d'horizons de sols organique et inorganique.

La récente conférence internationale sur le Hg comme polluant global (ICMGP 2009 à Guiyang, Chine) a confirmé la nécessité de comprendre et d'intégrer la dynamique du Hg à l'échelle d'un écosystème (Obrist et al 2009, Heyes et al 2009). Actuellement, la plupart des études sur le sujet sont limitées dans leurs interprétations par le fait que ce type de recherche nécessite un gros investissement matériel et financier. Dans cette thèse, nous avons privilégié une approche combinant les systèmes d'informations géographiques et les biomarqueurs qui nous a permis de mettre en évidence les facteurs clés dans le transfert du Hg depuis les milieux terrestres vers les lacs.

Dans une perspective de travaux futurs, les résultats des deux premiers chapitres pourraient être utilisés dans le développement d'un modèle dynamique et spatial de la matière organique terrigène. En effet, la composition de la matière organique terrigène, révélée par les biomarqueurs de la lignine sous les divers peuplements de la forêt boréale, pourrait être cartographiée grâce à l'utilisation de système d'information géographique. Cette cartographie des biomarqueurs permettrait de connaître la répartition spatiale du type et de la qualité de la MOT. Cette répartition spatiale pourrait être complétée d'une composante dynamique reliée aux changements d'utilisation du territoire, aux changements climatiques ou aux perturbations naturelles. Couplé aux caractéristiques topographiques de l'écosystème, il serait alors possible d'obtenir des cartes des apports potentiels de la MOT dans les lacs. Ces données auraient une utilité fondamentale en science de l'environnement permettant notamment de disposer des caractéristiques intrinsèques de la MOT dans les lacs. Ces caractéristiques pourraient être utilisées pour mieux comprendre le cycle du carbone dans ces environnements et plus spécifiquement les émissions de gaz à effet de serre, mais également le devenir des contaminants associés à la MO. Cette cartographie sera également un outil précieux dans la perspective de création d'un réservoir hydroélectrique.

Les résultats du chapitre II et III ont souligné l'importance de certaines variables morphoédaphiques. Ces résultats doivent être utilisés pour améliorer les modèles développés pour estimer la contamination des lacs et plus particulièrement des poissons par le Hg (Porvari 2003, Roué-Legall et al 2005, Beaulne et al 2009). La mise en évidence du rôle des processus pédologiques sur le devenir du Hg dans les lacs doit également encourager la recherche sur la dynamique combinée du Hg et de la MOT dans les sols. L'analyse du Hg et des biomarqueurs de la lignine dans les sols doit permettre de préciser l'association entre la MO et le Hg ainsi que leur évolution temporelle (perturbation, changement climatique). Finalement, les composés ligneux dans les sédiments et les sols possèdent le meilleur potentiel pour saisir et conserver dans le temps l'enregistrement des sources de matière organique et notamment la composition floristique source entre les angiospermes et les gymnospermes ou les tissus boisés ou non-boisés. Ces caractéristiques en font des traceurs idéaux de la MOT et donc de tous les contaminants qui sont associés à sa dynamique (Kolka et al 1999, Grigal 2002, Kainz et al 2003). Toutefois, les études ayant utilisé les biomarqueurs de la lignine pour aborder une problématique environnementale restent marginales et nous espérons que cette thèse participera à la promotion de cet outil pour les études environnementales.

Références de l'introduction et de la conclusion générale

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ANNEXE A

Table A.1

Nitrogen, Organic carbon and lignin parameters in organic and inorganic horizons of boreal soils. Abbreviations: %C, percentage of nitrogen; %OC, percentage of organic carbon; λ8, sum of 8 lignin phenols of vanillyl, syringyl, cinnamyl (mg/100 mg OC); Vl, vanillin; Vn, acetovanillone; Vd, vanillic acid; Sl, syringin; Sn, acetosyrigone; Sd, syringic acid; p-Cd, *p*-coumaric acid; Fd, ferulic acid; Pl, *p*-hydroxybenzaldehyde; Pn, *p*-hydroxyacetophenone; Pd, *p*-hydroxybenzoic acid; 3,5Bd, 3,5-dihydroxybenzoic acid; (mg/100 mg OC).

Soil horizon	Soil type	n	%N	%OC	λ8	Vl	Vn	Vd	Sl	Sn	Sd	p-Cd	Fd	Pl	Pn	Pd	3,5Bd
Organic	Maple	6	1.86 ± 0.33	43.37 ± 5.87	7.08 ± 2.90	1.90 ± 0.39	0.78 ± 0.18	1.86 ± 0.88	0.74 ± 0.57	0.57 ± 0.75	0.60 ± 0.57	0.24 ± 0.16	0.11 ± 0.05	0.23 ± 0.05	0.07 ± 0.01	0.21 ± 0.05	0.22 ± 0.04
	White birch	8	1.55 ± 0.30	44.94 ± 8.39	5.12 ± 1.01	1.72 ± 0.44	0.62 ± 0.18	1.47 ± 0.55	0.42 ± 0.28	0.17 ± 0.10	0.26 ± 0.13	0.17 ± 0.06	0.10 ± 0.05	0.26 ± 0.04	0.07 ± 0.01	0.23 ± 0.05	0.25 ± 0.08
	Yellow birch	8	1.59 ± 0,37	44.26 ± 7.93	3.52 ± 1.49	0.98 ± 0.70	0.38 ± 0.16	0.82 ± 0.44	0.44 ± 0.22	0.23 ± 0.11	0.21 ± 0.10	0.13 ± 0.03	0.19 ± 0.14	0.17 ± 0.05	0.05 ± 0.01	0.13 ± 0.04	0.17 ± 0.03
	Spruce	28	1.16 ± 0.31	46.10 ± 6.53	2.14 ± 1.46	0.75 ± 0.59	0.27 ± 0.22	0.46 ± 0.47	0.16 ± 0.18	0.06 ± 0.07	0.06 ± 0.06	0.12 ± 0.07	0.24 ± 0.13	0.13 ± 0.13	0.08 ± 0.07	0.10 ± 0.09	0.24 ± 0.08
	Peat	6	1.37 ± 0.77	42.41 ± 3.97	3.82 ± 2.35	0.81 ± 0.45	0.33 ± 0.19	0.72 ± 0.64	0.59 ± 0.60	0.29 ± 0.29	0.38 ± 0.38	0.36 ± 0.32	0.11 ± 0.07	0.51 ± 0.10	1.15 ± 0.86	0.56 ± 0.27	0.20 ± 0.10
Inorganic	Maple	7	0.17 ± 0.08	2.99 ± 1.40	1.83 ± 0.93	0.60 ± 0.38	0.22 ± 0.11	0.43 ± 0.23	0.20 ± 0.16	0.09 ± 0.06	0.14 ± 0.11	0.04 ± 0.02	0.04 ± 0.02	0.14 ± 0.07	0.03 ± 0.01	0.13 ± 0.05	0.17 ± 0.10
	White birch	9	0.14 ± 0.08	2.91 ± 1.80	1.80 ± 0.78	0.49 ± 0.22	0.24 ± 0.11	0.60 ± 0.37	0.11 ± 0.06	0.06 ± 0.03	0.09 ± 0.05	0.10 ± 0.12	0.05 ± 0.03	0.16 ± 0.09	0.05 ± 0.03	0.20 ± 0.10	0.25 ± 0.09
	Yellow birch	24	0.15 ± 0.07	3.12 ± 1.65	1.30 ± 0.96	0.33 ± 0.31	0.18 ± 0.15	0.55 ± 0.54	0.11 ± 0.14	0.06 ± 0.06	0.08 ± 0.07	0.07 ± 0.11	0.03 ± 0.05	0.12 ± 0.08	0.04 ± 0.05	0.25 ± 0.53	0.39 ± 0.51
	Spruce	18	0.11 ± 0.04	2.63 ± 1.70	0.76 ± 0.39	0.16 ± 0.15	0.07 ± 0.04	0.17 ± 0.11	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.26 ± 0.17	0.06 ± 0.04	0.17 ± 0.06	0.14 ± 0.10	0.16 ± 0.06	0.44 ± 0.18
	Peat	10	1.55 ± 0.77	42.51 ± 8.33	3.64 ± 1.83	0.83 ± 0.39	0.36 ± 0.19	0.86 ± 0.72	0.38 ± 0.21	0.17 ± 0.08	0.27 ± 0.24	0.47 ± 0.31	0.10 ± 0.02	0.48 ± 0.09	0.87 ± 0.74	0.54 ± 0.20	0.25 ± 0.10

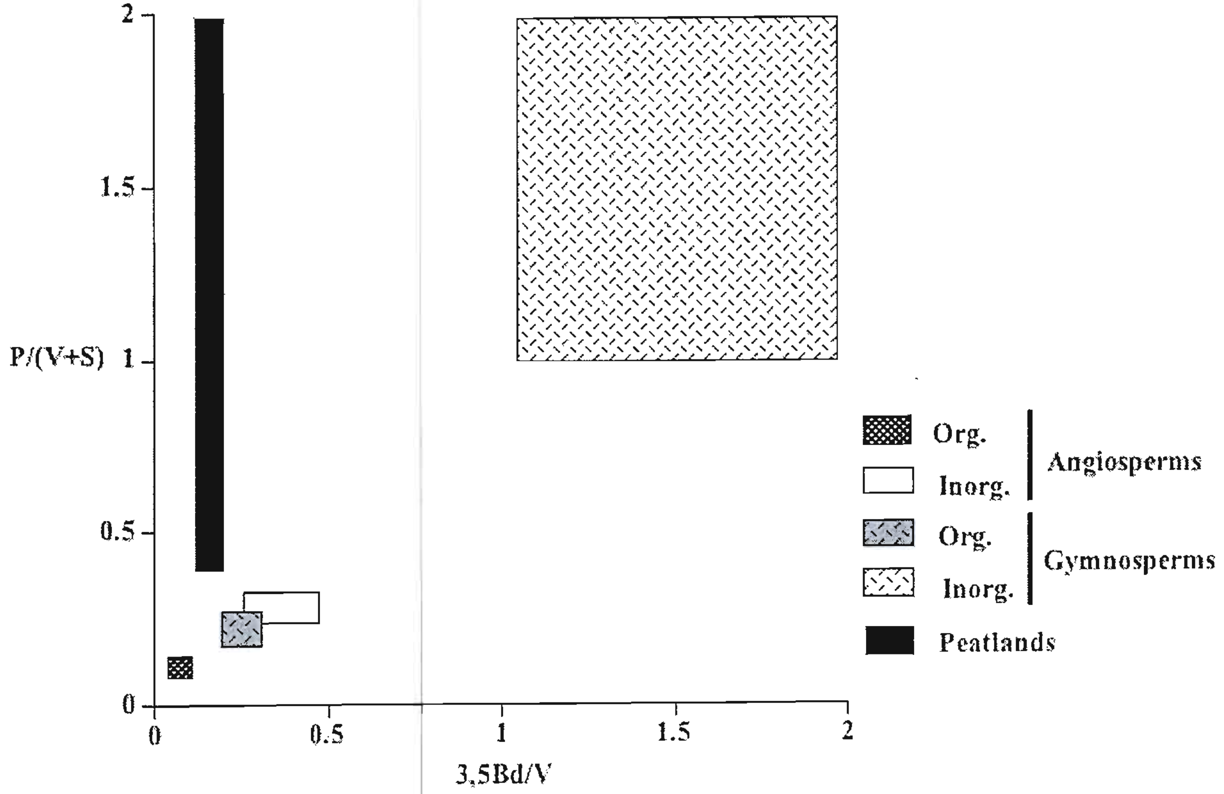

Figure A.1 : Mean P/(V+S) and 3,5Bd/V ratios in angiosperm, gymnosperm soils and peatlands. Boxes represent mean and 95% confidence interval.

ANNEXE B

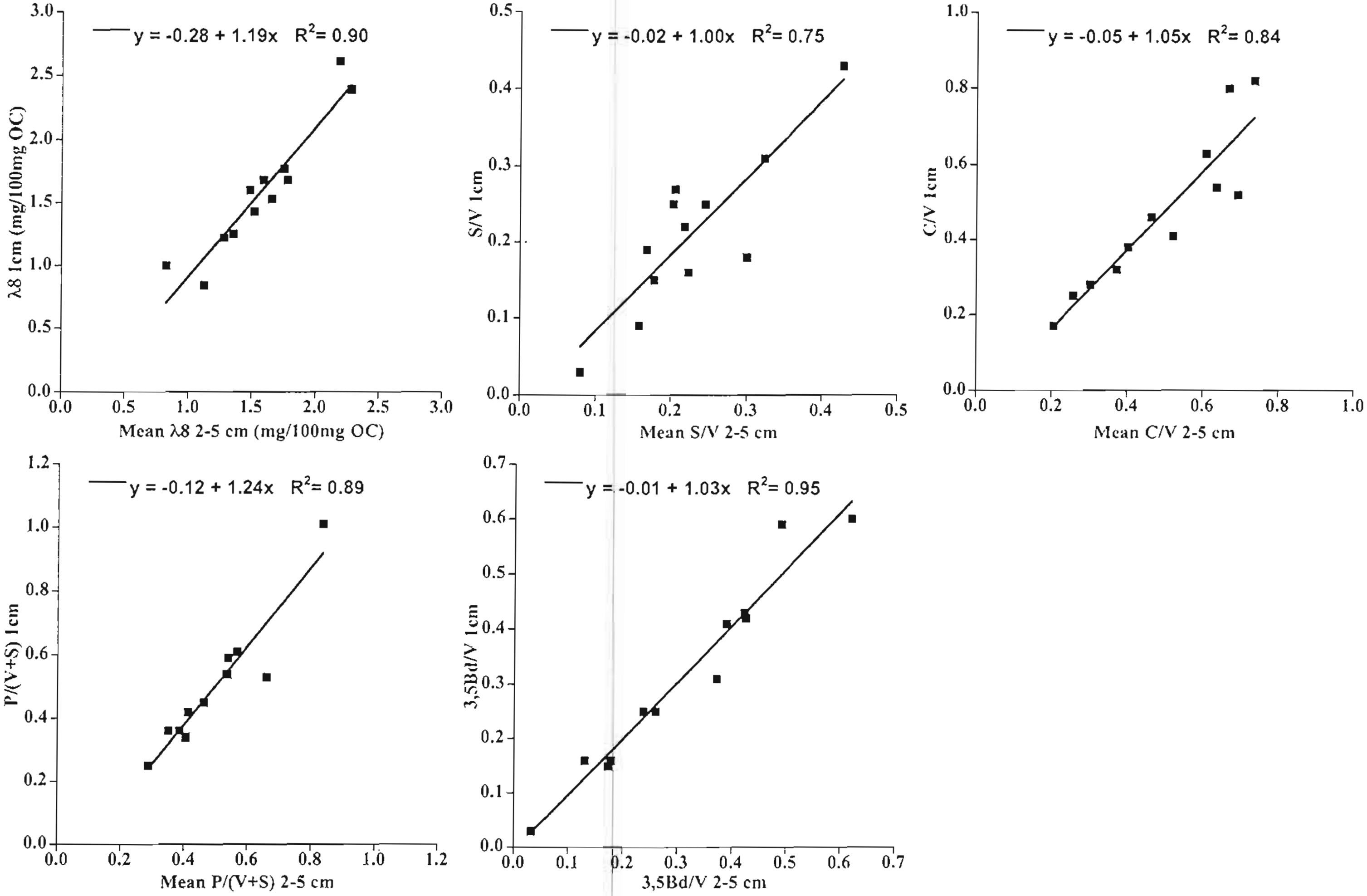

Figure B.1 : Comparison of each indicator measured in the first centimeter of the core and the mean value for centimeters 2-5.