UNIVERSITÉ DU QUÉBEC À MONTRÉAL

LINKING TERRESTRIAL LANDSCAPE TO AQUATIC CO2 THROUGH THE PROCESSING OF ORGANIC CARBON IN BOREAL FRESHWATERS

THÈSE
PRÉSENTÉE
COMME EXIGENCE PARTIELLE
DU DOCTORAT EN BIOLOGIE

PAR
JEAN-FRANÇOIS LAPIERRE

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LA DÉGRADATION DE CARBONE ORGANIQUE DANS LES EAUX DOUCES BORÉALES EN TANT QUE LIEN ENTRE LE PAYSAGE TERRESTRE ET LE CO2 AQUATIQUE

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RÉSUMÉ

Cette thèse a pour but commun d'améliorer notre compréhension du rôle que la dégradation de carbone organique dans les milieux aquatiques joue dans les flux de carbone entre le paysage terrestre, les milieux aquatiques et l'atmosphère. Ainsi, au cours des cinq dernières années, un survol de près de 500 lacs, rivières et milieux humides a été réalisé à travers différentes régions du biome boréal canadien afin de mieux comprendre comment le carbone organique dissous (COD), en termes de quantités et de qualité, est relié aux propriétés du paysage environnant. Ces caractéristiques ont ensuite servi à mieux comprendre le potentiel du COD à être dégradé par les processus biologiques et photochimiques ayant lieu dans l'eau, et ultimement, à mieux cerner le rôle que la dégradation de COD joue sur les émissions aquatiques de dioxyde de carbone (CO_2) dans le biome boréal.

Les résultats principaux ont d'abord démontré (Chapitre 1) qu'à travers un paysage boréal de près de 1 million km², le métabolisme des lacs était auto-corrélé spatialement, de telle sorte que les lacs près les uns des autres tendent à avoir des taux comparables de production et de dégradation de carbone organique et des concentrations comparables de CO_2. Ce sont largement les propriétés du climat et du paysage qui structurent le métabolisme des lacs dans l'espace, mais cet effet est presque entièrement intégré par les concentrations et la qualité des nutriments et du COD (aussi auto-corrélés spatialement), qui à leur tour ont un effet causal sur les processus qui contribuent au cycle du carbone dans l'environnement aquatique.

Cet effet contrôlant du COD sur le métabolisme aquatique se répercute spatialement au niveau du CO_2, comme en témoignent les diverses relations régionales existant entre CO_2 et COD (Chapitre 2). La nature et la force de cette relation, par contre, diffèrent grandement de région en région en fonction de la connectivité avec le milieu terrestre et des moyennes régionales en nutriments. Ces patrons supportent l'importance de l'effet intégrateur du COD, et exposent le besoin d'explorer les processus qui relient directement le COD au CO_2 aquatique.

Les concentrations, mais surtout la qualité du COD expliquent en grande partie les patrons de dégradation biologique et photochimique dans les lacs, rivières et milieux humides boréaux étudiés (Chapitre 3). Les analyses optiques ont révélé que même si les groupes de COD concernés diffèrent, le paysage terrestre exporte simultanément de grandes quantités de carbone biologiquement et photo-chimiquement dégradable. Les résultats montrent que le milieu terrestre exporte d'importantes quantités de carbone biodégradable qui ressemble beaucoup au carbone typiquement associé à des sources autochtones, provenant de la production primaire dans l'environnement aquatique, de telle sorte que le potentiel total de dégradation du COD, et donc de production de CO_2, semble augmenter plutôt que diminuer en s'approchant de l'interface sol-eau.

La dégradation de COD d'origine terrestre dans les écosystèmes aquatiques semble donc relier, causalement, le climat et le paysage terrestre au CO_2 aquatique. Des changements au niveau du climat et du paysage terrestre ont occasionné de considérables augmentations de concentrations en COD d'origine terrestre dans les écosystèmes aquatiques au cours des dernières décennies, et nos résultats démontrent qu'effectivement il y a un lien fort entre contenu en COD terrestre, dégradation de carbone organique, concentrations et flux de CO_2 dans à travers les lacs, rivières et milieux humides boréaux (Chapitre 4). En conséquence, les émissions de CO_2 par les écosystèmes aquatiques ont vraisemblablement augmenté de 10 à 50% au cours des 30 dernières années en réponse aux tendances temporelles en COD, et devraient continuer à augmenter proportionnellement aux tendances projetées.

L'ensemble des résultats présentés dans cette thèse démontre donc une dégradation efficace de carbone organique d'origine terrestre dans les eaux de surface, laquelle devrait résulter en une accélération considérable du retour de carbone terrestre vers l'atmosphère via la portion aquatique du paysage boréal en fonction des pressions environnementales actuelles. Il y a globalement, à chaque année, presque autant de carbone émis par les écosystèmes aquatiques de carbone stocké dans les sols. Les différents changements environnementaux dans le biome boréal à travers le monde devraient donc non seulement amplifier la perte de carbone terrestre vers les milieux aquatiques, mais aussi les flux de CO_2 de l'eau vers l'atmosphère, avec un impact majeur sur le cycle global du carbone.

Mots clés: Carbone organique dissous, écosystèmes aquatiques, paysage, climat, dégradation, flux

SUMMARY

The common goal of this thesis is better understand the role that organic carbon processing in aquatic environment plays in driving the carbon fluxes between the land, the water and the atmosphere. We surveyed over 500 lakes, rivers and wetlands across different North American boreal regions in order to better understand the landscape controls on aquatic dissolved organic carbon (DOC) properties, in terms of quantity and quality. DOC properties were then used to explore its susceptibility to biological and photochemical degradation in the water column and, ultimately, to better understand the role that DOC processing plays in driving aquatic carbon dioxide (CO_2) emissions in the boreal biome.

Main results first showed that lake metabolism was spatially auto-correlated across a 1 million km^2 boreal landscape (Chapter 1), resulting in comparable rates of production and degradation of organic carbon, as well as concentrations of CO_2 in nearby lakes. This was explained by nearby lakes sharing comparable climate and landscape properties, which were integrated in the concentration and quality of lake DOC and nutrients and on the effect of the latter variables on lake metabolism

This driving force of DOC on aquatic processes involved in the cycling of carbon was reflected in the spatial patterns in CO_2 concentrations, as reflected by the various regional relationships existing between DOC and CO_2 (Chapter 2). The nature and strength of this relationship, however, largely varies across regions according to connectivity with the landscape and regional averages in nutrient concentrations. These patterns thus support the integrative effect of DOC on lake CO_2, and further illustrate the need to explore the processes that may directly link DOC to aquatic CO_2.

The amounts and the quality of DOC largely explained the spatial patterns in its biological and photochemical degradation across the hundreds of boreal lakes, rivers and wetlands studied (Chapter 3). Optical analyses revealed that the DOC pools involved differ, but that biologically and photo-chemically degradable DOC were both largely originating from the terrestrial environment. Land appears to export biologically degradable DOC that closely resembles carbon typically associated to autochthonous carbon originating from aquatic primary production, such that the DOC degradation, and thus CO_2 production potentials tended to increase rather than decrease approaching the soil-water interface.

The degradation of terrestrial DOC in aquatic ecosystems thus appears to link, mechanistically, climate and landscape properties to aquatic CO_2. Changes in climate and landscape properties have caused considerable rises in terrestrially derived DOC content in aquatic environments across the boreal biome during the last decades, and we show that there is indeed a strong causal link between terrestrial DOC content, DOC processing and concentrations and fluxes of CO_2 across boreal aquatic ecosystems (Chapter 4). Aquatic emissions of CO_2 in these environments have thus conceivably increased from 10 to 50% in the last 30 years, and should continue increasing proportionally to projected trends in DOC.

Together, our different results demonstrate an efficient degradation of terrestrially derived organic carbon in inland waters, which should result in an accelerated return of terrestrial carbon to the atmosphere through the aquatic component of the boreal landscape in response to current environmental pressures. There is, every year, nearly as much carbon emitted from freshwaters than carbon being accumulated in the soils of the entire planet. The different climate and environmental changes taking place in the boreal biome should thus not only amplify the loss of carbon from land to water, but also the fluxes of CO_2 from water to the atmosphere, with a major impact on the global carbon cycle.

Keywords: Dissolved organic carbon, aquatic ecosystems, landscape, climate, degradation, flux

INTRODUCTION

0.1 Les écosystèmes aquatiques boréaux et le cycle global du carbone

Malgré leur faible couverture spatiale, les écosystèmes d'eau douce contribuent de façon démesurée au cycle global du carbone (Cole *et al.*, 2007 ; Raymond *et al.*, 2013 ; Tranvik *et al.*, 2009). Tandis que les combustibles fossiles sont responsables pour l'émission d'environ 7.6 Pg (10^{15}) de carbone par année, environ 2.2 et 2.8 Pg de carbone sont absorbés chaque année par les océans et les écosystèmes terrestres, respectivement, à travers le monde (Canadell *et al.*, 2007). Les eaux intérieures ne représentent que de 1 à 3% de la surface du globe, mais émettraient collectivement environ 2.1 Pg de carbone annuellement vers l'atmosphère (Raymond *et al.*, 2013), soit tout à fait dans le même ordre de grandeur que les émissions directement liées aux activités humaines, et environ la même quantité que ce qui est absorbé dans les océans et les sols du monde entier.

La contribution des écosystèmes aquatiques est particulièrement importante dans le biome boréal, là où on retrouve à la fois parmi les plus grandes quantités de carbone stocké dans les sols (Schlesinger, 1977) et les plus grandes densités d'eaux douces de surface au monde (Downing *et al.*, 2006). Les milieux terrestres et aquatiques y sont fortement connectés, de telle sorte que les lacs, rivières et milieux humides reçoivent et transforment des quantités phénoménales de carbone organique produit dans le paysage environnant (Battin *et al.*, 2009). Les milieux aquatiques réémettent donc vers l'atmosphère de grandes quantités de carbone qu'on croyait stocké dans les sols (McCallister et del Giorgio, 2012), mais les propriétés du paysage et les processus aquatiques qui régulent le retour de carbone terrestre vers l'atmosphère via les eaux de surface demeurent mal compris à de grandes échelles spatiales. Il est donc difficile de quantifier, ou même de prédire la direction future de la réponse du cycle du carbone boréal en réponse à des pressions environnementales répandues à l'ensemble du biome.

Les changements climatiques récents et à venir altèrent les patrons de précipitation et de température dans l'ensemble des écosystèmes nordiques, et les concentrations en carbone organique dissous (COD) augmentent un peu partout dans l'hémisphère nord, amplifiant ainsi la couleur brunâtre typique des eaux de surface dans ce qui a été nommé le "brunissement" des eaux continentales (Monteith *et al.*, 2007 ; Roulet et Moore, 2006). Si on en sait beaucoup sur effets individuel de la température ou du COD sur des processus isolés impliqués dans le cycle aquatique du carbone, on en sait très peu sur l'effet combiné réel de ces pressions environnementales sur des écosystèmes naturels dû à un manque d'études empiriques à des échelles spatiales pertinentes.

0.2 Patrons, processus, échelles et prédiction

"The key to prediction and understanding lies in the elucidation of the mechanisms underlying the observed patterns." (Levin, 1992)

Cette citation expose un problème majeur toujours présent en écologie: l'étude des patrons (variabilité prévisible dans l'environnement naturel) et des processus (mécanismes chimiques, physiques ou biologiques) est presque systématiquement découplée. Puisqu'ils sont rarement étudiés ensemble, il devient tentant, voire nécessaire de prédire les patrons (temporels ou spatiaux) à partir des processus étudiés en milieu contrôlé, ou, à l'inverse, de spéculer sur les processus à partir de patrons observés. Mais l'échelle étudiée, en termes de gradients temporel, spatial ou environnemental, est rarement transposable depuis les études sur les patrons vers les études sur les mécanismes, et vice-versa (Levin, 1992). Il demeure donc difficile d'identifier avec confiance les mécanismes à la base des patrons à grande échelle, ainsi que de déterminer comment les processus étudiés nous permettent de réellement comprendre et prédire des patrons naturels.

Prédire et extrapoler nécessite donc l'identification de processus clés, et les processus en question sont fonction de l'échelle étudiée. Par exemple, l'effet causal de la température, du carbone organique dissous (COD) et des nutriments sur le stockage de carbone organique (Gudasz *et al.*, 2010), la respiration bactérienne (McCallister et del Giorgio, 2008), la photo-oxidation (Graneli, Lindell et Tranvik, 1996) ou la production primaire (Finlay *et al.*, 2009) est bien connu, et cet effet se répercute concrètement dans la production, les émissions et le stockage de carbone dans les écosystèmes étudiés. L'effet causal de ces variables ne devrait pas varier signicativement dans le temps ou dans l'espace, mais selon l'échelle étudiée, l'impact individuel de chacune de ces variables sur les processus aquatiques sera plus ou moins significatif en fonction des conditions environnementales locales, telles que les propriétés du paysage environnant et l'hydrologie.

Ainsi, depuis l'équateur jusqu'au cercle polaire, on observe effectivement une augmentation de la productivité primaire et de l'efficacité de stockage du carbone dans les sédiments des grands lacs du monde (Alin et Johnson, 2007), conformément à l'effet causal théorique de la température (Gudasz *et al.*, 2010). Dans les patrons comme dans les processus, par contre, l'effet de la température (Gudasz *et al.*, 2010) et de la position géographique (Alin et Johnson, 2007) est clair sur des gradients représentatifs de l'ensemble du globe, mais négligeable à l'intérieur de quelques degrés celsius ou latitudinaux, représentatifs des changements projetés du climat au cours du prochain siècle (Solomon, 2007).

Dans le même ordre d'idées, on observe une relation globale significative, mais faible entre les concentrations en COD et en CO_2 (Sobek, Tranvik et Cole, 2005). Au niveau régional, par contre, la force de ces relations est en moyenne beaucoup plus forte, et la nature (pente et intercept) varie fortement (Finlay *et al.*, 2009 ; Jonsson, Karlsson et Jansson, 2003 ; Roehm, Prairie et del Giorgio, 2009); la relation change carrément de direction dans certaines régions (Finlay *et al.*, 2009). Ces études suggèrent donc un effet du COD sur les patrons spatiaux de CO_2, mais la grande disparité entre les différentes relations ne permet pas d'identifier un fort effet causal à cet échelle.

Ces différents exemples illustrent que même si l'effet causal de la température et du COD sur les processus aquatiques demeure, en théorie, présent et comparable dans tous les environnements, l'importance relative de ces variables comparativement aux autres forces en présence varie selon l'échelle. Quels sont donc les processus clés qui permettent de comprendre et prédire l'impact potentiel des changements environnementaux sur le cycle du carbone aquatique? La réponse varie, dans un premier temps, selon l'échelle à laquelle les changements environnementaux agissent dans le paysage, Ainsi, si le climat actuel et les changements prévus dans climat au cours du prochain siècle sont hautement prévisibles dans l'espace à l'échelle globale (Solomon, 2007), il y a des patrons apparamment régionaux d'augmentation des concentrations en COD à travers le biome boréal (Monteith *et al.*, 2007). Les processus clés devraient, dans un deuxième temps, agir à une échelle comparable à celle des patrons environnementaux en question, mais presque rien n'est connu sur l'échelle à laquelle varient les différents processus aquatiques impliqués dans la production et l'évasion de CO_2. Il est donc difficile d'identifier des variables intégratices qui permettent d'expliquer et de prédire l'effet des pressions environnementales régionales et continentales sur le cycle du carbone aquatique.

Il en résulte une apparente confusion, voire une contradiction dans la littérature sur le rôle que les différents processus jouent sur les émissions aquatiques de CO_2, et par le fait meme sur les sources de CO_2 émis par les écosystèmes aquatiques. Beaucoup d'énergie est ainsi investie à débattre des différents points de vue, et ce débat est essentiel puisque les conséquences des différentes pressions environnementales sur le cycle du carbone aquatique seront très différentes en fonction des processus impliqués. Cela dit, le débat doit éventuellement déboucher sur un consensus afin d'être réellement utile, mais un consensus demeure difficile tant que patrons et processus impliqués dans le cycle du carbone aquatique ne seront pas considérés sur des gradients et des échelles communs.

0.3 Le débat sur les sources de CO_2 en milieu aquatique

Il est généralement bien accepté que d'importantes quantités de carbone terrestre sont retournées vers l'atmosphère via la portion aquatique du paysage. Si la plupart s'entendent aussi sur l'ordre de grandeur des émissions globales de CO_2 par les écosystèmes aquatiques (Cole et al., 2007 ; Raymond et al., 2013 ; Tranvik et al., 2009), ce sont les processus impliqués qui sont âprement débattus.

De nombreux travaux ont démontré de façon convaincante que différents processus biologiques et photochimiques dégradent le COD dans les écosystèmes aquatiques et contribuent à la production de CO_2 dans les eaux de surface (Algesten *et al.*, 2004 ; del Giorgio *et al.*, 1999 ; Duarte et Prairie, 2005 ; Jonsson, Karlsson et Jansson, 2003). En contrepartie, des études plutôt axées sur les patrons et la quantification des émissions aquatiques suggèrent que le CO_2 émis a en grande partie été respiré dans les sols et importé par la suite par les eaux de ruissellement (Butman et Raymond, 2011 ; Humborg *et al.*, 2010 ; Maberly *et al.*, 2012 ; Wallin *et al.*, 2013). Ces dernières études ont cependant surtout été réalisées en milieu riverain ou dans des bassins versants de tête très près de l'interface sol-eau, où on retrouve de fortes proportions de CO_2 par unité de COD et où le COD est fraîchement importé et a été peu exposé à la dégradation. Les études mécanistiques sur le rôle de la dégradation de COD sur le CO_2 aquatique, quant à elles, proviennent surtout de millieux lacustres, typiquement beaucoup plus déconnectés de l'interface sol-eau. Le CO_2 d'origine terrestre dans de tels systèmes a donc été largement réémis vers l'atmosphère, et le COD terrestre qu'on y retrouve a été exposé à toutes sortes de mécanismes de dégradation lors de son parcours depuis la sortie des sols. Ces différences de contextes et d'échelles pourraient expliquer l'apparente contradiction entre les deux types d'études, mais d'importantes questions doivent d'abord être résolues avant de pouvoir placer ces différentes études sur un même gradient.

Une grande part du débat vient de l'incertitude entourant le potentiel de dégradation biologique du carbone organique d'origine terrestre à l'intérieur des écosystèmes aquatiques. Traditionnellement, la dégradabilité du COD était surtout étudiée dans les écosystèmes côtiers ou marins, où les concentrations en COD d'origine terrestre sont faibles et où contenu en COD terrestre est synonyme de matière vieille et altérée et donc de récalcitrance à la dégradation biologique (Dittmar et Kattner, 2003 ; Hedges, Clark et Cowie, 1988). Le COD terrestre provenant de ces environnements est, de ce fait, peu utilisé lors d'expériences contrôlées en laboratoire (Amon, 2004), suggérant ainsi qu'il participe peu aux processus biogéochimiques dans les grandes rivières arctiques, de même que dans les eaux côtières ou océaniques (Holmes *et al.*, 2008). Si ces patrons sont représentatifs de l'environnement où ils ont été étudiés, il n'est pas du tout évident qu'ils sont applicables aux eaux douces continentales. Dans les lacs, rivières et milieux humides, on retrouve de fortes concentrations de COD d'origine terrestre (Algesten *et al.*, 2004 ; Lapierre et Frenette, 2009 ; Wilkinson, Pace et Cole, 2013), lequel est typiquement beaucoup plus fraichement importé depuis les sols environnants. Le COD terrestre dans ces environnements tend à être plus dégradable que ne le laissaient penser les études en milieu marin (Holmes *et al.*, 2008 ; Ward *et al.*, 2013), et des études mécanistiques suggèrent qu'il contribue ainsi à la respiration, donc à la production de CO_2 dans certains milieux ciblés (Karlsson, Jansson et Jonsson, 2007 ; McCallister et del Giorgio, 2008).

Collectivement, nombre d'études récentes suggèrent ainsi que le COD d'origine terrestre ait le potentiel de soutenir la production et l'émission de CO_2 des eaux continentales, mais on en sait encore trop peu sur les patrons à grande échelle pour pouvoir démontrer ce point. Plus précisément, pour les mêmes raisons que la dégradabilité du COD terrestre observée en milieu marin s'applique mal dans les eaux continentales, sa dégradabilité mesurée en lacs ne s'applique pas nécessairement en rivières ou en milieus humides, qui sont de plus en plus reconnus pour leur rôle clé dans le cycle du carbone continental (Campeau *et al.*, 2014 ; Denfeld *et al.*, 2013 ; Raymond *et al.*, 2013). La contribution de la dégradation de COD aux flux mesurés de CO_2 à travers les lacs, rivières et milieux humides continentaux est fort probablement sous-estimée, puisque principalement basée sur des expériences effectuées dans des systèmes qui ne sont pas représentatifs de l'ensemble des eaux continentales; on ne sait presque rien sur la dégradabilité, et encore moins sur les taux de dégradation du COD à travers un gradient continu d'influence terrestre. Les eaux de surface occupent une toute petite partie du paysage, et par le fait même la quantité de CO_2 qui circule dans les écosystèmes aquatiques est une infime partie du carbone total qui circule dans le milieu terrestre. La perte d'une petite fraction de ce carbone vers les écosystèmes aquatiques est donc suffisante pour expliquer l'ensemble des émissions aquatiques. Dans un contexte de budget de CO_2 à grande échelle, il est logique d'attribuer à une source terrestre le manque à gagner dans les émissions aquatiques de CO_2, à défaut de pouvoir fournir des estimés satisfaisants de la dégradation de COD dans l'ensemble des eaux continentales.

Il est donc crucial de raffiner notre compréhension de la dégradabilité du COD d'origine terrestre dans les écosystèmes aquatiques, et du rôle que celui-ci joue sur les émissions aquatiques de CO_2; il devient par le fait même nécessaire d'élargir le gradient environnemental couvert afin que les processus mesurés soient applicables à l'ensemble du paysage. Seulement alors sera-t-il possible d'unifier patrons et processus sur un gradient commun, et donc de désenchvêtrer l'effet de diverses pressions environnementales ayant lieu dans le paysage sur les émissions de CO_2 par les écosystèmes aquatiques.

0.4 Objectifs de la thèse

L'objectif général de cette thèse est de comprendre et prédire la réponse des émissions aquatiques de CO_2 aux changements environnementaux majeurs ayant lieu dans le biome boréal, tels que le réchauffement climatique et l'augmentation de COD dans les eaux continentales. Cet objectif général est décomposé en une série de sous-objectifs, représentant les quatre chapitres de la thèse, chacun étant écrit sous forme d'article scientifique:

1- Déterminer le potentiel du COD à intégrer l'effet du climat et du paysage sur les processus aquatiques impliqués dans le cycle du carbone

2- Explorer les processus derrière les patrons régionaux existants entre CO_2 et COD dans les écosystèmes aquatiques boréaux

3- Expliquer le potentiel du COD à être dégradé par les processus biologiques et photochimiques dans les écosystèmes aquatiques à travers le paysage

4- Relier influence terrestre, dégradation de COD et émissions de CO_2 dans les eaux continentales

0.5 Approche générale

D'un point de vue plus technique, cette thèse a pour but commun d'identifier les liens existants entre climat, paysage terrestre, processus aquatiques et émissions de CO_2 par les eaux de surface. Une approche mixte explorant à la fois les patrons spatiaux en milieu naturel et les processus en milieu expérimental a donc été utilisée, et les patrons et les processus impliqués dans le cycle aquatique du carbone ont été étudiés sur des gradients environnementaux communs.

0.5.1 Survol spatial

Un échantillonnage intensif de centaines de lacs, rivières et milieux humides a eu lieu pendant quatre ans dans sept régions du Québec afin de bien capturer l'étendue des gradients climatiques et environnementaux ayant lieu dans le paysage du biome boréal (Fig. 0.1). Pour chaque système échantillonné, une série de mesures biologiques (concentrations en chlorophylle *a*), physiques (température, pH, turbulence) et chimiques (concentrations et propriétés optiques du COD, concentrations en nutriments) ont été effectuées afin de relier les conditions environnementales aux concentrations et flux de CO_2. À ces mesures s'ajoute une caractérisation du climat et du paysage environnant via l'analyse de cartes disponibles à l'utilisation publiques par des systèmes d'information géographique.

0.5.2 Expériences contrôlées

Pour chaque site étudié, des expériences contrôlées ont été effectuées en laboratoire afin d'explorer le rôle que les processus biologiques et photochimiques jouent sur les patrons observés dans les environnements naturels. Ces processus incluent les mesures standardisées de la dégradabilité biologique et photochimique du COD provenant des systèmes échantillonnés, de même que de la production et de la respiration bactériennes. Ces expériences ont été réalisées selon des protocoles bien établis, lesquels sont décrit en détails dans les chapitres respectifs.

0.5.3 Analyses statistiques

Plusieurs analyses de base, allant de la régression linéaire simple à l'analyse de redondance, ont été utilisées afin de caractériser les patrons de variation entre les différentes variables. Certains aspects de la thèse ont requis une analyse plus spécialisée. En particulier, une "parallel factor analysis" (Stedmon, Markager et Bro, 2003) a servi à modéliser les propriétés optiques du COD, et ainsi de relier sa composition à sa dégradabilité. La structure spatiale existant dans les différentes variables a été évaluée via l'analyse d'auto-corrélation spatiale et la mesure de l'indice Moran (Fortin et Dale, 2005). La série de liens potentiellement causaux reliant le COD d'origine terrestre aux émissions aquatiques de CO_2 a été analysée via le "Structural Equation Modeling" (Shipley, 2002). Cette thèse ne visait pas à développer ou à prouver l'utilité d'une technique en particulier. Il s'agit dans tous les cas d'analyses bien établies en écologie, et les analyses respectives ont été choisies en fonction de maximiser l'efficacité du message transmis par une base de données *a priori* complexe.

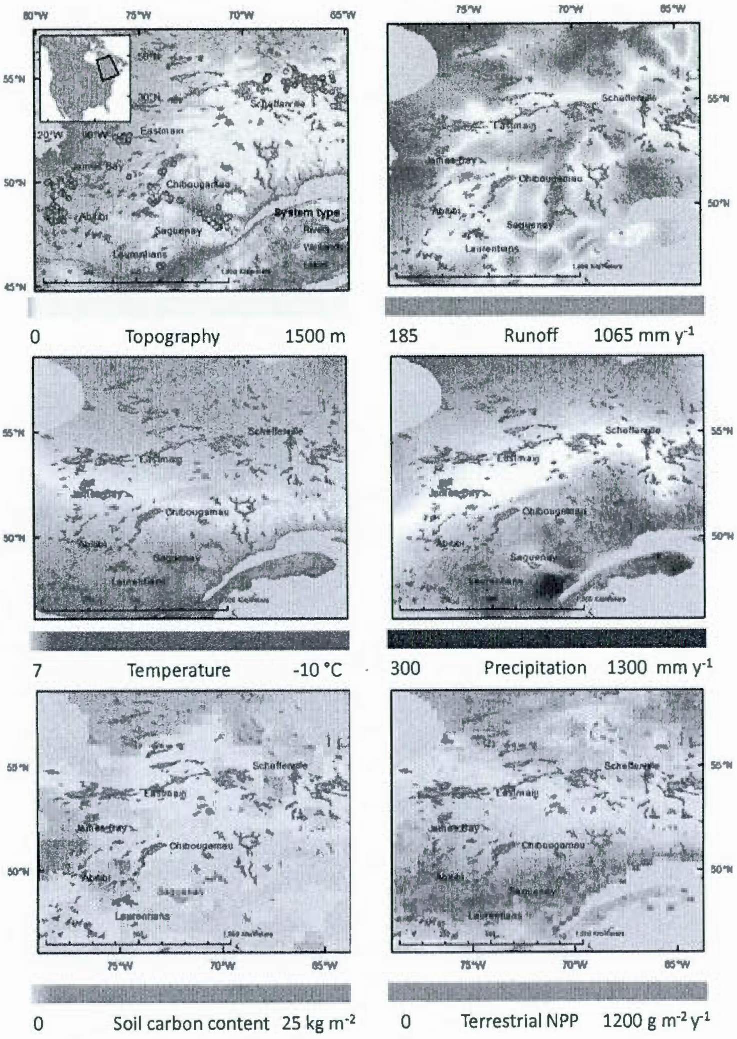

Figure 0.1. Gradients environnementaux et climatiques retrouvés dans le biome boréal québécois.

L'écoulement des eaux de surface (Runoff), la température, les précipitations et la production primaire terrestre (Terrestrial NPP) représentent les valeurs annuelles moyennes. Le contenu en carbone dans les sols (Soil carbon content) représente la quantité contenue dans les premiers cinquante centimètres. Les sites échantillonnés sont représentés sur la carte topographique.

CHAPITRE I

REGIONAL PATTERNS IN LAKE METABOLISM RESULTING FROM THE INTERPLAY OF CLIMATE, LANDSCAPE PROPERTIES AND LAKE ORGANIC MATTER AND NUTRIENTS

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Type of paper: Primary research article

N.B. References cited in this chapter are presented at the end of the thesis.

1.1 ABSTRACT

Aim: Climate affects ecosystem processes in many ways, but the direct effect of temperature on aquatic ecosystem functioning is unclear at regional scales, suggesting that additional pathways are needed. We explored how the delivery dissolved organic matter (DOM) and nutrients from land to water may link large-scale patterns in climate and landscape properties to spatial patterns in key proxies of lake metabolism.

Location: Eastern Canada temperate and boreal lakes.

Methods: For hundreds of lakes found in a large and complex landscape, we obtained a combination of field measurements of indices of lake metabolism, nutrients and DOM concentration and composition with landscape and climate variables. We compared the spatial auto-correlation measured in landscape and climate properties to that of DOM and nutrients, then explored the individual and overlapping effects of those different factors on lake metabolism using analyses of redundancy combined with variance partitioning.

Results: There were strong regional patterns in lake metabolism, which were almost entirely explained by DOM and nutrients. DOM and nutrients also showed regional patterns resulting from the interplay of continental and regional climate with landscape drivers related to temperature, primary productivity in the catchment, topography and hydrology. As a result, the effect of DOM and nutrients on lake metabolism largely overlapped with that of climate and landscape properties.

Main conclusions: There were spatially structured patterns in lake carbon cycling across a wide boreal landscape, where the metabolism of nearby lakes tended to be comparable as a consequence of similar climate, landscape, and ultimately, DOM and nutrient properties. It appears that the effect of climate and landscape on lake metabolism is mostly indirect and conveyed through the delivery of organic and inorganic matter which have a direct causal effect on the rates of production and degradation of organic carbon in aquatic ecosystems.

1.2 INTRODUCTION

Various environmental challenges are altering the boreal biome across the northern hemisphere, with major consequences for carbon cycling in the aquatic component of the landscape. Changing climate, precipitation and atmospheric deposition patterns are causing increasing water temperature and loss of terrestrial organic carbon to aquatic ecosystems (Freeman *et al.*, 2001; Monteith *et al.*, 2007; Zhang *et al.*, 2010), resulting in enhanced carbon degradation in the sediments and surface waters of continental watersheds (Gudasz *et al.*, 2010; Lapierre *et al.*, 2013). Temporal trends in climate have also been shown to drive regional synchrony in lake properties such as primary productivity, nutrients and dissolved organic matter (DOM) concentrations (Baines *et al.*, 2000; Pace & Cole, 2002); furthermore, concentrations and fluxes of CO_2 in the large lakes of the world tend to increase globally with increasing latitude (Alin & Johnson, 2007). Temporal and large-scale spatial environmental patterns are thus apparently reflected in aquatic processes involved in the cycling of carbon, but the pathways involved remain unclear. A better understanding of the pathways involved will allow to better assess the potential direct and indirect impacts of changing climate on the aquatic carbon cycle.

There is a clear role of climate in the synchronous and latitudinal lake patterns mentioned above, but the direct effect of temperature, in turn, is not always obvious. Multi-year synchrony across northern Wisconsin lakes was stronger for water temperature than for chlorophyll concentrations (Baines *et al.*, 2000), reflecting the effect of local environmental conditions on aquatic primary production which were not directly climate-driven. Likewise, there is a convincing effect of climate and temperature on lake carbon cycling over gradients representative of the whole biosphere(Alin & Johnson, 2007; Gudasz *et al.*, 2010), but this direct effect appears ambiguous at a regional scale where temperature and latitude vary by only a few degrees, but where water chemistry may still vary by orders of magnitude (Sobek *et al.*, 2003; Cheruvelil *et al.*, 2008; Lapierre & del Giorgio, 2012). Climate, however, may further influence aquatic ecosystems through its effect on hydrology and landscape properties that dictate the delivery of organic and inorganic matter from land to water (McKnight *et al.*, 1996; Schindler, 1997; Pace & Cole, 2002). The effect of climate is thus also indirect and further conveyed by variables such as dissolved organic matter (DOM) or nutrients which may have a clearer mechanistic effect on aquatic processes involved in the cycling of carbon at sub-global scales (Lapierre and del Giorgio, submitted;Pace & Prairie, 2005).

Climate and landscape properties (e.g., temperature, precipitation, topography) are highly structured in space over continental and global spatial scales (IGBP-DIS, 1998; Hansen *et al.*, 2003; Hijmans *et al.*, 2005), implying that nearby environments tend to share, among other characteristics, similar climate, hydrology and terrestrial vegetation. Some degree of spatial structure would be expected in aquatic processes if such climate and landscape properties were major drivers. Recent studies indeed showed strong regionality in the concentrations of DOC and nutrients (Cheruvelil *et al.*, 2008; Seekell *et al.*, 2014), which in turn are reflected, for example, in surface water CO_2 concentrations (Lapierre & del Giorgio, 2012). This suggests that metabolic processes involved in the cycling of organic carbon may also vary predictably over space as a result of spatially structured patterns in lake DOM and nutrients. DOM and nutrients, however, are driven by different factors depending on the spatial scale studied (Table 1), with variables such as lake area and percent wetlands in the catchment having a stronger impact at local scale while climate and hydrology become increasingly important as the spatial scale broadens. There are thus potentially complex, multi-scale interactions between climate, landscape properties, DOM and nutrients occurring over large landscapes that renders it challenging to disentangle the effect of those different drivers on aquatic processes at regional scales, relevant for projected climate changes over the next decades or century (Solomon, 2007).

Here we aim at assessing the role of climate, landscape properties, DOM and nutrients in driving the spatial patterns in lake metabolism over a large boreal landscape. We explored whether variables such as DOM and nutrients could integrate the effect of climate and landscape properties on aquatic processes related to the production and degradation of carbon in lakes. To do so, we first performed spatial auto-correlation analyses on a large field data set composed of lake biogeochemical variables, combined publicly available climatic and landscape properties in order to compare the spatial structure in lake metabolism to that of its potential drivers. We then explored the individual and overlapping effect of different groups of drivers on lake metabolism using redundancy analyses and variance partitioning in order to test the ability of DOM and nutrients to integrate climate and landscape properties.

1.3 METHODS

1.3.1 Sampling

Over the course of four years, we surveyed lakes situated in seven distinct biogeographic regions of Québec, Eastern Canada (Fig. 1.1a), allowing for a multi-scale comparison where the distance between lakes ranged from less than one kilometer to up to 1300 km. From 2009 to 2012, 239 individual lakes were sampled once or twice between May and August for a total of 280 observations; means have been used for multiple lake samples.

Water was sampled for chemical and gas analyses from the deepest measured point in the lake at 0.5 m from the surface. Water temperature was measured from a multiprobe (Yellow Springs Instruments, OH, USA). A portion of the water was filtered through 0.45 initial pore size cartridge filters (Sarstedt, OH, USA) and stored in 40 ml acid-washed glass vials for subsequent dissolved organic carbon (DOC) and optical measurements. Unfiltered water was added to 60 ml acid-washed glass vials for subsequent nutrient analyses. All samples were immediately stored in the cold and dark and kept under those conditions until laboratory analyses.

1.3.2 GIS analyses

The surface and catchment areas, as well as elevation of the lakes we sampled were determined using the ArcGIS v.10.1 software applied on the EM derived from (1:50000) maps. The source of complementary geographic data is presented in Table 2.

1.3.3 Biological and chemical analyses

DOC concentration were measured on an OI 1010 TOC-TIC (Aurora, TX, USA) analyzer following sodium persulfate digestion. Total phosphorus (TP) was analyzed spectrophotometrically after persulfate digestion. Total nitrogen was analyzed as nitrates following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV autoanalyzer.

1.3.4 Optical analyses

We used a combination of chemical (DOC concentration, see above) and optical analyses to explore the dynamics in the concentration and composition of DOM, respectively. A PARAFAC model (Stedmon *et al.*, 2003) was performed to identify and quantify fluorescence components, i.-e. groups of DOM that had similar optical properties and distribution across the lakes, and which presumably shared common sources and sinks. Fluorescence data was first corrected for inner-filter effect and standardized to Raman units using the FDOMcorr 1.6 toolbox (Murphy *et al.*, 2011) in MATLAB (MathWorks, MA, USA). The model was then performed on corrected data using the DOMfluor 1.7 toolbox (Stedmon & Bro, 2008). We calculated the percent that each component contributed to the total fluorescence in a given sample to more directly the composition of DOM. Additional details on the modeling procedure are provided in Lapierre and del Giorgio (submitted).

Fluorescence intensity was measured on a Shimadzu RF5301 PC (Shimadzu, Kyoto, Japan), across excitation wavelengths of 250 – 450nm (5 nm increments) and emission wavelengths of 280–600 nm (2nm increments). Absorbance measurements were performed on a UV-visible Ultrospec 2100 spectrometer (Biochrom, Cambridge, UK) using a 2-cm quartz cuvette, and corrected by subtracting nanopure water blanks. Absorbance at 440 nm was used as an indicator of the concentration of colored dissolved organic matter (CDOM). All measurements were performed within 2 weeks after collection.

Here we use the PARAFAC model previously described in Stubbins et al. (submitted) and Lapierre and del Giorgio (submitted). We summarize the main points emerging from those studies that are useful to interpret the results from the present study. The model, based on 1349 samples from temperate and boreal aquatic environments, identified six different fluorescence components. Components 1-3 (C1-3) were associated to biologically refractory, humic- and fulvic-like material with high C:N ratios; component C3 was extremely sensitive to photo-chemical degradation. Components C4-6 were associated to more biologically labile, freshly-produced DOM with higher proportions of N. Component C6 in particular had a fluorescence signature typical of protein-like material and was the strongest driver of DOC biological degradability across hundreds of boreal lakes, rivers and wetlands.

1.3.5 Lake metabolism

We explored lake metabolism through key variables related to the production and mineralisation of organic carbon in lakes. Primary production (PP) rates were estimated from Chl *a* concentrations following del Giorgio and Peters (1994). Chl *a* concentrations were measured spectrophotometrically, in duplicates, following filtration on Whatman (GF/F) filters and hot ethanol (90 %) extraction. Filters were sonicated prior to extraction. For all variables measured in duplicate, we used the mean value. Bacterial respiration (BR) was determined from changes in oxygen concentrations during in vitro incubations in the dark and at site temperature. Oxygen was measured from filtered water (2.7 μm) in 500 ml sealed erlenmeyers using optical sensors (Fibox 3, PreSens, Regensburg, Germany) following Marchand et al. (2009). The P:R ratio was measured as the ratio of Chl *a*-derived rates of PP to rates of BR. Bacterial production (BP) based on rates of radioactive leucine incorporation (Marchand *et al.*, 2009)in standardized conditions. Finally, surface water CO_2 concentration (expressed as the partial pressure of CO_2, pCO_2, in μatm) was measured in situ using an EGM-4 infrared gas analyzer (PP-systems, Boston, MA, USA), after equilibration by pumping water through a Liqui-Cel Mini Module (Charlotte, NC, USA) contactor membrane.

1.3.6 Statistical analyses

We We scaled the variation in lake metabolism and its drivers using Moran's index (Moran's I) for spatial auto-correlation in order to distinguish how similar lakes are to each other within a given distance interval in regards to any given variable. More detailed explanations on Moran's I can be found in Fortin and Dale (2005). Briefly, for each variable we built a correlogram representing average Moran's I for 20 groups (comprising between 2842 and 2844 pairs of lakes) of sites that were within a certain distance interval from one another. For each variable, we determined the maximum distance at which there was positive spatial auto-correlation disappears between two lakes using SAM 4.0 software (Rangel *et al.*, 2010), i.-e. the average distance at which two lakes tend to become completely independent in regards to the variable in question.

We explored how different categories of predictors explain the measured proxies of lake metabolism with a redundancy analysis (RDA), using the Vegan package (Oksanen *et* *al.*, 2013) in R 3.0 (R Core Team, 2013). We further explored how DOM and nutrient integrate the effect of climate and landscape properties by partitioning the variance explained by those three different groups of variables (Legendre & Legendre, 1998)); significance of the different fractions was verified by bootstrapping (Peres-Neto *et al.*, 2006). The effect of the different predictors in driving the spatial structure in lake metabolism was assessed by comparing the spatial auto-correlation remaining in the sample scores on the first two axis of the RDAs performed with different combinations of variables. The same series of analyses was performed in order to assess how climate and landscape properties with contrasting scale of variation explained the spatial structure in DOM and nutrients. Finally, the apparent visual regional patterns in the RDA analyses were validated using a linear discriminant analysis (LDA) with pre-determined regions (illustrated in Fig. 1a) as categories; the LDA results presented below correspond to the Jackknifed classification matrix. The LDA analyses were performed in JMP (v. 7.0.1, SAS institute, Cary, NC).

Table 1.1 Key variables related to DOM and nutrients at different spatial scales, based on published studies.

Reference i: (Frost *et al.*, 2006), ii: (Xenopoulos *et al.*, 2003), iii: (Fergus *et al.*, 2011), iv: (Wilson & Xenopoulos, 2008), v: (Williams *et al.*, 2010), vi: (Rantakari & Kortelainen, 2008), vii: (Larsen *et al.*, 2011), viii: (Sobek *et al.*, 2005). % Wetlands, Slope, % Poorly drained soils, NDVI, Runoff, % Bog, Soil C, Soil C:N refer to catchment properties, whereas climate variables refer to annual means. NDVI means "Normalized Difference Vegetation Index". More details provided in the respective references.

Ref	Study scale	Main drivers of DOM or nutrients
i	local-regional, 10^1km	Lake area and Perimeter, % Wetlands, Slope
ii	local-regional, 10^2km	Watershed area, % Wetlands, Slope
iii	local and regional	% Wetlands and Land use
iv	regional, 10^2 km	% Poorly drained soils, Hydrology
v	regional, 10^2 km	Land use, % Wetlands, Temperature
vi	continental, $10^{2\text{-}3}$ km	Nutrients, Iron
vii	continental, $10^{2\text{-}3}$ km	NDVI, Runoff, Temperature, Slope, % Bog
viii	global, $10^{3\text{-}4}$ km	Precipitation, Runoff, Soil C, Soil C:N, Elevation, Conductivity

Table 1.2 Source of the geographic data processed in this study.

Variable	Source
Mean annual Temperature, Precipitation	WordClim, (Hijmans *et al.*, 2005)
Vegetation density in the catchment	Global forest monitoring program, (Hansen *et al.*, 2003)
Soil carbon content	The Atlas of the Biosphere, (IGBP-DIS, 1998)
% Wetlands in the catchment	Geobase(Geobase, 2009)
Lake area	Geobase(Geobase, 2009)
Catchment area	Geobase(Geobase, 2009)
Catchment slope	Geobase(Geobase, 2009)
Mean annual runoff	UNH/GRDC, (Fekete, Vorosmarty et Grabs, 2000)

1.4 RESULTS

1.4.1 Spatial structure in climate, landscape and lake properties

The variables studied here span a wide range in spatial structure. At the upper end of the spectrum, mean annual temperature and precipitation tended to vary at a very large (hereafter "continental") scale with lakes spatially auto-correlated within a radius of 741 and 566 km of each other, respectively, indicating that mean annual temperature at any given site can be partly predicted from the mean annual temperature observed at any other site situated within 741 km. At the other end of the spectrum were lake and catchment area, which varied at local scale, i.e., any pair of lakes situated more than 12 km apart tended to be completely independent in terms of those variables. Varying at an intermediate, regional scale were proxies of lakes metabolism, for which lakes tended to be spatially auto-correlated at distances ranging between 38 and 351 km (Fig, 1.1b). Production to respiration (P:R) ratio and CO_2 concentration (expressed as pCO_2, see Methods) occupy the upper and lower range, respectively, while bacterial respiration (BR), bacterial production (BP) and primary production (PP) were spatially auto-correlated for lakes situated within around 200 km from each other.

Variables associated to DOM and nutrients, including concentration (DOC) and composition (% contribution of PARAFAC components (C1-C6) to total fluorescence) as well as TP and TN were spatially structured at comparable scales. In particular, total DOC, CDOM and humic- or fulvic-like components of DOM (C1-C4) tended to be spatially auto-correlated over larger scales than the typically labile and freshly-produced protein-like components C5 and C6. For those typically labile DOM groups, auto-correlation disappeared at a scale (75 km) comparable to soil organic carbon content in the top 50 cm (Fig. 1.1b). Landscape properties such as vegetation density in the catchment (VCF, see Table 1.1), catchment slope (Slope), mean annual runoff (Runoff), and percent area covered by wetlands (% Wetlands), were located between those different DOM groups and tended to be auto-correlated at scales of 141 to 241 km (Fig. 1.1b).

1.4.2 Spatial patterns in lake metabolism

The different climate, landscape and limnological variables collectively explained 49% of the variation in the five measured proxies of lake metabolism (Fig. 1.2a). Not all variables were significant predictors of lake metabolism, but DOM and nutrient concentrations and DOM composition (as shown by %C2, %C3, %C5, %C6) were significantly driving lake metabolism (Fig. 1.2a). Mean annual temperature and runoff, catchment elevation and VCF were also significant predictors. The five indices of lake metabolism (BR, PP, P:R, pCO_2, BP) tended to be positively related to high DOM and nutrient concentrations, mean annual temperatures and proportions of fluorescence component C3, but negatively to fluorescence components C2, C5 and C6, as well as to elevation and runoff. Water temperature at the moment of sampling was a weak but significant predictor of BP ($r^2 = 0.07$, $p = 0.002$), PP ($r^2 = 0.14$, $p < 0.001$) and P:R ($r^2 = 0.10$, $p < 0.001$) but did not significantly explain BR and pCO_2 ($p = 0.90$ and $p = 0.15$, respectively) in simple linear regressions; water temperature was not a significant predictor of lake metabolism in the RDA analysis once the other predictors were included.

Dissolved organic matter and nutrient collectively explained 43 % of the variance in lake metabolism, corresponding to the majority of the variance explained when all drivers are included (49 %, Fig. 1.2b). Climate and landscape properties also explained a considerable amount of the total variance in lake metabolism (27 % and 31 %, respectively), but most of their effect overlapped with that of DOM and nutrients (Fig. 1.2b). There was a strong overlap between the effect of climate with that of lake and landscape properties on lake metabolism, suggesting that the climatic effect is largely integrated by landscape properties; DOM and nutrients, in turn, appear to integrate the effect of both climate and landscape properties on lake metabolism.

There was strong spatial structure measured in lake metabolism. In addition to the spatial auto-correlation that was measured for individual proxies of lake metabolism (Fig. 1.1b), the Moran's I measured on the scores of the sampled lakes on the first two axis of the RDA (which represent the two strongest linear combinations of the different proxies of lake metabolism) were significantly positive for lakes situated within around 200 km from each other (Fig. 2c, d), typical of the geographic range of the *a priori* determined sampling regions

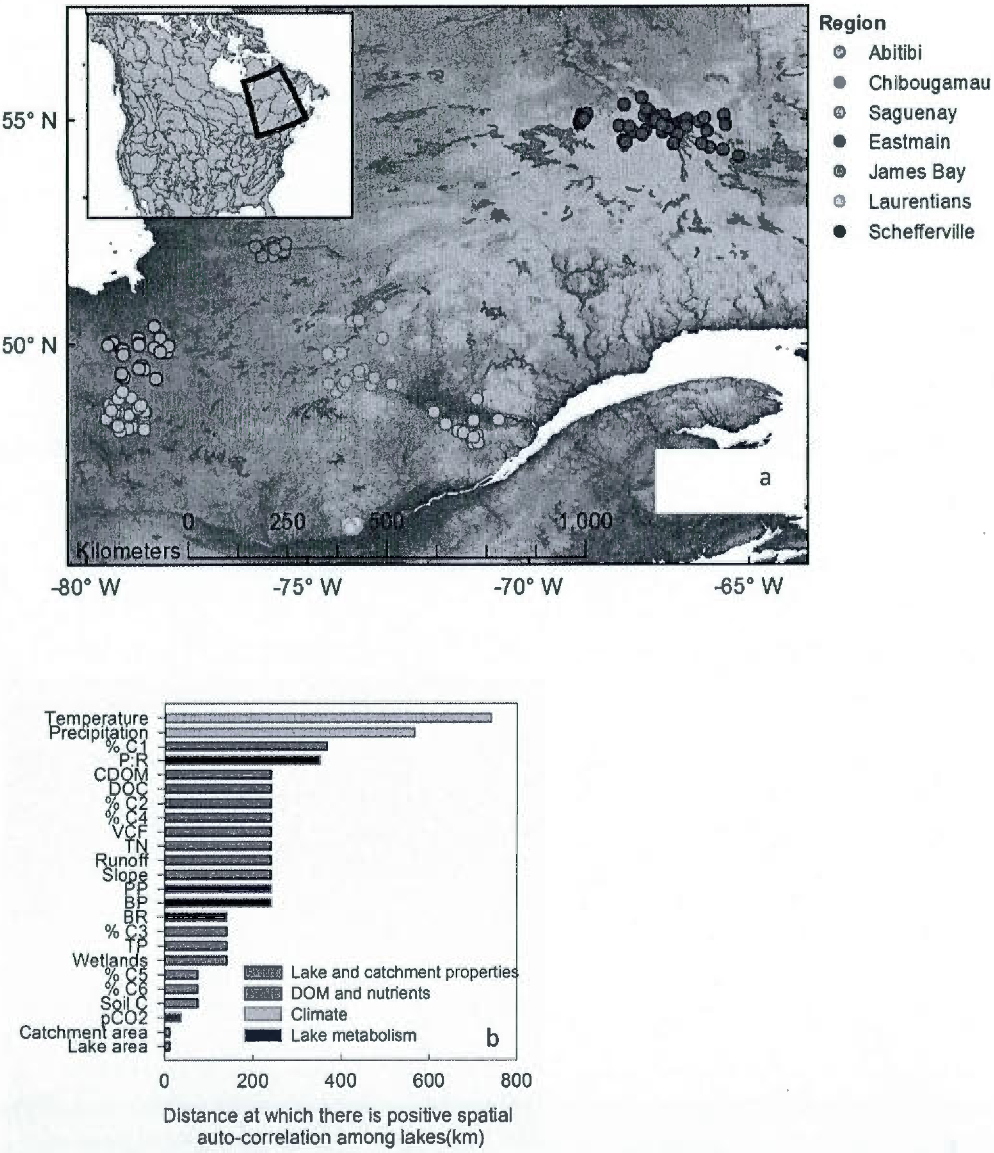

Figure 1.1. The spatial structure in the measured variables across a large boreal landscape.

a) Distribution of the sampling sites across Québec biogeographical regions. b) Spatial scales of variation of climate, landscape and lake properties depicted as the distance at which spatial auto-correlation reaches 0. The map is scaled such that the distances in lower panel are directly transposable. Climate variables are long-term mean annual averages. %C1-6 represent the percent contribution of a specific DOM group to total fluorescence in a sample; it is an index of DOM composition. P:R, PP, BP and BR represent production to respiration ratio, primary production, bacterial production and bacterial respiration rates, respectively. CDOM, DOC, TN and TP represent concentrations of colored dissolved organic matter, dissolved organic carbon, total Nitrogen and total Phosphorus, respectively. VCF stands for vegetation continuous field; it denotes vegetation density in the catchment.

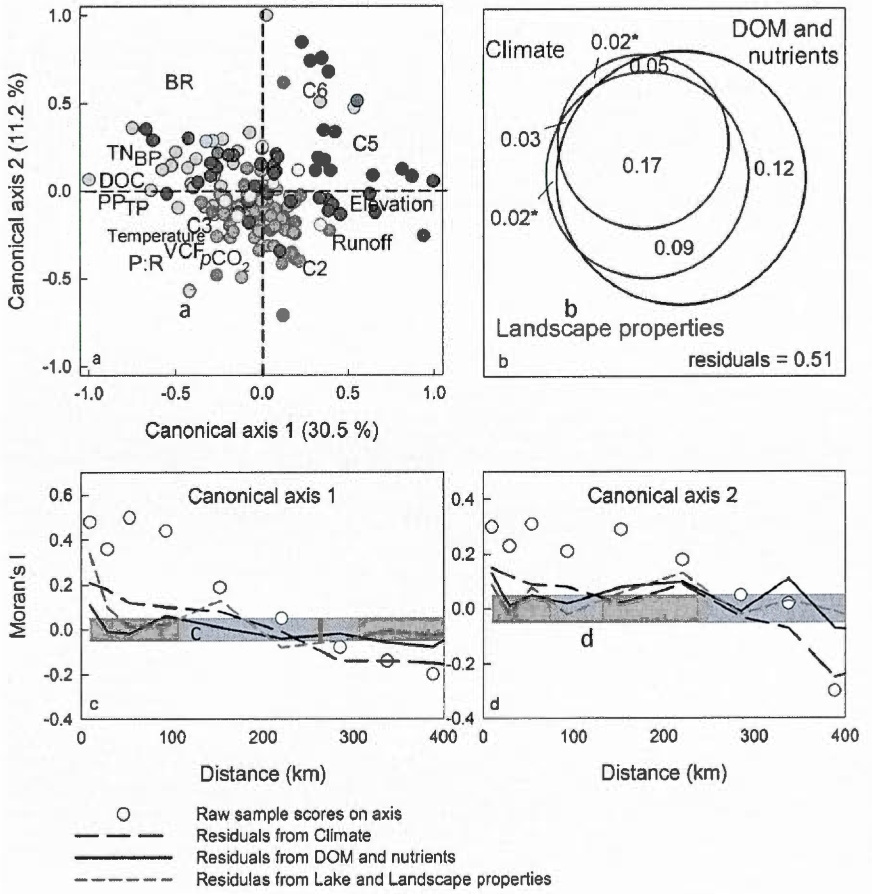

Figure 1.2. Climate, landscape, DOM and nutrient controls on the spatial patterns in lake metabolism.

a) RDA of lake metabolism as a function of climate, landscape properties and DOM and nutrients. Color codes match map's legend. $r^2 = 0.49$, $n = 157$, $p < 0.001$. b) Partitioning the variance explained in lake metabolism by "Climate" (mean annual temperature (Temperature)), "Landscape properties" (vegetation density in the catchment (VCF), mean catchment Elevation and Runoff) and "DOM and nutrients" (total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), percent contribution of a DOM group to total fluorescence (C2, C3, C5, C6)). Not all the variables included in Fig. 1b were significant predictors of lake metabolism. * : Fraction not significant. c) and d) Spatial structure remaining in the residuals of RDAs performed with subsets of the predictors, based on the above categories.

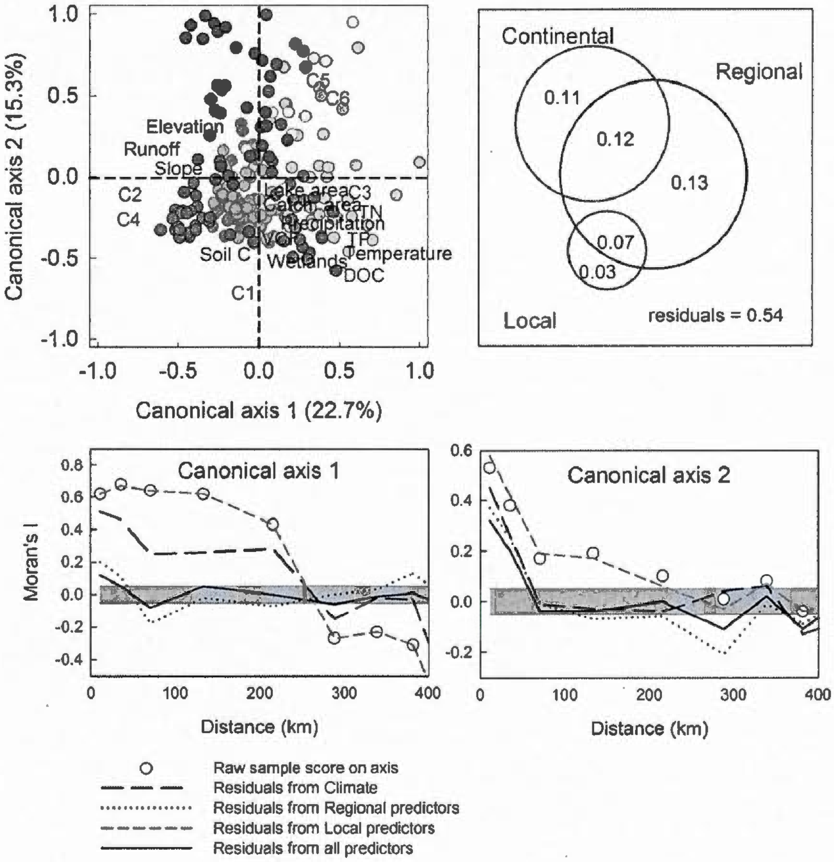

Figure 1.3 Multi-scale predictors of the spatial patterns un lake DOM and nutrients.

a) RDA of DOM as a function of lake, landscape and climate drivers. Color codes match map's legend. $r^2 = 0.45$, $n = 239$, $p < 0.001$. b) Partitioning the variance explained in DOM and nutrients by drivers that vary at different scales. "Continental" includes mean annual Temperature and Precipitation, "Regional" includes catchment mean Runoff, Elevation, soil carbon content (Soil C) and Slope, vegetation density (VCF) and % Wetlands in the catchment. "Local" includes Lake and Catchment area. Categories are based on the scale of spatial auto-correlation presented in Fig. 1.1b. c and d) Spatial structure remaining in the residuals of RDAs performed with subsets of the predictors, based on the above categories.

(see Fig. 1.1a). There were indeed apparent regional signatures in Fig.1. 2a, which were validated by a linear discriminant analysis (LDA): 73 % of lakes were classified in the right *a priori* determined sampling region (n= 158, $p < 0.001$) based on lake metabolism.

Not all predictors contributed equally to this regional structure in lake metabolism. Substantial spatial structure remained in the residuals of the RDA performed with climate and landscape properties on axis 1 (Fig. 1.2c), but there was virtually no spatial structure remaining in the residuals of the RDA performed with DOM and nutrients as the only predictors (Fig. 1.2c), suggesting that the latter variables were mostly responsible for the regional structure observed in lake metabolism.

1.4.3 Spatial patterns in lake DOM and nutrients

A combination of continental, climate drivers (mean annual precipitation and temperature) with local (lake and catchment area) and regional (mean catchment slope and elevation, percent wetlands in the catchment, soil C content, runoff, VCF) lake and landscape properties explained nearly half (46 %) of the variation in lake DOM (concentration and composition) and nutrients (Fig 1.3a, b). Lakes for which catchments are characterized by high slope and runoff tend to have higher proportions of components C2 and C4 and low proportions of component C3, whereas all the other predictors were contained in (or very close to) the lower right quadrant of the RDA (Fig. 1.3a), along with DOC, C3, total nitrogen (TN) and total phosphorus (TP). This suggests that at the landscape level, climate, catchment productivity, percent area covered by wetlands and soil C content tend to co-vary. Thus, the lakes located in catchments characterized by the highest values of these variables tend to have higher concentrations of DOC and nutrient and higher proportions of humic fluorescence component C3, whereas DOC- and nutrient-poor lakes typically have higher proportions of humic- and fulvic-like DOM components C2 and C4 and higher proportions of protein-like components C5 and C6.

The majority of the variance in lake DOM and nutrient was explained by predictors that were spatially structured at regional scales (Fig. 1.3b), similar to DOM and nutrients themselves (Fig. 1.1b). There was, nonetheless, some overlap between the effect those regional landscape predictors with that of climate, which was structured at a continental scale

(Fig. 1.3b). This suggests that the effect of climate on DOM and nutrients is partly integrated by landscape properties related to the production and delivery of carbon from the catchment to the lake. About half of the effect of continental predictors, however, was direct and was not shared with either regional or local predictors. Local predictors (lake and catchment area) explained the smallest fraction of the variance in DOM and nutrients, and most of their effect was also integrated by regional predictors (Fig. 1.3b); there was no overlap between the effect of local and continental predictors.

There were even stronger regional patterns in lake DOM and nutrient than in lake metabolism (Fig. 1.3a *vs* Fig. 2a); 93 % of lakes were classified in the right *a priori* determined sampling "region" (LDA, n= 239, $p < 0.001$) based on their nutrient and DOM content. Similar to lake metabolism, the Moran's I measured on the scores of the sampled lakes on the first two axis of the RDA were significantly positive for lakes situated within over 200 km from each other (Fig. 1.3c, d), but the drivers of the spatial structure in DOM and nutrients were different. Local drivers (lake and catchment area) did not account for any of the spatial structure in DOM and nutrients (Fig. 1.3c, d), and there was considerable spatial structure remaining in the residuals of the RDA performed with continental predictors (climate) for lakes situated up to around 200 km. The remaining regional, landscape properties explained nearly as much spatial structure in DOM and nutrients as the whole model (Fig. 1.3c, d). It thus appears that there are spatially structured patterns in lake DOM and nutrients resulting from the interplay of continental-scale climate properties and regional-scale landscape properties.

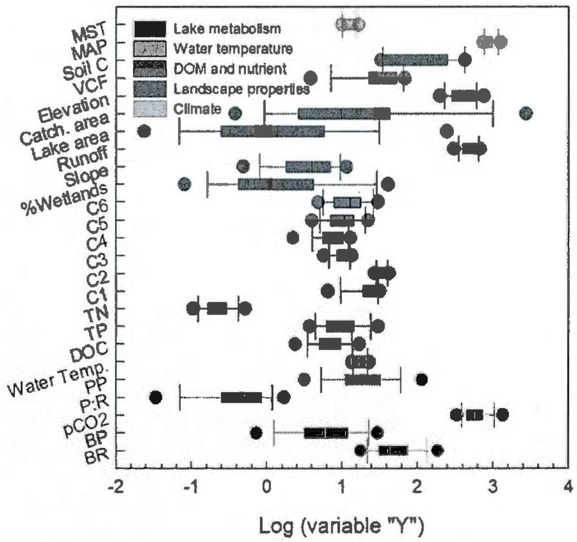

Figure 1.4. Range of variation of the reported variables across the sampled lakes

All variables are presented on a log scale in order to emphasize the orders of magnitude of variability; one unit on the "X" scale represents one order of magnitude variation. MAP denotes mean annual precipitation and MST denotes mean summer temperature. We used MST rather than mean annual temperature (MAT) for this analysis in order to avoid negative values that could not be logged and to have a range of temperature that is comparable to the water temperature reported; using one or another would not meaningfully alter the range in terms of order of magnitude (logMST range: 0.97-1.25; logMAT range: 0.59-1.16). Points represent the 5th and 95th percentiles, and vertical lines represent the 10th, 25th, 50th, 75th and 90th percentiles.

1.5 DISCUSSION

This study provides empirical evidence of biogeochemical pathways linking large-scale environmental patterns to local aquatic carbon cycling through the delivery of organic and inorganic matter from land to water, illustrated here by the interplay of climate, landscape and limnological variables with different spatial structures. We showed that across the area spanning over 1 million km², some variables (i.e., mean annual temperature and precipitation) tended to vary slowly and gradually along geographic gradients, while others, namely lake and catchment area, varied in a much less structured way and were nearly unpredictable over space across the study region. Between those extremes were a series of lake and landscape properties varying at intermediate regional scales, and the combined effect of those different drivers resulted in strong regional patterns in lake metabolism. Lake DOM and nutrients not only integrated the effect of climate and landscape properties on lake metabolism, but further drove spatially structured patterns in some key processes and properties involved in the aquatic carbon cycling across this large and complex boreal landscape.

1.5.1 Climate and landscape controls on DOM and nutrient

Mean annual temperature and precipitation at the sampling sites explained nearly a quarter of the variation in lake DOM and nutrient (Fig. 1.3b), and half of that explanatory power was shared with regionally structured landscape properties. Several of the landscape variables such as surface runoff, soil carbon content, vegetation density in the catchment and perhaps even percent wetlands in the catchment are likely, at least partly, climate-driven. The overlap between the effect of continental climate variables with regional landscape properties on lake DOM and nutrients (Fig. 1.3b) suggests that climate indeed exerts an indirect control via its effect on factors such as terrestrial vegetation and hydrology in the catchment; this statistical overlap between the effect of very rough measures of climate (long-term mean annual averages in temperature and precipitation) and a handful of widely reported landscape properties on mid-summer, punctual measurements of DOM and nutrient likely underestimates the underlying effect of climate. Regardless of the actual strength of the direct and indirect statistical links between climate and lake DOM and nutrient, our results provide strong empirical support to the hypothesis that lake DOM and nutrient respond to climatic pressures via the effect of climate-sensitive landscape properties.

1.5.2 The indirect effect of climate

Climate could have been expected to have a strong impact on lake metabolism, considering the direct impact of temperature on the aquatic processes involved in aquatic metabolism (Apple *et al.*, 2006; Gudasz *et al.*, 2010; Yvon-Durocher *et al.*, 2012). Water temperature, however, was weakly or not related to the different lake processes associated to metabolism, and it was not a significant predictor in the RDA performed on lake metabolism either (Fig. 2a).

This lack of direct effect of temperature can be explained by the mismatch in terms of environmental gradients covered. While variables such as DOM, nutrient and several landscape properties varied by roughly an order of magnitude across the study area, comparable to the range of variability observed in the measured proxies of lake metabolism, water temperature at the moment of sampling barely varied twofold (Fig. 1.4). It is thus unlikely that the small changes in water temperature across the study area can explain the large changes in lake metabolism. Conversely, lake and catchment area varied by close to four orders of magnitude across the study region (Fig. 1.4), well beyond the range of variation observed in lake metabolism; neither was a significant predictor of lake metabolism at that scale.

It is interesting to note that whereas the range in measured water temperature was relatively narrow, (5^{th} and 95^{th} percentiles = 12.7 and 23.1 °C, respectively), mean annual temperature at the sampled sites ranged from -5.7 to 3.9 °C (5^{th} and 95^{th} percentiles, respectively) was almost symmetrically distributed around the freezing point. This range of temperature is crucial in determining the balance between production, decomposition and transport of terrestrial material to aquatic environments due to a combination of hydrology, primary productivity and vegetation type in the catchment (Laudon *et al.*, 2012). The latitudinal gradients in climate across our study area were indeed reflected in proxies of terrestrial primary productivity (i.-e. vegetation density in the landscape, Fig. 1.2a), consistent with a general decrease in soil carbon content along a South-North gradient

(IGBP-DIS, 1998), and dominant vegetation in the catchment varied from deciduous and mixed forest in the Southernmost Laurentians region to scarce spruce-moss forest in the Northernmost Schefferville region (Geobase, 2009). Thus, the absence of a direct effect of mid-summer water temperature on lake metabolism across the study area is not incompatible with the fairly strong effect of climate (Fig. 1.2b), but rather suggests that the effect of climate is indirect and conveyed by drivers other than temperature.

In this regard, DOM and nutrients have a more obvious causal effect than climate or landscape properties on lake metabolism, and there was a significant overlap in the effect of those different drivers (Fig. 1.2b). There was a strong coherence between the spatial patterns in DOM and nutrient and spatial patterns in climate, soil carbon concentrations, runoff, vegetation density and percent wetlands in the catchment, implying that those different variables tend to co-vary at the landscape level. Although the large number of predictors and the high overlap in the effect of those different predictors do not allow a robust interpretation of the individual effect of any single variable, the overall patterns suggest that it is DOM and nutrient that are mechanistically driving lake metabolism, and that the effect of landscape properties on lake metabolism is expressed through both quantitative and qualitative aspects of DOM. The co-variation between those different potential drivers of lake metabolism further suggests the presence of a common, gradual and diffuse driving force over the study area, and the very strong spatial structure observed in mean annual temperature and precipitation (Fig. 1.1b) suggests that climate is that underlying driver.

1.5.3 Regional structure in lake metabolism, DOM and nutrients

The major role of DOM and nutrients on lake metabolism (Fig. 1.2) is not unexpected, as their impact on individual aspects of metabolism has been widely studied. It is well established, for example, that the concentrations of DOM and nutrients drive the rates of respiration, as well as primary and secondary production in lakes, or the ratio between both (Smith, 1979; del Giorgio & Peters, 1994; Pace & Prairie, 2005). Likewise, different DOM groups from contrasting sources and origins are known for their different composition and degradability in aquatic environments (Wickland *et al.*, 2007; Fellman *et al.*, 2008, Lapierre and del Giorgio, submitted). Little was known, however, on how those different DOM pools respond to contrasting drivers in the landscape and how they interact in driving lake metabolism over large spatial and environmental gradients. The results presented here show that DOM and nutrients allow to understand the spatial patterns in key proxies of lake metabolism across a wide number and variety of natural aquatic environments situated across large geographic gradients, and perhaps less intuitively, that the spatial patterns in DOM and nutrient are driving strong spatial structure in lake metabolism.

The presence of spatial auto-correlation in lake metabolism, DOM and nutrients suggests that variables with strong spatial structure are driving those lake properties. In community ecology, spatial auto-correlation is often explained by connectivity and thus dispersal (Cottenie, 2005; Beisner *et al.*, 2006), such that "space" in itself is a causal predictor of the spatial patterns. Here DOM and nutrients are indeed moving through the aquatic networks in the landscape, but in a non-conservative manner, i.-e. they are gradually removed from the environment and replaced by local inputs (Mattsson *et al.*, 2005; Weyhenmeyer *et al.*, 2012; Lottig *et al.*, 2013). Moreover, the sampled lakes are almost never hydrologically connected across the study areas. Thus, connectivity cannot play a large role in explaining the similarity of nearby lakes. Taking the effect of environmental variables into account almost entirely removed spatial auto-correlation in DOM, nutrients and lake metabolism, further supporting that there is no clear effect of connectivity or proximity *per se* underlying the patterns presented here. It thus appears that there are predictable spatial patterns in lakes across this boreal landscape, resulting in strong regional signatures as nearby lakes tend share comparable climate, landscape and aquatic properties which are ultimately reflected in comparable metabolism.

1.5.4 Conclusions and implications

The different results presented in this study suggest an effect of climate on the aquatic carbon cycle that is not mediated by water temperature at regional scales. Instead, the effect of climate appears indirect and mediated by co-varying landscape properties and their effect on DOM and nutrient. This indirect effect of climate combined with the strong spatial structure in aquatic processes suggests that gradual and diffuse changes in the environment should have a stronger effect on lake metabolism at the landscape level than punctual changes in land use. Moreover, the co-variation of climate and several landscape properties with DOM and nutrient proposes that these variables may co-vary, temporally and perhaps latitudinally, as climate keeps changing; these changes should in turn will be reflected in lake functioning.

Previous evidence with reduced sets of variables, originating from systems with stronger human influence, have shown region-specific relationships between nutrients, DOC and proxies of lake metabolism (Fergus *et al.*, 2011; Wagner *et al.*, 2011; Lapierre & del Giorgio, 2012), implying that extrapolation of regional relationships should be done with caution and proper knowledge on the underlying regional characteristics. The results we present here, however, show that at least in boreal landscapes with low human influence, DOM concentration, composition, and nutrient respond similarly to common environmental drivers and convey a similar effect on lake metabolism. Moreover, considering that DOM and nutrients themselves were regionally structured as a function of climate and landscape properties, and further integrated the effect of the latter variables on lake metabolism, it appears that the relationships that we report here could be extrapolated to other undisturbed northern landscapes beyond the studied region. There are thus several potential pathways linking climate and landscape properties to aquatic metabolism and carbon cycling across large boreal landscapes, and our results suggest that the delivery of DOM and nutrients from land to water is a key pathway at regional scales, where the direct impact of temperature may not be fully expressed.

1.6 ACKNOWLEDGEMENTS

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1.7 SUPPORTING INFORMATION

1.7.1 Supplementary Figure

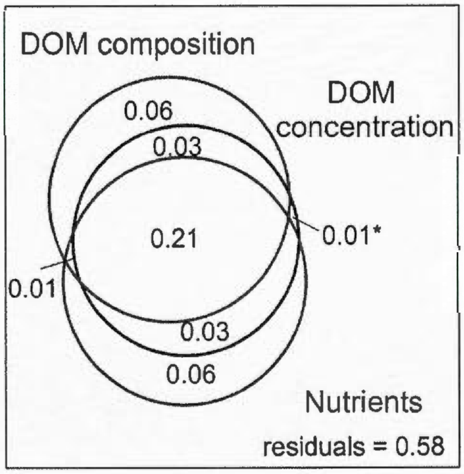

Figure 1.5 Partitioning the variance explained in lake metabolism by DOM composition, DOM concentration and nutrient concentration.

* : Fraction not significant. "DOM composition" includes the percent contribution of fluorescence components C2, C3, C5 and C6 to total fluorescence. "DOM concentration" represents dissolved organic carbon concentration, and "Nutrient concentration" represent total nitrogen and total phosphorus concentration.

1.7.2 Supplementary Discussion

1.7.2.1 *Quantized distribution of spatial auto-correlation*

We estimated spatial structure (expressed here as the maximum distance at which there was significant positive spatial auto-correlation, Fig. 1b) directly from the correlograms, such that there were only 20 possible distance intervals at which auto-correlation crosses zero. Considering the number of variables studied and that most variables were not spatially auto-correlated beyond a few hundred kilometers, this analysis generated the quantized distribution shown in Fig. 1.1b and provides only a rough estimation of the spatial structure measured in the different variables.

1.7.2.2 *The effect of DOM vs nutrients on lake metabolism*

Partitioning the variance explained by DOM concentration, composition, and by nutrient reveals that those three groups of drivers are significant predictors of lake metabolism at large spatial scales, and more importantly, that there is a strong overlap between the effect of those different drivers (Fig. 1.5). Although both nutrients and DOM composition individually explained only small, yet significant, fractions of the variance in lake metabolism, the effect of DOM concentration was almost entirely shared with DOM composition and nutrient concentration (Fig. 1.5). Both nutrient concentration and DOM composition thus improved the amount of variance explained in lake metabolism compared to DOM concentration alone, and most of the effect of nutrients on lake metabolism was taken into account when DOM concentration and composition were combined (Fig. 1.5).

1.7.2.3 *The influence of study design on the estimation of spatial auto-correlation*

It should be noted that it is the overall pattern that is of interest here rather than the actual distances at which spatial autocorrelation disappears for any given variable (which we use as a measure of spatial structure). This absolute distance may be slightly underestimated and not necessarily transposable globally. Firstly, geostatistical analyses are typically performed on more homogenous sampling schemes (Goovaerts, 1997). Our aggregated sampling scheme could have inflated the regional behavior of certain variables; thus, artificially decreasing the estimated distance at which they are auto-correlated due to the large gaps in space between the sampling regions (Fig. 1a). The large number of sites studied here and the very wide environmental and spatial gradients, however, resulted in robust estimations of spatial auto-correlation. In particular, average Moran's I reported here were always measured on more than 2800 pairs of lakes within a certain distance interval, and distance intervals were between 25 and 114 km (average = 60 km). Considering that the closest pair of lakes was less than 100 m apart and that the farthest pair of lakes was separated by 1230 km, this shows that our sampling scheme yielded an adequately regular distribution of the estimations of auto-correlation across different scales. Secondly, the main underlying drivers (e.g. climate, geology, topography) of the spatial structure of the variables that we report here are likely to behave differently in space in other landscapes of the world, such that the scale of variation that we report here may not directly apply elsewhere. Finally, the results presented here include data collected over four years of sampling, covering the period of May to August; however, this temporal component was not taken into account in the present study. Thus, there is undoubtedly a portion of spatially stochastic variability (e.g. weather, irradiation, hydrology) that is not taken into account by the measured variables, which on the other hand, highlights the strength of the spatial patterns presented here. Regardless, the patterns are clear: DOM concentration and composition, nutrients and lake metabolism showed spatially structured patterns at regional scales over the entire study area, which is a consequence of the interplay of drivers varying at local, continental, but mostly regional scales.

CHAPITRE II

GEOGRAPHICAL AND ENVIRONMENTAL DRIVERS OF REGIONAL DIFFERENCES IN THE LAKE PCO2 VS DOC RELATIONSHIP ACROSS NORTHERN LANDSCAPES

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N.B. References cited in this chapter are presented at the end of the thesis.

2.1 ABSTRACT

Several recent studies have identified dissolved organic carbon (DOC) as playing a key role in determining surface water partial pressure of CO_2 (pCO_2) in northern lakes, and in particular, in shaping the commonly observed patterns of CO_2 supersaturation. The nature of this role, however, is unclear and appears to vary regionally, as evidenced by the contrasting strength and shape of the diverse pCO_2 versus DOC (pCO_2-DOC) relationships. Here we combine original data on lake pCO_2 from 6 boreal and temperate regions of Québec (Canada) with 13 studies from northern temperate and boreal aquatic landscapes published in the past 15 years to explore the factors that explain the differences in regional pCO_2 baselines (pCO_2 at low DOC), and in the slopes of the pCO_2-DOC relationships. Mean elevation was the best predictor of the regional pCO_2 baselines, suggesting that lake position in the landscape determines the contribution of terrestrially-derived CO_2 to lake pCO_2. In contrast, the slope of the pCO_2-DOC relationships was strongly negatively correlated to the mean regional TP:DOC ratio. The relationship between DOC and TP varied at the cross-regional scale and there was a large increase in the TP:DOC ratio at $TP > 20\ \mu g\ L^{-1}$, resulting in negative slopes of the pCO_2-DOC relationships for regions situated in that part of the TP gradient. These results highlight the interplay that exists between geographical gradients, large-scale biogeochemical patterns in regional lake trophic status and the associated metabolic balance in determining pCO_2 dynamics in northern lakes.

2.2 INTRODUCTION

Lakes act as funnels for materials derived from soils, including organic and inorganic nutrients and carbon exported from their terrestrial catchments (Cole *et al.*, 2007 ; Prairie, 2008). This supplementary material is responsible for a large fraction of the flow of carbon through aquatic biogeochemical cycles and impacts aquatic ecosystems in several ways. In particular, organic carbon exported from the terrestrial landscape contributes to the widespread supersaturation of CO_2 in surface waters in lakes in northern landscapes, and to its subsequent evasion to the atmosphere (Jonsson *et al.*, 2007 ; Kling, Kipphut et Miller, 1991), which is now recognized as a globally significant component of the biosperical CO_2 budget (Battin *et al.*, 2009 ; Tranvik *et al.*, 2009).

The drivers of this outgassing, however, are not well understood, which in turn limits our understanding of the role of lakes in temperate and boreal carbon budgets. There is a large degree of variability at different spatial scales across lakes, both in the partial pressure of CO_2 (pCO_2), and in the contribution of the different processes that supply pCO_2. For example, it has been widely reported that biological mineralization of allochthonous organic carbon is a major source of excess CO_2 in lakes (del Giorgio et Peters, 1994 ; Duarte et Prairie, 2005 ; Sobek *et al.*, 2003), but other studies have shown that the apparent net heterotrophy is insufficient to sustain the observed CO_2 supersaturation, and have pointed to inputs of CO_2 from the catchment as playing a key role (Dubois, Carignan et Veizer, 2009 ; Finlay *et al.*, 2009 ; Stets *et al.*, 2009). Likewise, photo-oxidation of DOC was found to account for essentially all of the DOC loss to CO_2 in boreal Canadian lakes (Molot et Dillon, 1997), whereas respiration was shown to account for most of the mineralization in Swedish lakes with a comparable DOC range (Graneli, Lindell et Tranvik, 1996 ; Jonsson *et al.*, 2001).

These apparently conflicting observations suggest that different processes are simultaneously active in all lakes and that their relative contribution to surface water pCO_2 varies greatly, both temporally and along lake gradients, leading to a large heterogeneity both within (Aberg *et al.*, 2004 ; Kelly *et al.*, 2001) and across (Sobek, Tranvik et Cole, 2005) lakes. Several studies have nevertheless identified broad patterns in lake surface water pCO_2 along, for example, gradients of lake size (Alin et Johnson, 2007 ; Marchand, Prairie et del

Giorgio, 2009 ; Urabe *et al.*, 2011), nutrients (Huttunen *et al.*, 2003 ; Rantakari et Kortelainen, 2008), and DOC concentration (Bergstrom *et al.*, 2004 ; Hope, Kratz et Riera, 1996 ; Kritzberg *et al.*, 2005 ; Larsen, Andersen et Hessen, 2011a).

These patterns with DOC concentration have generally been interpreted as evidence that C export from the terrestrial landscape fuels CO_2 supersaturation in lakes, wherein DOC would either act as the direct substrate for CO_2 production, or as a proxy for the loading of inorganic C (Humborg *et al.*, 2010). In this regard, the relationship between pCO_2 and DOC appears to be a key property that may account for the regional differences in the regulation of lake pCO_2. For example, the pCO_2 at very low DOC concentrations may reflect, for any given region, the level of CO_2 that is present at low rates of in situ DOC consumption and degradation, and thus may be an indication of landscape scale export of CO_2 to lakes. Likewise, a strong positive relationship between DOC and pCO_2 would suggest a dominant role of in situ oxidation of terrestrial organic carbon (biological or photo-chemical) in generating excess CO_2 in lakes, or a significant contribution of associated drivers of DOC with a similar impact on pCO_2. Conversely, a weak, or a negative relationship would indicate either a strong contribution from other drivers that are not correlated to DOC, or from drivers that are correlated with DOC but have a contrasting impact on pCO_2, respectively.

In this context, it is interesting to note that whereas there have been a number of pCO_2-DOC relationships reported for a variety of northern regions, there is a remarkable range in the strength and, more importantly, in the shape of these relationships (Roehm, Prairie et del Giorgio, 2009). Several factors could explain these regional discrepancies. For example, regional patterns in DOC composition and susceptibility to biological and photochemical degradation could lead to contrasting pCO_2 levels per unit of ambient DOC, and potentially to a different slope and intercept of the regional pCO_2-DOC relationships. Likewise, regional patterns in landscape morphology and lake position in the landscape may dictate the amount and relative proportions of DOC and CO_2 exports from land to lakes. Further, regional patterns in lake trophic status and the ensuing patterns in lake metabolism may modulate the impact of increasing DOC concentration, and presumably processing, on ambient pCO_2 dynamics. Those different scenarios imply a very different pCO_2 for any given amount of DOC present in lakes, and assessing such scenarios requires exploring how the

pCO$_2$-DOC relationship behaves at scales that are broader than those reported in individual field studies. This approach, however, also limits the number of variables available for an inter-regional comparison. Here we combine our own empirical results of a large-scale study across temperate and boreal lakes in Québec, with an extensive literature analysis of published data on pCO$_2$ for a wide range of northern temperate and boreal lakes across the world in order to explore the latter two scenarios that we introduced. We show that integrative geographical and environmental variables, such as elevation and the ratio of TP to DOC, predict well the inter-regional patterns in the pCO$_2$-DOC relationships across northern landscapes.

2.3 METHODS

2.3.1 Study area

The experimental portion of this study was conducted over 3 years in 6 boreal regions from Québec, Canada. We sampled the Eastmain region (52°N, 75°W) in 2009, the Abitibi (48.5°N, 79°W), James Bay (51°N, 79°W) and Laurentians (46°N, 74°W) regions in 2010, and the Chibougamau (49.5°N, 74°W) and Chicoutimi (48°N, 71°W) regions in 2011. These regions are part of the temperate and boreal biomes of Québec and cover a large span of characteristics in terms of climate, land cover and geomorphology. Sites within a region were typically found within a 50 km radius within which lakes and catchment properties were rather homogeneous, whereas different regions were several hundreds of kilometers afar and were represented by contrasting climate, vegetation cover and catchment morphometry. Briefly, from South to North, mean annual temperature ranges from 4.9 °C in the Laurentians to -2.0 °C in the Eastmain region. Mean annual precipitation ranges from 1050 mm y^{-1} in the Laurentians to 695 mm y^{-1} in the Eastmain regions, and between 900 and 1000 mm y^{-1} for the remainder of the regions. Dominant vegetation cover shifts from deciduous forest in the Laurentians to mixed deciduous and conifer forest in the Abitibi and Chicoutimi regions; the James Bay, Chibougamau and Eastmain regions are characterized by spruce-moss forest. Relief is generally flat and lakes are typically shallow and turbid in the Abitibi and James Bay regions, which are situated in the Abitibi clay belt; elevation and landscape steepness were the highest in Laurentians and Chicoutimi regions. High densities of beavers (*Castor canadensis*) typically alter the landscape hydrology, especially in the Abitibi region, due to the construction of dams of various sizes that flood rivers shores and increase water residence time.

2.3.2 Sampling and analyses

A total of 198 different lakes were sampled from June to August over the three sampling years by boat or hydroplane depending on accessibility. Most lakes were sampled once, but some were sampled twice over a two-month interval; averages have been used in the latter case. Water was pumped at a depth of 0.5 m from the deepest measured point of the lake for in situ and lab measurements. In situ $p\text{CO}_2$ was measured using a PP-Systems EGM-4 infrared gas analyzer (IRGA) receiving air equilibrated with the water by pumping lake water through a Liqui-Cel MiniModule contactor membrane. Total phosphorus (TP) was analyzed spectrophotometrically after persulfate digestion. Total nitrogen was analyzed as nitrates following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV autoanalyzer. Chlorophyll *a* (Chl *a*) was determined spectrophotometrically following filtration on Whatman (GF/F) filters and hot ethanol (90 %) extraction. Filters were sonicated prior to extraction. Lake water filtered through 0.45 µm porosity PES cartridges (Sarstedt) was analyzed for DOC concentration on an OI 1010 TOC analyzer following sodium persulfate digestion. The surface and catchment areas, as well as elevation of the lakes we sampled were determined using the ArcView 3.2 and ArcGIS v.9 software applied on the DEM derived from (1 : 50000) maps.

2.3.3 Literature analysis

In addition to articles from our existing database, we searched "Web of Science" for articles containing "DOC", "CO_2" or "pCO_2" or "carbon dioxide", and "lake*" as topical keywords, and extended our search for the past 25 years. We selected studies that had focused on temperate and boreal regions that provided DOC and $p\text{CO}_2$ data on enough number of lakes to allow building a significant $p\text{CO}_2$-DOC relationship. In cases where published data were available for regions that we sampled ourselves, we gave priority to our own data. Although there have been substantial numbers of papers that have reported lake CO_2 in the past decades, many fewer have reported both DOC and CO_2 across a range of lakes. We ended up collecting published data on lake $p\text{CO}_2$, DOC and ancillary lake and watershed properties taken directly from tables and figures from 13 papers published from 1996 to 2011. Five of the 13 studies did not simultaneously present DOC and $p\text{CO}_2$ data but were still used to explore the link between $p\text{CO}_2$ and lake and watershed morphometry. The data cover lakes from boreal and northern temperate regions in Canada, the United States, Sweden and Finland. Because the studies presented in this paper have typically conducted sampling in a specific region of the temperate or boreal landscape, we use the term "regional" to refer to study-specific patterns or averages hereon, even though the spatial scale of the different regions differs across studies: Tables 2.1 and 2.2 describe the environmental and geographical gradients for the different regions comprised in this literature analysis.

Different techniques have been used across studies to determine lake pCO_2, including calculation from DIC, alkalinity, temperature and pH (Rantakari et Kortelainen, 2005), direct measurement by gas chromatograph (Algesten *et al.*, 2004) and infra-red gas analyzer (Aberg *et al.*, 2004) of CO_2 equilibrated between water and air by headspace equilibration (Cole *et al.*, 1994) or equilibrating devices such as contactor membrane (Roehm, Prairie et del Giorgio, 2009). These methods have very different levels of resolution, but previous studies have shown that both the magntitude and the patterns are highly comparable across studies using different measurement techniques (del Giorgio *et al.*, 1999 ; Prairie, Bird et Cole, 2002). Although there is clearly additional noise introduced by comparing the pCO_2 values obtained from different techniques, we contend that the large gradients covered in this paper greatly limit the impact of these cross-method differences, and that the resulting noise does not introduce a systematic bias to the large-scale patterns presented here. We have thus used the pCO_2 data from the different studies as reported without any further correction or manipulation to account for potential methodological issues.

The sampling timing and frequency also varied among studies, but in all cases there was sampling at least during mid-summer. For studies with a single sampling date, we used the published data directly. Some studies reported several measurements throughout the ice-free period, and when averages for this period were presented in the study, we used those means. When data were available for different sampling dates but no mean was reported, we calculated averages for the ice-free season, more specifically, from May to October, such that there was no systematic seasonal effect among the studies that could bias the relationships presented here.

2.3.4 Data manipulation and statistical analyses

In this paper we compare how the pCO_2-DOC relationships vary across regions and explore factors that may explain these differences. One major problem in this analysis is that the key environmental and geographic variables considered here, in addition to pCO_2 and DOC, were not systematically included or reported in the various studies. As a result, the use of multivariate analyses would necessarily lead to either the removal of a large number of regions (which had incomplete variables sets) or the use of a very restricted set of variables that were reported for the largest number of regions, which would clearly undermine the main objective and the reach of this study.

To circumvent this problem, we first fit orthogonal (variance allocated to both explanatory and response variables)(Legendre et Legendre, 1998) linear regressions on log-transformed data from our own and published studies ($\log(pCO_2) = a \log(DOC) + b$), using JMP software (SAS institute, NC, USA), and generated study-specific, regional pCO_2-DOC models. We then used the resulting regression equations to estimate a regional pCO_2 baseline at very low DOC (pCO_2 at the 5th percentile of DOC concentrations for all available data; 1.9 mg L^{-1}). No baseline was estimated in the absence of a significant regression. We also used the slopes of the relationships as indicators of the effect of DOC on pCO_2 at the regional scale, more particularly, of how much pCO_2 increases for a given increase in DOC in each study. These new response variables (pCO_2 baseline and slope) were then analyzed individually against regional means of commonly measured geographical/morphological (latitude, elevation, mean annual temperature, lake size, mean depth), and lake environmental (Chl *a,* TP, TN, pH) predictors. Piece-wise regressions (Toms et Lesperance, 2003) were performed to identify break points in the orthogonal relationships of DOC and pCO_2 against TP, using the "Segmented" package (Muggeo, 2008) on R software (R development core team, 2010).

Variables were log-transformed to meet normality assumptions of linear regression. In one of the reported study, however, the non-transformed pCO_2-DOC relationship was linear and would not require transformation. In this case, the coefficient of correlation differed by only 0.01 between transformed *vs* non-transformed data, and not transforming data would greatly limit the comparability of the resulting parameters with that of other regions. Therefore, we only present here the results obtained from the fits to log-transformed data.

2.4 RESULTS

2.4.1 General lake properties

Table 2.1 presents the ranges and averages of lake properties, both for our study lakes and for the lakes for which we gathered published data. There was approximately an order of magnitude in range for most variables, both for our own and published data, showing the wide gradients in environmental and geographical conditions of the systems included in our analysis. Range, average and median TP and pCO_2 were comparable between Québec lakes and published estimates from other northern landscapes, but DOC tended to be higher and elevation to be lower in Québec lakes. Average lake area and maximum depth were skewed toward higher values due to a few extreme measurements, but medians suggest that the distribution of lake morphometric characteristics were also comparable between Québec and other northern temperate and boreal lakes (Table 2.1).

2.4.2 Regional pCO_2-DOC relationships

Out of the six regional pCO_2-DOC relationships that we obtained from our own field study, four were significant and positive while the remaining two (Abitibi and Laurentians regions) were not significant (Fig. 2.1, Table 2.2). There were strong regional differences in the strength and in the shape (slope and pCO_2 baseline) of these relationships, relative to each other and to those reported for other northern regions (Table 2.2). In particular, the pCO_2 baseline for Chicoutimi and Chibougamau regions of Québec were among the highest when all studies were considered together, and the slope of the pCO_2-DOC relationship for the Chibougamau region was the lowest positive relationship (Table 2.2).

Our literature analysis yielded a total of 8 additional regional studies that had reported concomitant surface water pCO_2 and DOC data. Out of the 8 regional studies, seven yielded significant positive relationships and one yielded a significant negative relationship (Table 2.2, Fig. 2.2). The average r^2 for the 14 individual relationships (8 published + our 6) presented in Figure 2.2 ($r^2 = 0.46$) was twice that obtained by fitting a log-log curve to all the points together ($r^2 = 0.23$, Table 2.2, "All data"), suggesting that the predictive power of DOC is much stronger at smaller, regional scales, and drastically declines as the scale is broadened. Taken together, our field data plus the published data show that there is over an order of magnitude range in $p\mathrm{CO}_2$ at any given concentration of DOC, but that there are regional trends in this scatter, reflected in widely varying slopes and $p\mathrm{CO}_2$ baselines at low DOC between regional models (Fig. 2.2, Table 2.2).

2.4.3 Patterns in regional $p\mathrm{CO}_2$ baseline

The regional $p\mathrm{CO}_2$ baselines were not correlated to water chemistry or other geographical variables but were strongly positively correlated to the average lake elevation in each study region (Fig. 2.3). Lake elevation is presumably a proxy of other catchment and lake morphometric variables with a more direct impact on lake $p\mathrm{CO}_2$, but unlike elevation, such variables were not commonly measured in studies reporting concomitant $p\mathrm{CO}_2$ and DOC values. The relationship of lake elevation with catchment and lake morphometric variables, available for individual lakes in some regions, provides a more causative assessment of the potential role of lake elevation on $p\mathrm{CO}_2$ dynamics. Individual lake elevation was negatively correlated with lake catchment area (Fig. 2.4a), which was, in turn, negatively correlated with the individual lakes $p\mathrm{CO}_2$ per unit DOC (Fig. 2.4b). Lakes situated in higher catchments also tended to be smaller (Fig. 2.5a), and smaller lakes tended to be more supersaturated in CO_2 (Fig. 2.5b). There was a large degree of variability in $p\mathrm{CO}_2$ for a given lake size, but small lakes tended to be systematically supersaturated, whereas $p\mathrm{CO}_2$ converges to equilibrium and even under-saturation with increasing lake area (Fig. 2.5b).

2.4.4 Patterns in the regional $p\mathrm{CO}_2$-DOC slopes

The slope of the $p\mathrm{CO}_2$-DOC relationships, on the other hand, was not correlated to the regional averages of most geographical or morphometric variables, weakly correlated to the average regional concentrations of TP ($r^2 = 0.34$, $p = 0.04$), but rather was strongly and negatively correlated to the average regional TP:DOC ratio (Fig. 2.6a). This relationship suggests that a given increase in DOC is associated with a lower increase in $p\mathrm{CO}_2$ at higher TP:DOC ratios, coherent with the trend of the decreasing $p\mathrm{CO}_2$ per unit DOC as TP increases in individual lakes (Fig. 2.6b), and with the observation that past a certain threshold in the TP:DOC ratio, increases in DOC do not imply higher $p\mathrm{CO}_2$.

The relationships of DOC and pCO_2 with TP (Fig. 2.7) are consistent with this pattern. At TP < 20.2 μg L^{-1}, DOC increases faster than TP (log slope = 1.22, Fig. 2.7a), and in this same range, pCO_2 increases as does TP (log-slope = 0.83, Fig. 7b). At TP = 20.2 μg L^{-1} (95 % confidence interval = 13.8 μg L^{-1} – 29.0 μg L^{-1}, based on the piece-wise regression), there is a significant shift in the TP - DOC relationship (Fig. 2.7a), wherein both variables become more loosely coupled and DOC increases at a slower rate than TP (log slope = 0.77), leading to higherTP:DOC values as TP increases in this part of the gradient. The relationship between pCO_2 and TP also drastically shifts at a comparable TP value (14.8 μg L^{-1}; 95% confidence interval =13.1 μg L^{-1} – 16.8 μg L^{-1}), switching from positive to negative. Therefore, at low TP:DOC ratios, there is a positive relationship between pCO_2 and both DOC (Fig. 2.7) and TP (Fig.2.7b), but the slopes become shallower, and even negative, as TP increases disproportionately relative to DOC (Fig. 7a).

Tableau 2.2 Mean and range of the major variables for the lakes sampled in this study and for the published data used in this analysis.

Variable	Range (min ; max)	
	This study	Published
Lake area (km²)	0.01 ; 2335	0.0007 ; 378 400
Elevation (m)	121 ; 856	81 ; 1140
Maximum depth (m)	0.50 ; 44.5	0.7 ; 680
DOC (mgL^{-1})	0.76 ; 22.3	0.7 ; 21
TP (µgL^{-1})	2.88 ; 153.2	0.25 ; 201
pCO$_2$ (µatm)	102 ; 2391	103 ; 3629
	Average ; Median	
	This study	Published
Lake area (km²)	54.9 ; 1.1	3128 ; 0.88
Elevation (m)	368 ; 299	404 ; 370
Maximum depth (m)	8.5 ; 7.1	28.6 ; 8.4
DOC (mgL^{-1})	8.4 ; 7.5	5.6 ; 5.2
TP (µgL^{-1})	14.5 ; 8.8	13.0 ; 8.3
pCO$_2$ (µatm)	687 ; 606	723 ; 590

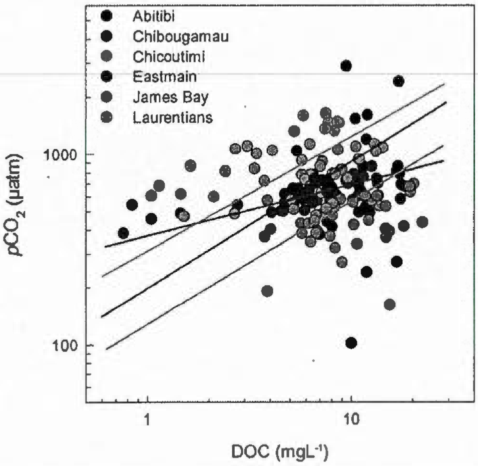

Figure 2.1 Relationships of pCO$_2$ vs DOC for lakes sampled in temperate and boreal Québec, Canada.

Regression lines are presented for significant relationships. The parameters are included in Table 2.2.

Tableau 2.3 Parameters obtained from the $p\mathrm{CO}_2$-DOC relationships for original and published data among northern landscapes.

The slope was obtained from the log ($p\mathrm{CO}_2$) vs log (DOC) relationships. The $p\mathrm{CO}_2$ baseline (µatm) corresponds to the estimated $p\mathrm{CO}_2$ (µatm) at DOC = 1.9 mgL^{-1} for each region, obtained from the corresponding regional equations. No $p\mathrm{CO}_2$ baseline was calculated for non-significant relationships. * = not significant. Parameters have also been estimated for the overall relationship when all data, published and from this study, are analyzed together (All data).

Reference	Region	r^2	$p\mathrm{CO}_2$ baseline	Slope	Geographical range
This study	Abitibi, Can.	0.00*	n.a.	n.a.	48.0°-49.0°N, 78.2°-79.6°W
	Chibougamau, Can.	0.52	553	0.27	48.9°-50.9°N, 72.7°-74.7°W
	Chicoutimi, Can.	0.21	633	0.52	47.7°-48.8°N, 70.5°-72.2°W
	Eastmain, Can.	0.39	350	0.64	51.9°-52.4°N, 75.3°-76.5°W
	James Bay, Can.	0.17	225	0.55	49.0°-50.6°N, 78.0°-79.6°W
	Laurentians, Can.	0.02*	n.a.	n.a.	45.8°-46.1°N, 73.8°-74.2°W
Bergstrom et al. 2004	Northern Swe.	0.56	474	0.38	63°-67°N, 13°-19°W
del Giorgio et al. 1999	Estrie, Eastern Can.	0.45	299	1.10	45.0°-45.9°N, 71.0°-72.7°W
Finlay et al. 2009	Prairies, Central Can.	0.82	1410	-1.05	50.0°-51.3°N, 101.3°-107.1°W
Hope et al. 1996	Wisconsin, Northern Us.	0.18	179	0.92	45.5°-46.6°N, 89.2°-89.6°W
Jonsson et al. 2003	Abisko, Northern Swe.	0.62	455	0.55	67.5°-68.5°N, 18.0°-22.0°E
Kelly et al. 2001	Northwestern Ontario, Can.	0.58	136	1.18	48°-51°N, 88°-94°W
Kritzberg et al. 2005	Wisconsin, Northern Us.	0.53	591	0.79	46.1°-46.3°N, 89.3°-89.6°W
Sobek et al. 2003	Sweden	0.51	210	1.15	57°-64°N
	All data	0.23	282	0.86	45°-69°N, 107°W-22°E

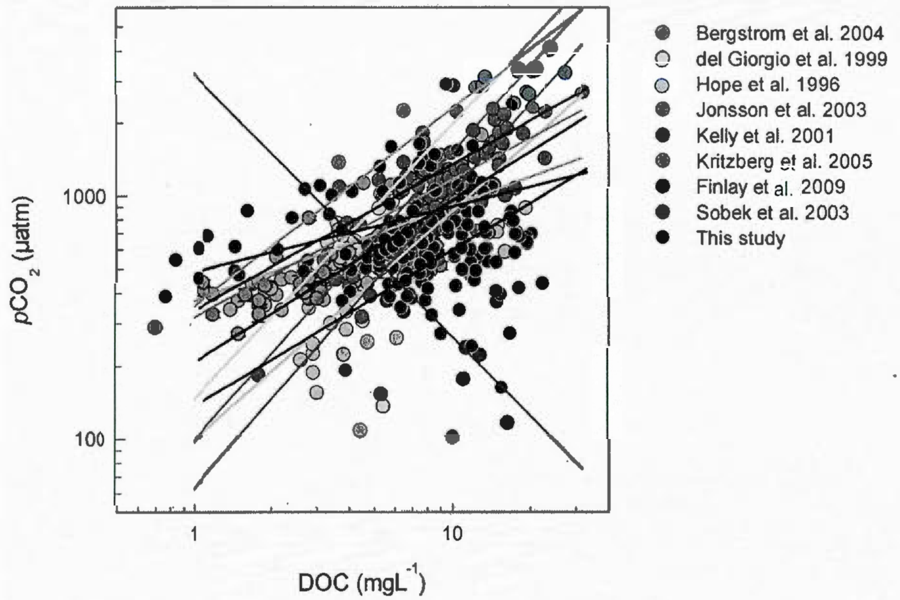

Figure 2.2 Relationships of $p\mathrm{CO}_2$ vs DOC for our own and published data among the boreal landscape.

Error bars represent standard deviation for temporally replicated measurements, when available. The regression parameters are presented in Table 2.2.

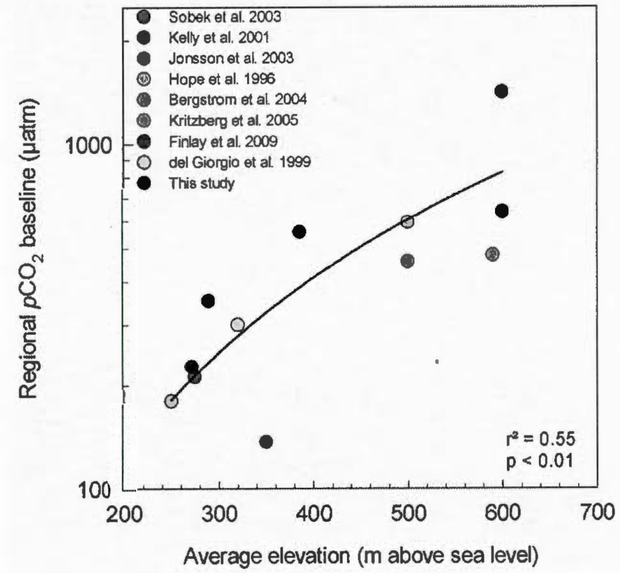

Figure 2.3 Relationship between mean regional altitude and pCO_2 baseline.

pCO_2 baseline represents the estimated pCO_2 at DOC = 1.9 mg L^{-1}, calculated from the corresponding fit (parameters presented in Table 2.2). Lake altitude was not available for the study of Hope et al. [1996]; individual lakes altitude were not available for the study of Sobek et al. [2003] but we used pro-rated regional averages presented in the paper.

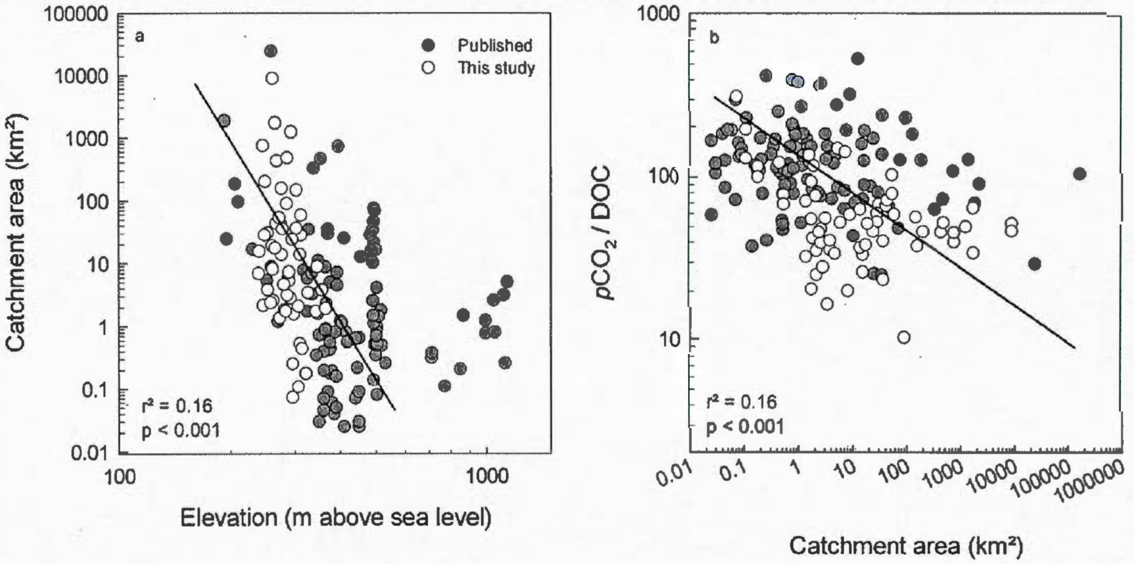

Figure 2.4 Relationship between lake elevation and catchment area (a), and between lake catchment area and $p\text{CO}_2$ per unit DOC (b).

"Published" data originate from del Giorgio et al. (1999), Hope et al. (1996), Jonsson et al. (2003) and Kelly et al. (2001). Equation for panel a : log(catchment area) = -7.85 log(elevation) + 20.7. Equation for panel b: log($p\text{CO}_2$/DOC) = -0.24log(catchment area) + 2.02. Equations, p-values and r² for all data analyzed together.

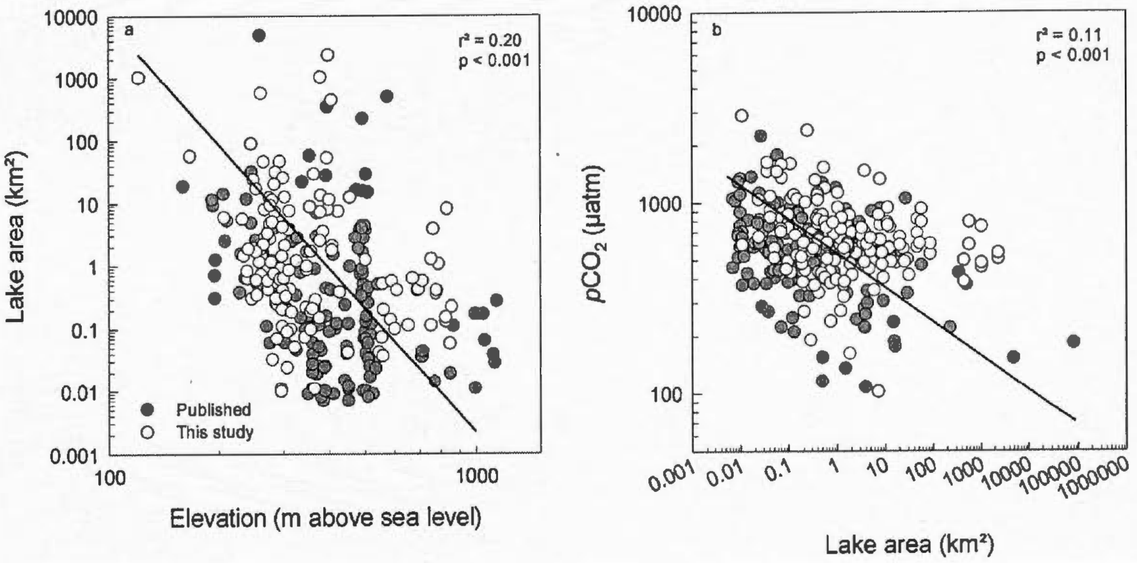

Figure 2.5 Lake area as a function of elevation (a) and the relationship between *p*CO_2 and lake area (b).

''Published'' data originates from del Giorgio et al. (1999), Hope et al. (1996), Jonsson et al. (2003), Kelly et al. (2001), Kritzberg et al. (2005) and Finlay et al. (2009). Equation for panel a: log(lake area) = -6.89log(elevation) + 17.56) . Equation for panel b: log(*p*CO_2) = -0.18log(lake area) + 2.74. Equations, *p*-values and r² for all data analyzed together.

2.5 DISCUSSION

The dynamics of CO_2 in lakes have received increasing attention in the past decade, and many different factors have been linked to lake pCO_2 and CO_2 fluxes. One of the few recurrent patterns across landscapes that have been identified is the relationship between surface water pCO_2 and DOC concentration (Roehm, Prairie et del Giorgio, 2009). Inspection of Table 2.2 quickly reveals that while these relationships exist for many regions, there is a large degree of variability in their strength and shape, and thus the interpretation of the underlying basis of this relationship is far from straightforward. We contend that the variability in the pCO_2-DOC relationship reflects fundamental environmental gradients that can only be detected on a comparative basis over very large geographical scales, and there is now a sufficient mass and diversity of available data to allow this type of comparison. In this regard, our own results combined with the existing published data, when placed together in a broader context of northern landscapes, demonstrate that the different regional relationships in fact fit a cross-regional pattern that appears to be driven by a combination of geographic, morphometric and biogeochemical properties.

Combining our own and published data allowed us to explore two basic scenarios that could account for the contrasting parameters of the regional pCO_2-DOC relationships: regional differences in the amount and relative proportions of DOC and CO_2 exports from land to lakes, and regional patterns in lake trophic status that may mediate the above patterns in C and nutrient loadings. In order to explore these scenarios, we used the slopes and calculated regional pCO_2 baselines from the regional pCO_2-DOC relationships as response variables and found that they were indeed well explained by proxies of trophic status and terrestrial influence, i.e. the TP:DOC ratio and lake elevation, respectively. The strength of the inter-regional relationships presented here (Figs. 2.3 and 2.6), despite all the unaccounted variability induced, for example, by differing DOC composition, land use, lake mixing regime, climate, inter-seasonal and inter-annual patterns across the different studies, as well as by the inclusion of pCO_2 values obtained from different measurement techniques, suggest that these basic relationships effectively capture some of the key mechanisms that regulate lake pCO_2 in northern landscapes.

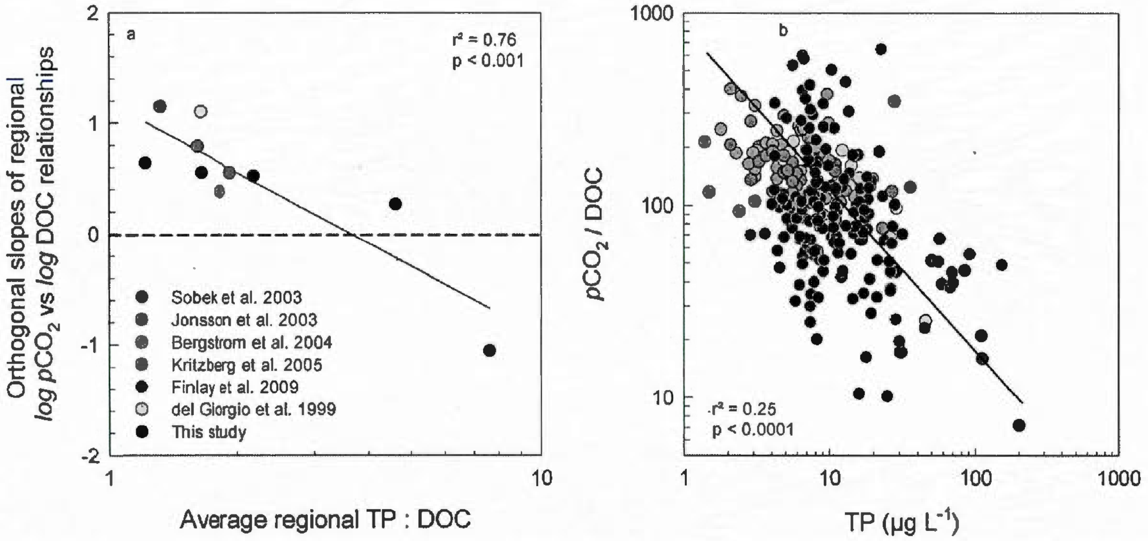

Figure 2.6 The slopes of the regional *p*CO_2-DOC relationships as a function of average regional TP:DOC ratio and b) the *p*CO_2 per unit DOC as a function of TP for individual lakes.

Equation for panel a: $y = -1.02\log(\text{average regional TP:DOC}) + 1.24$. Equation for panel b: $y = -0.92\log(\text{TP}) + 2.93$. Equations, *p*-values and r^2 for all data analyzed together.

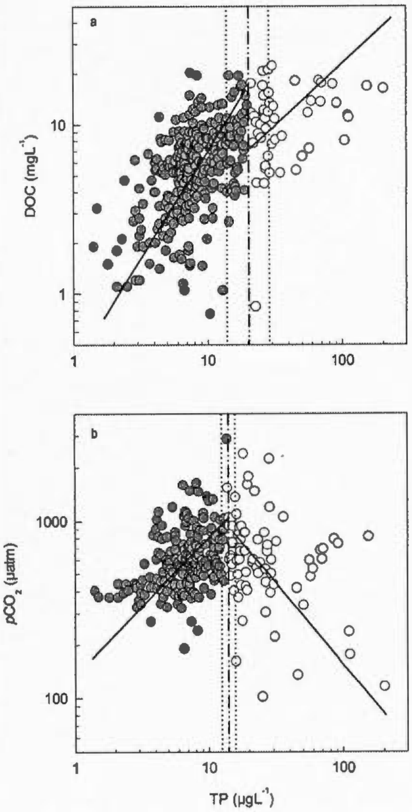

Figure 2.7 Piece-wise regression of DOC (top panel, a) and pCO$_2$ (bottom panel, b) against TP.

Panel a: TP < 20.2 (black symbols): log(DOC) = 1.22 log(TP) – 0.38, $r^2 = 0.34$, $p < 0.001$; TP > 20.2 (white symbols): log(DOC) = 0.77 log(TP) – 0.15, $r^2 = 0.11$, $p = 0.03$. Panel b: TP < 14.8 (black symbols): log(pCO$_2$) = 0.83 log(TP) + 2.15, $r^2 = 0.24$, $p < 0.001$; TP > 14.8 (white symbols): log(pCO$_2$) = -0.99log(TP) + 4.30, $r^2 = 0.17$, $p < 0.001$. "Published" data for panel a originate from Bergstrom et al. (2004), del Giorgio et al. (1999), Jonsson et al. (2003), Kritzberg et al. (2005), and Finlay et al. (2009). "Published" data for panel b originate from Bergstrom et al. (2004), del Giorgio et al. (1999), Hope et al. (1996), Jonsson et al. (2003), Kelly et al. (2001), Kritzberg et al. (2005), and Finlay et al. (2009). All data have been analyzed together in the regression. Dash-dot line represents the break point and the dotted bars represent the confidence interval (95%).

2.5.1 The $p\text{CO}_2$ regional baseline and elevation

Recent studies have provided evidence for a strong hydrologic control of lake $p\text{CO}_2$ that is decoupled from net ecosystem production (Dubois, Carignan et Veizer, 2009 ; Stets *et al.*, 2009), partly due to imports of terrestrially-produced CO_2 (Humborg *et al.*, 2010 ; Jones *et al.*, 2001 ; Walvoord et Striegl, 2007). If this DIC subsidy were dependent on region-specific drivers, it would induce cross-regional variation in the concentration of CO_2 for a given amount of DOC, regardless of the slope of the relationship between both variables. This pattern was indeed observed in the relationships we presented here (Fig. 2.2), and we further showed that the regional $p\text{CO}_2$ baseline was positively correlated to mean regional elevation (Fig. 2.3)

This result may seem counter-intuitive, as terrestrial net primary production, and the associated absolute exports of DOC and CO_2 from land to water, tend to decrease with altitude (Jansson *et al.*, 2008). At higher elevation, however, aquatic ecosystems also tend to be more closely coupled to their surrounding landscape and thus more responsive to catchment processes. Riverine networks, especially small, headwater streams, carry large quantities of CO_2 (Teodoru *et al.*, 2009 ; Wallin *et al.*, 2010), much of which originates from terrestrial respiration (Johnson *et al.*, 2008). Landscape position and topography are further related to key aspects of the delivery of water and C to lakes, including water transit time (McGuire *et al.*, 2005), catchment and lake area (Figs. 2.4 and 2.5) and position in the catchment (Tetzlaff *et al.*, 2011), groundwater flow (Jones et Mulholland, 1998), and type of soils and land cover (Tetzlaff, Seibert et Soulsby, 2009). These elements favor higher hydrologic responsiveness in higher elevation catchments (Tetzlaff *et al.*, 2011), resulting in shorter residence time and dominance of terrestrial over aquatic processes in determining the amount of organic and inorganic carbon circulating in surface waters. In this context, we interpret elevation as an integrative variable reflecting a large number of factors that couple lakes to the surrounding landscape. Higher proportions of terrestrially-derived CO_2 are thus expected to circulate in higher altitude watersheds with smaller catchments, independent of aquatic DOC content (Fig. 2.4), whereas in lower elevation lakes with larger catchments *in situ* lake processes play a larger role in regulating surface water CO_2 levels.

Our results further indicate that elevation is not only linked to the watershed properties, but also correlates to the regional lake size distribution. On average, lakes in higher elevation landscapes tend to be smaller, and this pattern further has the potential to influence both DOC and pCO_2 (Fig. 2.5). Similar to higher altitude watersheds, smaller lakes tend to be more responsive to the delivery of organic and inorganic C from the catchment, due to higher drainage ratios (Hope, Kratz et Riera, 1996), lower residence time (Kelly *et al.*, 2001) and a higher relative contact surface with the basin. All these features result in higher terrestrial C import per unit lake volume or area, and thus a higher potential for terrestrially-derived C to influence both the DOC and the CO_2 dynamics in these lakes. Conversely, larger lakes with longer residence times are expected to have smaller ranges of variation due to their capacity to buffer shifts in hydrology and C loadings through longer renewal time (Roehm, Prairie et del Giorgio, 2009). Larger lakes are also exposed to stronger winds and have higher rates of degassing for a given wind speed (Vachon and Prairie submitted), which would tend to dampen pCO_2 levels.

The idea of a direct terrestrial origin of lake pCO_2 is not, however, in contradiction with the widespread notion that net heterotrophy supports excess CO_2 in boreal lakes (del Giorgio *et al.*, 1999 ; Duarte et Prairie, 2005 ; Sobek *et al.*, 2003). Together, these various studies rather show that there are several pathways supporting lake pCO_2, and suggest that the balance between the contribution of these pathways differs not only among lakes, but also more broadly across regions. In this regard, it appears that high regional pCO_2 baselines are related to a higher degree of coupling between lake and catchment processes, and this coupling is reflected here in the relationships of catchment and lake area with lake surface water pCO_2.

2.5.2 Slope and TP:DOC ratio

The main reason DOC is an overall good predictor of pCO_2 at the regional scale is because it acts both directly as a substrate for the production of CO_2 within lakes, and as a proxy for variables that also influence pCO_2 (Larsen, Andersen et Hessen, 2011a). Our results suggest that this is also the case at a cross-regional scale, over the temperate and boreal landscapes, but in a different manner. The "substrate" role of DOC would lead to the positive relationship that is generally found, while the "proxy" role would modulate the regional differences in this relationship. The drastic decrease in the predictive power of DOC at the cross-regional scale (Table 2.2) supports this view, and highlights the emerging role of associated drivers of $p\text{CO}_2$ as the spatial scale broadens, especially if the relationship between DOC and these drivers differs across regions. For example, in the case of negative $p\text{CO}_2$-DOC relationships, it is clear that more DOC cannot result in less $p\text{CO}_2$ *per se*, and that this pattern is driven by other variables and related processes.

In this context, Figure 2.7 illustrates the importance of the relationship between DOC and TP in shaping $p\text{CO}_2$ dynamics. Because DOC and TP tend to co-vary, they also both tend have positive individual relationships with $p\text{CO}_2$ (left portion of Fig. 7). However, in the higher end of the TP gradient, where TP increases faster than DOC and the TP:DOC ratio is highest (past TP ≐ 20 µg L^{-1} Fig. 2.7a), the relationship between $p\text{CO}_2$ and TP becomes negative (Fig. 2.7b), and the increase in $p\text{CO}_2$ resulting from any given DOC increase becomes gradually lower, and eventually negative at high TP:DOC (Fig. 2.6a). This suggests that TP and DOC are strong, opposite drivers of $p\text{CO}_2$, and that the manner in which they co-vary has a major impact on lake CO_2 dynamics, both at the intra- (Fig. 2.6b) and an inter-regional (Fig. 2.6a) scales.

Our results suggest that the TP:DOC ratio may act as a proxy for the balance between primary production and respiration, and thus support the widespread idea that lake ecosystem metabolism is an important driver of lake $p\text{CO}_2$ (Duarte et Prairie, 2005). Our results further suggest that there are regional patterns in lake net metabolic balance that could account for the differences observed in $p\text{CO}_2$ dynamics across northern landscapes, more specifically, in modulating the $p\text{CO}_2$-DOC relationships. The relatively steep slope of the DOC-TP relationship below 20 ug L^{-1} suggests that terrestrial exports of organic matter constitute the major P source in more pristine lakes situated in less perturbed regions, while the weaker slope above 20 ug L^{-1} may reflect the increasing contribution of inorganic P due to anthropogenic and other sources. In lakes with a higher average TP:DOC ratio, DOC-driven increases in respiration and photo-production of CO_2 would thus be compensated by P-driven increases in primary production, and the role of DOC as a substrate for mineralization would be secondary to its role as a proxy of nutrient inputs from the catchment, leading to the negative slopes of the $p\text{CO}_2$-DOC relationships in the most productive regions. In addition, as

TP increases and lakes become more productive, an increasing fraction of the ambient DOC available to respiration would be of autochthonous origin and would not contribute to further CO_2 super-saturation. Those combined effects would tend to maintain lower surface water pCO_2 for a given concentration of DOC.

The intra-regional patterns observed within the overall pCO_2-TP relationship support this argument. On an individual basis, the studies that have measured TP concentrations beyond the thresholds presented in Figure 2.7 have been conducted in four regions: Abitibi and James Bay (this study), the Eastern Townships region (del Giorgio *et al.*, 1999), and the Canadian Prairies (Finlay *et al.*, 2009). Each area is characterized by either anthropogenic perturbations or natural features in their landscapes that favor increased P but not necessarily DOC loadings, such as agriculture (Abell *et al.*, 2011 ; Merilainen *et al.*, 2000), urban development (Schindler, 2006), forestry (Pinel-Alloul *et al.*, 2002), or beaver dams (Roy, Amyot et Carignan, 2009). As opposed to the significant positive relationship found in the lower part of the TP gradient (Fig. 2.7b), the relationship between pCO_2 and TP was not significant for the Abitibi and James Bay lakes, and was strong and negative for the other two regions mentioned ($p < 0.001$). These observations further support the conclusion that the role of DOC as a predictor of pCO_2 is modulated by regional trends in lake metabolic balance, which are in turn driven by regional patterns in the proportion of the terrestrial loadings of TP and DOC.

2.5.3 Conclusions and Implications

Our analysis shows that what appear to be scattered and sometimes contradictory results in fact yield a coherent portrait of the regulation of lake pCO_2 in northern landscapes when placed together along common environmental and geographical gradients. The differences in the pCO_2-DOC relationships appear to be driven by the same key factors which are integrated by the mean regional TP:DOC ratio and elevation. We found that proxies of lake metabolic balance and terrestrial CO_2 exports account for a large portion of these patterns in the lake pCO_2-DOC relationships, but additional underlying, correlated factors not reported here, such as regional patterns in DOC composition due to contrasting terrestrial influence and trophic status, also likely play a role and may further account for significant portion of the remaining, unexplained variability. Nonetheless, our results provide a synthetic view of the role of terrestrial exports of organic and inorganic nutrients and carbon in regulating northern lakes CO_2 dynamics, and illustrate the importance of taking background regional geographic and environmental patterns into account at the time of evaluating how future changes in environmental and climatic conditions may affect CO_2 dynamics in inland waters in northern landscapes.

2.5.4 Acknowledgements

We thank two anonymous reviewers for constructive comments and P. Massicotte for help with analyses. JFL was supported by a doctoral scholarship from the National Science and Engineering Research Council of Canada (NSERC). This project is part of the program of the Industrial Research Chair in Carbon Biogeochemistry in Boreal Aquatic Systems (CarBBAS), and was co-funded by the National Science and Engineering Research Council of Canada (NSERC) and Hydro-Québec.

CHAPITRE III

PARTIAL COUPLING AND DIFFERENTIAL REGULATION OG BIOLOGICALLY AND PHOTO-CHEMICALLY LABILE DISSOLVED ORGANIC CARBON ACROSS BOREAL AQUATIC NETWORKS

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N.B. References cited in this chapter are presented at the end of the thesis.

3.2 ACKNOWLEDGEMENTS

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3.3 ABSTRACT

Despite the rapidly increasing volume of research on the biological and photochemical degradation of DOC in aquatic environments, little is known on the large-scale patterns in biologically and photo-chemically degradable DOC (Bd-DOC and Pd-DOC, respectively) in continental watersheds, and on the links that exist between these two key properties that greatly influence the flow of carbon from continents to oceans. Here we explore the patterns in the concentrations and proportions of Bd- and Pd-DOC across hundreds of boreal lakes, rivers and wetlands spanning a large range of system trophy and terrestrial influence, and compared the drivers of these two reactive pools of DOC at the landscape level. Using standardized incubations of natural waters, we found that the concentrations of Bd- and Pd-DOC co-varied across all systems studied but were nevertheless related to different pools of dissolved organic matter (DOM, identified by fluorescence analyses) in ambient waters. Concentrations of nutrients and protein-like fluorescent DOM (FDOM) explained nearly half of the variation in Bd-DOC, whereas Pd-DOC was exclusively predicted by DOM optical properties, consistent with the photochemical degradability of specific FDOM pools that we experimentally determined. The concentrations of colored DOM (CDOM), which we use here as a proxy of terrestrial influence, almost entirely accounted for the observed relationship between FDOM and the concentrations of both Bd- and Pd-DOC. The concentrations of CDOM and of the putative bio-labile fluorescence component shifted from complete decoupling in clear-water environments to strong coupling in darker streams and wetlands. This suggests a baseline autochthonous Bd-DOC pool fuelled by internal production that is gradually overwhelmed by land-derived Bd-DOC as terrestrial influence increases across landscape gradients. The importance of land as a major source of both biologically and photo-chemically degradable DOC for continental watersheds resulted in a partial coupling of those carbon pools in natural freshwaters, despite fundamental contrasts in terms of their composition and regulation.

3.4 INTRODUCTION

The movement of terrestrial dissolved organic carbon (DOC) from the land-water interface to the oceans is mediated by its transit through complex and highly heterogeneous continental freshwater networks, where DOC from different sources and origins is simultaneously produced and removed via biotic and abiotic processes (Battin *et al.*, 2008 ; Cole *et al.*, 2007 ; Massicotte et Frenette, 2011). The overall role that DOC plays on aquatic ecosystems is well recognized (Findlay et Sinsabaugh, 2002), but there is still debate regarding the direct role of terrestrially derived organic carbon as a substrate for ecological and biogeochemical processes in freshwater ecosystems. More specifically, it is generally accepted that terrestrial DOC may support foodwebs at various trophic levels (Berggren *et al.*, 2010b ; Jansson *et al.*, 2007 ; Karlsson *et al.*, 2003), as well as fuel CO_2 evasion from these systems (Algesten *et al.*, 2004 ; Berggren, Lapierre et del Giorgio, 2012 ; Lapierre *et al.*, 2013b), but the relative importance for those processes compared to that of autochthonous sources of organic C (Brett *et al.*, 2009 ; Wenzel *et al.*, 2012), or terrestrially derived CO_2 (Butman et Raymond, 2011 ; Wallin *et al.*, 2013), respectively, is still questioned. This questioning largely emerges from unresolved issues concerning terrestrial organic carbon degradability in aquatic ecosystems, which then determines the ability of this carbon to enter aquatic foodwebs and biogeochemical cycles.

Microbial and photochemical degradation are the two main pathways by which terrestrial DOC may influence aquatic metabolism (Bertilsson et Tranvik, 1998 ; del Giorgio *et al.*, 1999 ; Obernosterer et Benner, 2004) and gas dynamics (Jonsson *et al.*, 2001 ; Lapierre *et al.*, 2013b ; Molot et Dillon, 1997), and both processes operate simultaneously in ambient waters. Their magnitude and relative contribution in natural systems depend on environmental factors, such as light availability, water residence time and dissolved ions (Soumis *et al.*, 2007), as well as on factors that are intrinsic to DOC (Guillemette et del Giorgio, 2011). Microbial degradation is thought to preferentially target freshly produced, low-molecular weight molecules with low aromaticity (Amon et Benner, 1996 ; Wickland, Neff et Aiken, 2007), whereas photochemical degradation mainly acts on colored, photo-reactive molecules generally associated to high molecular weight and aromaticity (Benner et Kaiser, 2011 ; Bertilsson et Tranvik, 1998 ; Stubbins *et al.*, 2010). These broad chemical properties have thus been associated to distinct pools of DOC with distinct sources (i.-e. the process that imported DOC in the environment, e.g. leaching, exudation) and origins (i.-e. the environment where these processes take place, e.g. terrestrial, riverine, marine).

Transposing the mechanistic evidence described above to natural landscapes would suggest a shift in the relative importance of these DOC degradation pathways, from a dominance of biological degradation in systems dominated by autochthonous carbon sources, to a dominance of photo-chemical degradation in environments with high terrestrial influence. This scenario, which is based on the simplistic assumption that biological degradability is mostly linked to autochthonous DOC, and that photochemical degradability is mostly associated to terrestrially derived DOC, would lead to a compensatory dynamic wherein the overall (biological + photochemical) degradability of DOC would be to some extent buffered across different environments and along a gradient of terrestrial influence.

Although the above assumption may hold for specific aquatic environments, it is unlikely that it applies at the landscape level, in part because there is increasing evidence that land exports to continental waters not only photo-chemically degradable DOC (Jonsson *et al.*, 2001 ; Molot et Dillon, 1997 ; Weyhenmeyer *et al.*, 2012), but also significant amounts of biologically degradable DOC (Berggren *et al.*, 2010a ; Fellman *et al.*, 2008 ; Guillemette, McCallister et del Giorgio, 2013). For example, significant concentrations of protein-like DOC and small organic acids, typically attributed to autochthonous and bio-labile material, have been measured in soils and headwater streams (Berggren *et al.*, 2010a ; Fellman *et al.*, 2009), and carbon pools that are considered recalcitrant from a geochemical perspective (based on their molecular properties) may actually be biologically degradable under the right environmental conditions, in soils (Schmidt *et al.*, 2011) or in the water (Marín-Spiotta *et al.*, 2014 ; Ward *et al.*, 2013). This implies that there may be faster turnover of terrestrially derived DOC in inland waters than what was previously thought, yet there is a large volume of literature documenting the recalcitrance of this carbon in marine or riverine environments with high residence time (see synthesis by Marín-Spiotta *et al.*, 2014). This would suggest that the degradability of terrestrial DOC may be very different in contrasting aquatic environments, and in particular, that it is becoming increasingly stable with time as it circulates through continental watersheds, where the labile portions of the DOC pool imported from upstream are gradually processed and removed from the bulk.

It thus appears that land delivers to inland waters a DOC pool that, depending on the environmental context, may be both biologically and photo-chemically degradable. If indeed biologically and photo-chemically degradable DOC share, to a certain degree, similar sources and origins, one could expect both functional pools of DOC to co-vary across aquatic environments. This would lead to an additive rather than compensatory dynamic, wherein the overall degradability of DOC would increase as a function of increasing terrestrial export with major implications for the aquatic carbon cycle. Previous evidence has shown that both Bd-DOC and Pd-DOC tend to increase in boreal freshwaters with increasing terrestrial influence (Lapierre *et al.*, 2013b), but the respective drivers of those pools and the degree to which they are coupled across a large diversity of freshwater environments, remain unclear; few if any studies have simultaneously assessed the magnitude and regulation of biological and photochemical degradability across gradients representative of aquatic ecosystems at a landscape-level. Here we explore the patterns in the concentrations and proportions of biologically and photo-chemically degradable DOC across boreal lakes, rivers and wetlands, and the degree to which those distinct pools of DOC co-vary in natural waters. We then use a combination of optical and chemical properties in order to explore how intrinsic DOC composition and extrinsic environmental properties respectively drive the concentrations of Bd- and Pd-DOC in boreal natural waters. Finally, we explore how a continuous gradient of terrestrial influence (using CDOM as a proxy, see Lapierre et al. (2013b) may explain the patterns in the concentrations of degradable DOC across diverse and complex freshwater environments.

3.5 METHODS

3.5.1 Study regions and sampling

Over the summer period from 2009 to 2013 we sampled a wide range of lakes (236), streams (204), rivers and wetlands (83; mostly beaver ponds). Those systems span over a very large geographic range (Fig. 3.1), which translates into very diverse climate, landscape and limnological properties. In particular, mean annual temperature and precipitation ranged from -5.7 to 4.8 °C and from 334 to 1289 mm, respectively, and catchment vegetation ranged from mixed conifer and deciduous in the south to black spruce moss forest in the north; tundra-type vegetation covered the northern-most, highest altitude sites. Aquatic environmental properties spanned over most of the freshwater gradients reported in the literature, with DOC, CDOM (a440 nm, naperian units), TN, TP and Chl *a* concentrations ranging from 0.4 - 123.9 mg L^{-1}, 0.05 - 30.0 m^{-1}, 0.03 - 1.90 mg L^{-1}, 2.24-248.2 μg L^{-1} and 2.2 - 248.2 μg L^{-1}, respectively, across the sampling sites (Lapierre et al. 2013). Hydrology and morphometry were also very different across the systems studied, with rivers ranging from Strahler order 1 to 6, and lakes and wetlands ranging from 0.01 to 2300 km^2 (Lapierre *et al.*, 2013a), as well as mean depth and discharge ranging over several orders of magnitude (Campeau *et al.*, 2014 ; Lapierre et del Giorgio, 2012). The different sites were almost never included in a common catchment except for the largest lakes and rivers that drained vast territories.

Water was sampled at 0.5 m from the surface from the deepest measured point of lakes. It was sampled near the shore of streams, rivers and wetlands and in all cases, it was immediately filtered (0.45 μm) and stored in acid-washed glass vials for DOC, optical analyses and inorganic N. Samples for total nitrogen (TN) and phosphorus (TP) were also stored in acid-washed glass vials but were not filtered. All samples were immediately stored in cold and dark conditions. Analyses were typically performed within a month; optical measurements and inorganic Nwere typically performed within two weeks..

3.5.2 Biological and chemical analyses

DOC concentration was measured on an OI 1010 TIC-TOC (TX, USA) analyzer following sodium persulfate digestion. We analyzed TP spectrophotometrically after persulfate digestion and TN was analyzed as nitrate following alkaline persulfate digestion and measured on an Alpkem FlowSolution IV autoanalyzer; ambient nitrites and nitrates were measured individually prior to persulfate digestion (APHA, 1998). Ammonium was measured by fluorescence following Holmes et al. (1999). Chl *a* samples were analyzed spectrophotometrically after filtration on Whatman (GF/F) filters and hot ethanol (90 %) extraction (Marker et Nusch, 1980). Filters were sonicated prior to extraction. Each of those variables has been collected in duplicates in the field; we present the mean here.

3.5.3 Optical analyses

The absorbance of colored dissolved organic matter (CDOM) was measured on nanopure-corrected samples of filtered ambient water from 230 to 700 nm, using a UV-visible Ultrospec 2100 spectrometer (Biochrom, Cambridge, UK) and a 2-cm quartz cuvette. We report CDOM as the absorption coefficient at 440 nm (in m^{-1}, naperian units), calculated by dividing the optical absorbance at 440 nm by the path length in meters and multiplying by 2.303 (Cuthbert and del Giorgio, 1992). We also calculated proxies of DOC aromaticity and molecular weight by estimating the DOC specific absorbance at 254 nm ($SUVA_{254}$) and the ratio of absorbance at 250 nm to 365 nm (Spencer et al., 2009a), respectively. The former was calculated by dividing absorption coefficients at 254 nm by DOC concentration and the latter was directly obtained from the ratio of absorption coefficients at these specified wavelengths.

Fluorescence intensity was measured on a Shimadzu RF5301 PC (Shimadzu, Kyoto, Japan), across excitation wavelengths of 275– 450nm (5 nm increments) and emission wavelengths of 280–600 nm (2nm increments) in order to build excitation-emission matrices (EEMs). A parallel factor (PARAFAC) model (Stedmon et al., 2003) was developed to identify and quantify groups of DOM that shared similar optical properties and distribution across the sampled sites. Fluorescence data were corrected for inner-filter effect and

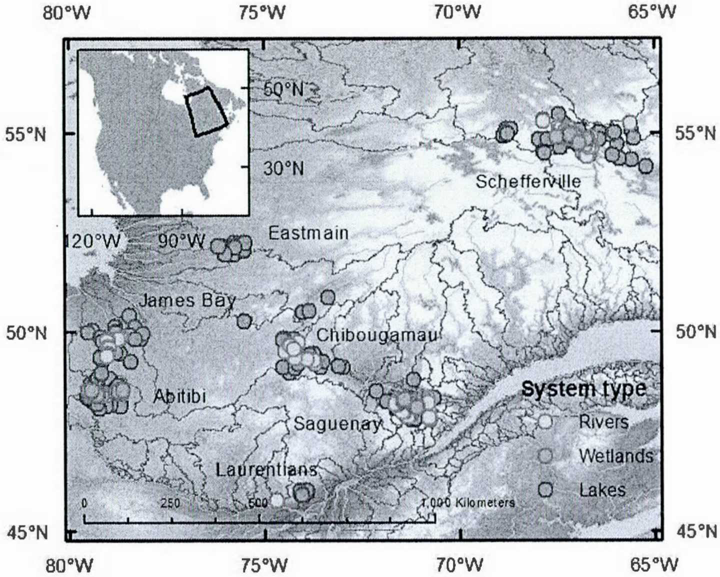

Figure 3.1 Distribution of the sampling sites across seven boreal regions (James Bay, Abitibi, Laurentians, Saguenay, Chibougamau, Schefferville) of Quebec, Canada.

Grey lines and area represent large rivers and lakes; green lines delimit the main watersheds in Quebec.

standardized to Raman units using the FDOMcorr 1.6 toolbox (Murphy et al., 2010) in MATLAB (MathWorks, Natick, MA, USA). The model was based on 1349 samples from ambient waters and from photochemical degradation experiments, and was performed on corrected data using the DOMfluor 1.7 toolbox (Stedmon and Bro, 2008); only part of the data are reported here. The initial dataset comprised 1577 samples; samples for which absorbance within the 1 cm cuvette was higher than 0.6 at 254 nm were excluded due to potential for ineffective inner filter effect correction (Miller et al., 2010), which could bias the final model. We express the "concentrations" of fluorescence components as the maximum fluorescence intensity at the peak. These represent relative concentrations that may be used to explore the cross-sample patterns for a given component, but this does not necessarily that one unit of a given component represents equal DOM amount compared to one unit of any other component.

3.5.4 Biological and photochemical degradation

We carried out standardized biological and photochemical degradation experiments in order to derive a concentration of degradable DOC that did not depend on varying incubation conditions and would thus be fully comparable across ecosystems and in time (Lapierre et al., 2013). The experiments were started on the same day that the samples were collected. Biological degradation experiments were carried out in water filtered through 2.8 µm nominal pore size GF/D filters (Whatman) in order to maintain the *in situ* bacterial community and thus to avoid re-inoculation. Unfiltered water samples were incubated in the dark at a fixed incubation time (14 days) and temperature (20°C). The results presented in Figs. 2 and 3 correspond to the concentrations in biologically degradable DOC (Bd-DOC), expressed as the absolute amount of DOC removed over a period of 14 days, calculated as the difference in concentration before and after degradation. Percent degradable DOC was calculated as the difference between DOC concentration at the start of the experiment and Bd-DOC, multiplied by 100.

A subset of the filtered water (2.8 µm) was used for photochemical degradation experiments, which were carried out in a solar simulator (Qsun XE1-BC, Qlab, FL, USA) under a standard light dose (0.68 W m^{-2} at 340 nm, spectrum representative of natural sunlight) in 24 mm diameter glass tubes disposed horizontally. Given the strong light dose and the small cross-section of the tubes, there was a negligible effect of the CDOM concentrations on the effective light dose inside the tubes, even for the most colored samples (See Appendix A for details). The amount of light energy available for wavelengths comprised between 300 and 450 nm, responsible for most photochemical processing of DOC (Vähätalo et al., 2000), averaged 130.8 W m^{-2} and did not vary substantially across samples (std.dev. = 9.2 W m^{-2}; 10th and 90th percentiles = 118.4 and 140.4 W m^{-2}, respectively) compared to the range of variation measured in the concentrations of photo-chemically degradable DOC (Pd-DOC), which spanned several orders of magnitude. Consequently, standardizing the concentrations in Pd-DOC for the corrected light dose in the corresponding tubes could in no way alter the patterns and conclusions of the current study (see Figure A2). We therefore report the uncorrected values (in mg C L^{-1} of photo-chemically degradable DOC). We assumed that most bacteria could not survive the very strong UV dose and thus contribute meaningfully to the DOC loss in irradiation experiments; even if that were not the case, the DOC loss rates (expressed per day) were always at least one order of magnitude higher in photochemical degradation experiments compared to biological degradation experiments conducted in the dark (Lapierre et al., 2013).

Photo-exposure time (24 hours) and temperature (24 °C) were the same for all experiments (Lapierre et al., 2013). The data presented in Figs. 3.2 and 3.3 correspond to the amount of DOC removed in 1 day under those conditions; considering diel light cycles and the natural light intensity at the studied latitudes, this would roughly correspond to six days of natural light exposure in the sampled regions. Irradiated samples were stored in 40 ml glass tubes and directly analyzed for DOC concentration. We also measured DOM optical properties before and after irradiation for a subset (n = 187) of the samples. The fluorescence data were included in the PARAFAC model.

3.5.5 Statistical analyses

Analyses of variance, simple and multiple linear regressions and principal components analyses (PCA) were performed on log-transformed data in JMP 7.0.1 software. Data have been centered and standardized before performing the PCA. The best multiple linear regression (MLR) models were identified using forward step-wise selection based on change in Akaike information criterion (AIC.) Moving window regressions (MWR) of fluorescence component C6 against CDOM concentrations were performed successively on subsets of 250 samples (about half of the sample size) sorted by increasing CDOM.

3.6 RESULTS

3.6.1 Patterns in the amounts and proportions of degradable DOC

The amounts of DOC removed in these standardized incubations ranged from 0.05 to 15.2 mg L^{-1} and from almost 0 to 26.0 mg L^{-1}, for biological and photochemical degradation, respectively (Fig. 3.2). This represented 0.13% to 54.3%, and from 0.04 to 72.6% of the ambient DOC pool where those samples were collected, respectively (Fig. 3.2). These numbers represent potential degradation under standardized conditions and depending on environmental conditions may not be expressed in situ; they should not be considered as representative of ambient rates. They do allow, however, to isolate DOC degradability while minimizing the influence of site-specific conditions, such as temperature or irradiation, and thus to explore the patterns and drivers of this degradability over a large range of DOC properties.

The amounts and proportions of degradable DOC were typically lower in lakes than in rivers and wetlands (Fig. 3.2). Both the amounts and proportions of Bd-DOC were highest in wetlands, whereas rivers contained the highest proportions of Pd-DOC, but similar amounts of Pd-DOC compared to wetlands (Fig. 3.2). There was no relationship at all between the percent Bd-DOC and Pd-DOC across the ensemble of almost 300 lakes, rivers and wetlands for which those measurements were available (Fig. 3.3a). There was, however, a significant positive relationship between the absolute amounts of Bd-DOC and Pd-DOC in lakes, rivers and wetlands separately. There was thus a significant coupling between both pools of DOC when all the systems were considered together , and this coupling was typically stronger in rivers and wetlands than in lakes (Fig. 3.3b). There was a very large scatter around the regression, however, and concentrations of Pd-DOC ranged by more than one order of magnitude for any given amount of Bd-DOC, and *vice-versa.*

3.6.2 The PARAFAC model

The PARAFAC model identified six fluorescence components (Fig. 3.4), corresponding to humic-, fulvic- and protein-like material which are widely reported in

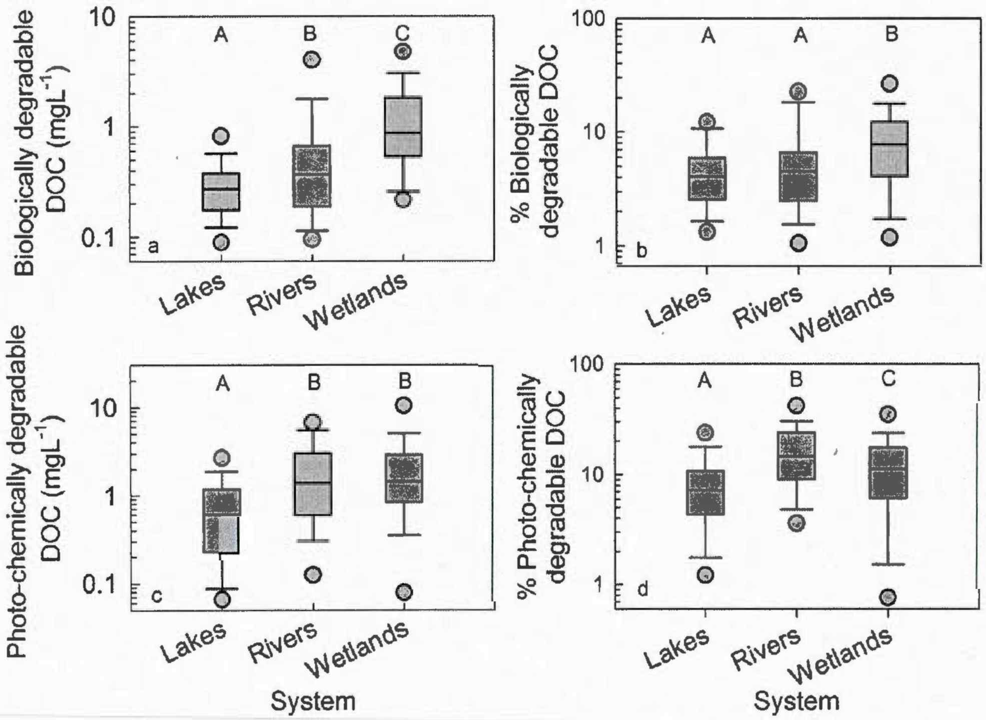

Figure 3.2 Amounts and proportions of biologically and photo-chemically degradable DOC across the three main types of systems studied.

Lines represent the 25, 50 and 75 percentiles, points, 5 and 95 percentiles. Different letters denote statistically different ($p < 0.01$) means across groups, based on ANOVA and Tukey-Kramer post-hoc analyses. Bd-DOC (percent and absolute) : n = 201 for lakes, n = 71 for rivers, n = 53 for wetlands. Pd-DOC (percent and absolute): n = 193 for lakes, n = 136 for rivers, n = 67 for wetlands.

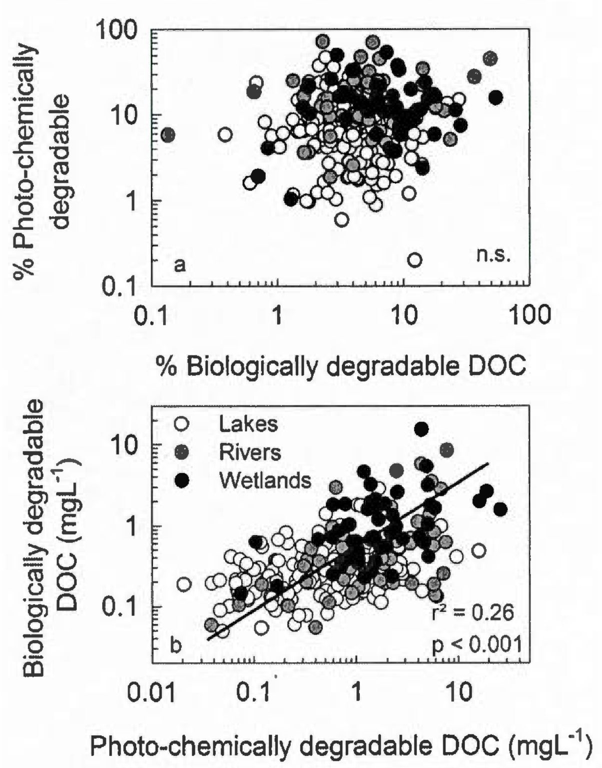

Figure 3.3. Relationship between the proportions (a) and amounts (b) of biologically and photo-chemically degradable DOC across boreal lakes, rivers and wetlands.

a) $n = 262$, not significant. b) lakes: $\log(\text{Bd-DOC}) = 0.16\log(\text{Pd-DOC}) - 1.67$, $p = 0.0003$, $r^2 = 0.11$, $n = 161$; rivers: ($\log(\text{Bd-DOC}) = 0.88\log(\text{Pd-DOC}) - 1.59$, $p < 0.0001$, $r^2 = 0.33$, $n = 58$); wetlands ($\log(\text{Bd-DOC}) = 0.78\log(\text{Pd-DOC}) - 1.34$, $p < 0.0001$, $r^2 = 0.23$, $n = 50$; overall relationship: $\log(\text{Bd-DOC}) = 0.71 \log(\text{Pd-DOC}) -1.48$, $p < 0.001$, $n = 268$.

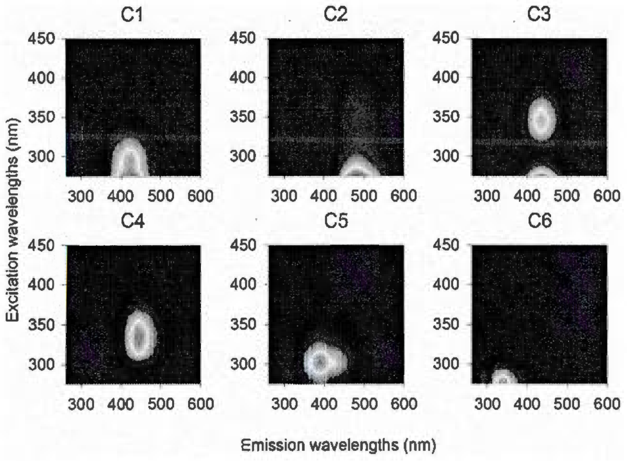

Figure 3.4. Fluorescence signatures of the components identified by the PARAFAC model.

Fluorescence peaks are observed at the following wavelengths (nm), for excitation and emission,respectively (secondary peak in parentheses): C1: 275, 424; C2: 275(340), 484; C3: 275(345), 436; C4: 334, 446; C5: 300, 388; C6: 275, 334 freshwaters. In particular, quantitative comparison of our components to published components (using OpenFluor database, (Murphy et al., 2014)) revealed that components C1 and C2 reportedhere matched very well previously reported humic material identified in a variety of aquatic environments (Stedmon et al., 2003). Component C5 and C6 matched widely reported components (Cory and McKnight, 2005;Fellman et al., 2008;Kothawala et al., 2013b, among others), which have been associated to microbially-derived humic-like and freshly produced protein-like material, respectively. The whole spectra of components C3 and C4 did not show a strong match with any fluorescence component published in the OpenFluor database, but had fluorescence peaks comparable to other published humic- and fulvic like material (Guillemette and del Giorgio 2012, Lu et al 2013); these components had excitation spectra ranging in the UV-B and UV-A regions (Fig. 3.4), indicating that they strongly absorb light at those wavelengths.

Although the model was not run with samples with highest absorbances, as described in the Methods section, it was subsequently used to estimate the concentration of fluorescence components in highly colored samples for which the inner-effect correction may not optimal. Hence, for the 43 samples with absorbance ranging from 0.6 to up to 1.2 at 254 nm (cm^{-1}), the concentration of tryptophan-like component C6 may have been slightly under-estimated whereas the concentration of the remaining fulvic- and humic-like components may have been over-estimated by up to 20% (Miller et al., 2010); recent findings suggest that this bias may actually be much smaller (Kothawala et al., 2013a) Similar to the range of variation in Pd-DOC, the concentrations in the different fluorescence components varied by several orders of magnitude across the sampled sites, and thus the small bias that may be present in these 43 highly colored samples is unlikely to influence the patterns reported here.

3.6.3 Linking patterns in DOC degradability to DOM composition and nutrients

There were significant differences in the amounts and proportions of degradable DOC across different types of systems (Figure 3.2), and a principal component analysis (PCA) further shows that lakes, rivers and wetlands tend to group not only in terms of concentrations of total and degradable DOC, but also in terms of DOM composition and nutrient concentrations (Fig. 3.5). The concentrations of DOC, CDOM, the individual fluorescence components identified by the PARAFAC model, and nutrients all tended to co-vary along a "concentration" axis (Component 1 of the PCA plot), which explained 45.4% of the total variability in the measured variables (Fig. 3.5). Fluorescence components C1, C2 and C3, as well as CDOM had the highest loadings on axis 1, and rivers and wetlands tended to have the highest scores on this axis. The absolute amounts of Bd-DOC and Pd-DOC were also positively associated to this axis, implying that systems with higher amounts of DOM and nutrients tended to have overall more degradable DOC.

The links between DOC degradability and composition are captured by the second axis of the PCA, which explained 23.7% of the variability. Concentrations of nutrients, as well as concentrations and proportions of protein-like C5 and C6 are all situated in the top half of the PCA, along with the a250:365 absorbance ratio (proxy of low molecular weight) and Bd-DOC, whereas the amounts and proportions of humic- or fulvic-like C1, C2 and C4, as well as $SUVA_{254}$ and Pd-DOC, clustered in the lower half of the PCA (Fig. 3.5); there was no clear system-specific distinction on that "composition" axis. These results suggest that the absolute amounts of biological and photochemical degradability are both associated to the total amount of DOC, but also that these two aspects of degradability are further linked to distinct pools within the bulk DOC.

3.6.4 Drivers of the amount of biologically and photo-chemically degradable DOC

The differential regulation of Bd-DOC and Pd-DOC is more clearly expressed by their direct relationships with nutrients and the various DOM components (Table 3.1); pH and the concentration of Chl *a* were not significant predictors when the variables presented in Table 1 were included. Likewise, the inclusion of a categorical variable for system type (Lake, River, Wetland), or for the sampling region (see Fig. 3.1) did not improve the fit in multiple regression models predicting either component of degradability. There was thus no systematic ecosystem- or region-specific differences in the relationship between Bd-DOC its predictors, suggesting that the amount of biologically degradable DOC in the studied systems is mainly a function of DOM composition and nutrients regardless of the type of aquatic environment and the region where they lie.

Bd-DOC was strongly related to both DOM and nutrient concentrations (Fig. 3.5, Table 3.1), and TN was the strongest single predictor (Table 3.1). Among the fluorescence components, the concentration of protein-like component C6 was the strongest predictor of Bd-DOC (Model a, Table 3.1); no other component had a significant effect on Bd-DOC once C6 was included. In contrast to Bd-DOC, DOM optical properties played a greater role as predictors of Pd-DOC. The best MLR models for Pd-DOC included a positive relationship with both the abundance and the relative proportions of component C3, and negative relationships with the proportions of components C5 and C6 (Table 3.1). The EEMs analysis allowed to identify specific pools of DOM that are particularly linked to ambient DOC biological or photochemical degradability, but the concentration aspect was mostly captured by CDOM (measured as absorbance at 440 nm, see methods) alone in both cases (Table 3.1, model c, g). In particular, when concentrations of CDOM were included in MLR, no other variable associated to concentration of DOM was significant in predicting Pd-DOC, but qualitative aspects of DOM, such as the percent contribution of C3 and C6 (the latter negatively related) still significantly improved the model.

3.6.5 Factors influencing the relationship between biological and photochemical degradability

The above patterns in nutrients and DOM concentration and composition were reflected in the residuals of the relationship between Bd-DOC and Pd-DOC. Sites with higher concentrations of CDOM and proportions of the very photo-chemically degradable fluorescence component C3 (see below) tended to contain more Pd-DOC per unit Bd-DOC (Table 1, model h). Conversely, sites with higher proportions of protein-like component C6 and higher nutrient concentrations tended to have a DOC pool that was more biologically degradable per unit Pd-DOC.

3.6.6 Susceptibility of DOM components to photochemical degradation

We further explored the photochemical degradability of specific pools of DOM in a subset of the irradiation experiments. Component C3, which emerged as one of the main drivers of Pd-DOC, was extremely photosensitive and was often completely removed after 12 or 24 hours of irradiation. In contrast, components C5 and C6, the latter being a major driver of Bd-DOC (Table 3.1), appeared to be largely un-reactive to irradiation, whereas the concentration of component C4 systematically increased following irradiation, suggesting the photo-chemically mediated production of this component. Components 1 and 2 showed an intermediate photochemical degradability, with an average loss of 24% and 57%, respectively, of their initial fluorescence during incubations (Fig. 3.6). It is interesting to note that these patterns of selective photochemical degradation of specific DOC components were very consistent among ecosystem types and regions (see error bars in Fig. 3.6).

3.6.7 Patterns of biologically and photo-chemically degradable DOC across gradients of terrestrial influence

Despite the fact that different pools of DOM were linked to the concentrations of Pd-DOC vs Bd-DOC (Table 3.1), CDOM itself accounted for as much variability in both Pd-DOC and Bd-DOC as any combination of fluorescence components, in terms of concentration. Coherent with the PCA (Fig. 3.5), this suggests that environments with high terrestrial influence also have higher concentrations of specific DOC pools associated to both Pd-DOC or Bd-DOC. Figure 3.5 shows the very strong relationships that exist between CDOM and the photo-sensitive fluorescence components C2 and C3. The relationship between CDOM and component C6, which was linked to Bd-DOC, was less obvious in the PCA (Fig. 3.5). In this regard, there was an overall weak positive relationship between CDOM and C6 (Fig. 3.7a). Interestingly, the shape of this relationship varied greatly over a gradient of terrestrial influence (using CDOM as a proxy, see (Lapierre et al., 2013)). An analysis of discrete portions of this gradient using moving window regression (MWR) showed that the relationship between C6 and CDOM was not significant in low-CDOM environments (Fig. 3.7b), but became significant at CDOM (a440) concentrations of approximately 3 m^{-1}. Beyond this point, both the r^2 and the slope of the relationship consistently increased with CDOM concentration until the slope stabilized when the lowest CDOM in the MWR was around 4 m^{-1}. There was thus a strong link between CDOM and C6 in systems with elevated CDOM concentrations ranging from 4 to 30 m^{-1}. These results indicate that the amount of bio-labile DOC, as reflected by the C6 component of DOM, is completely uncoupled to CDOM at low levels of water color, but that the two become strongly coupled in systems with stronger terrestrial influence.

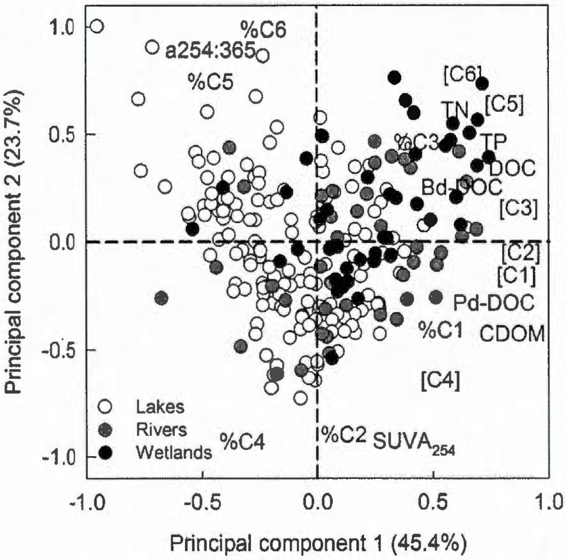

Figure 3.5. Principal component analysis of concentrations of degradable DOM, DOM optical properties and nutrients across boreal lakes, rivers and wetlands.

Abbreviations are defined in the text. Fluorescence components in square brackets correspond to the absolute concentration of the specified component.

Table 3.1. Multiple linear regression models predicting the concentrations of photo-chemically and biologically degradable DOC across boreal lakes, rivers and wetlands.

Abbreviations are defined in the text. Fluorescence components in square brackets correspond to the absolute concentration of the specified component. The sign in parentheses denotes the sign of the coefficient in the MLR model.

Response variable	Model	Predictors	n	adj. r^2	AIC
Bd-DOC	a	(+)[C6]	323	0.35	-675
	b	(+)TN	319	0.40	-683
	c	(+)TN, (+)CDOM	317	0.45	-696
	d	(+)TN, (+)[C6]	317	0.45	-693
	e	(+)TN, (+)[C6], (+)TP	316	0.46	-699
Pd-DOC	f	(+) [C3], (-) %C5, (-) %C6	392	0.67	-818
	g	(+) CDOM, (+) %C3, (-) %C6	392	0.73	-887
Residuals of Pd-DOC vs Bd-DOC	h	(+)%C3, (+)CDOM, (-)%C6, (-)TP	264	0.27	-406

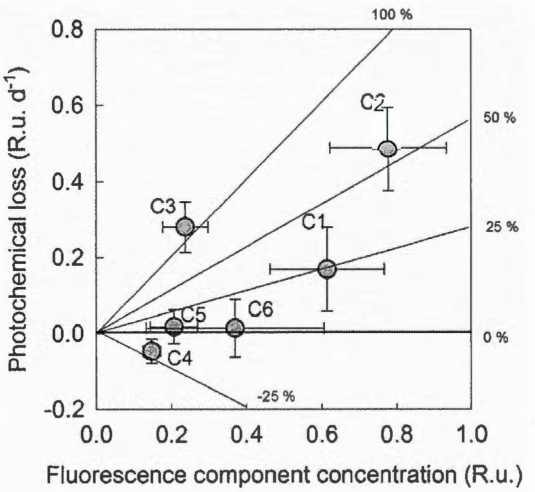

Figure 3.6. Average loss of specific fluorescence components based on the difference in concentration before and after irradiation for samples originating across boreal lakes, rivers and wetlands.

Rates have been reported on a per day basis based on the average of the FDOM loss measured after 12 and 24 hours; this allowed to better quantify the photochemical susceptibility of C3 which was commonly completely degraded after 24 hours, hence the average per day loss of over 100 %. n = 121

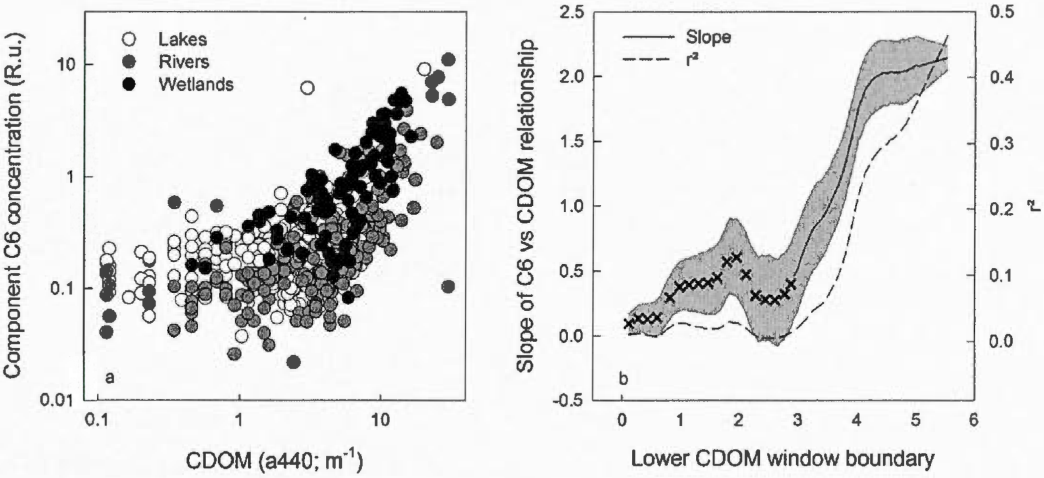

Figure 3.7. Concentrations of protein-like C6 as a function of CDOM in lakes, rivers and wetlands.

a: $r^2 = 0.32$, $p < 0.001$, n = 519. b: Parameters of moving window regressions performed on discrete portions of the dataset based on increasing CDOM. Total sample size was 519, but individual regressions were performed on subsets of 250 samples; a total of 270 regressions were thus performed. "x" signs denote non-significant regressions. X axis shows the lowest CDOM concentration included in the regression for which the parameters are reported. The first regression was thus performed on samples for which CDOM ranged from 0.12 to 3.11 m^{-1}, whereas the last regression was performed on samples for which CDOM ranged from 5.55 to 30.0. Note that the slope characterizes the log(C6) vs log(CDOM) relationship.

3.7 DISCUSSION

3.7.1 Origin, age, freshness and DOC degradability

The core result that we report here is that the concentrations of biologically and photochemically degradable DOC are uncoupled within any particular site, but that they nevertheless tend to positively co-vary across large geographical and environmental gradients, and in particular, along a gradient of terrestrial influence (Fig. 3.3b). These two functional groups of DOC are associated to compositionally distinct pools which are subject to differential regulation across the landscape, and their coupling is only apparent when both aspects of DOC degradability are assessed simultaneously over very broad gradients of terrestrial influence and across a wide range of aquatic ecosystems, as we have done in this study. This pattern likely reflects the expression of the different intrinsic DOC properties as well as environmental conditions (Guillemette and del Giorgio, 2011;Marín-Spiotta et al., 2014) that are encountered across the very diverse natural freshwater environments studied here.

The prevailing view on aquatic DOC biological degradability has been based on the notion that material from autochthonous origin is typically fresh and highly degradable whereas material from terrestrial origin tends to be old and highly altered, and thus does not contribute much to microbial processes (Hedges et al., 1988;Dittmar and Kattner, 2003;Amon and Benner, 1996). Origin and age, however, have different implications and different links to the notion of "freshness" (defined as the time relative to when it left its site of production and was imported into the aquatic environment) in different types of systems. For instance, in the open-ocean, freshly produced is synonymous withautochthonous and young, whereas terrestrially derived implies leftovers of a pool that entered the aquatic network months, years or even centuries before (Anderson and Williams, 1999), and is therefore both old and diagenetically altered. The terrestrially derived DOC pool in such systems is not expected to contain significant amounts of highly labile (consumed within hours to days), or even semi-labile (consumed within months to years, see Carlson (2002)) compounds. In contrast, most continental aquatic environments are directly connected to a terrestrial source that delivers DOC within a time frame of hours or days (Müller et al., 2013), and terrestrial DOC is therefore freshly imported, but may still be either young or old (Mayorga et al., 2005;Raymond et al., 2007;Marín-Spiotta et al., 2014). Recent work suggests that freshly imported terrestrial organic carbon can be readily degraded in lakes and rivers even if it is extremely old (McCallister and del Giorgio, 2012;Kleber et al., 2011), thus suggesting that age and origin may not be the best predictors of DOC biological degradability across continental and marine waters.

Freshness thus appears to be a better common driver than age or origin to place apparently differing patterns of DOC biological degradability on a common gradient, regardless of the type of system studied. In this regard, studies in arctic rivers have shown that DOC is typically more labile during the spring freshet (Mann et al., 2012;Holmes et al., 2008), when DOC has been freshly imported into the aquatic environment. Likewise, DOC was more labile in temperate streams characterized by low temperatures, presumably because it has been less altered than the DOC found in warmer streams and thus conserved in a "fresher" state (Lu et al., 2013). Our results suggest that the same basic pattern may apply not only seasonally, but rather across the whole boreal aquatic network: Close to the land-water interface, most of the biologically labile DOC appears to be of terrestrial origin, as suggested by the increasingly tight coupling between CDOM (measured as absorbance at 440 nm, see methods) and bio-labile component C6 as CDOM increases (Fig. 3.7). Furthermore, the highest concentrations and proportions of both biologically and photo-chemically labile DOC are found in low order rivers and wetlands (Fig. 3.2), supporting the notion that these are major hotspots for biogeochemical processes in continental waters (Denfeld et al., 2013;Campeau et al., 2014).. Systems with greater CDOM content thus tend to contain higher concentrations of biologically and photo-chemically degradable DOC (Lapierre et al., 2013), because in such environments the DOM pool is fresher and contains high amounts of photo-sensitive DOM (Fig. 3.6, Table 3.1), as well as bio-labile, protein-like DOM (Fig. 3.7, Table 3.1), which interestingly, closely resembles DOM from autochthonous origin (Stedmon et al., 2007;Lapierre and Frenette, 2009, Fig. 3.7).

3.7.2 The underlying basis of DOC degradability patterns

The patterns in the concentrations of biologically and photo-chemically degradable DOC reported here allow to identify DOM pools and environmental factors that are linked to DOC degradability in boreal freshwater networks. In our study the amounts of Bd-DOC and Pd-DOC were measured separately, however, and there are known synergistic effects between the biological and photochemical processing of DOC in natural environments (Miller and Moran, 1997), wherein biological and photochemical processes may operate on the same DOM pool (Koehler et al., 2012). The overall degradation potential of DOC could thus be different in ambient waters where these processes actually co-occur, as opposed to our experimental conditions where no such interaction was possible. The objective of this study, however, was not to estimate the total concentration of degradable DOC, or the realized expression of this potential degradability *in situ*, but rather to explore the large-scale patterns in Bd-DOC and Pd-DOC and their respective drivers across a wide variety of aquatic environments in the most comparable manner possible.

Both intrinsic DOM properties and environmental conditions appeared to play a role in determining the concentrations and relative proportions of degradable DOC observed in these boreal freshwater environments. Bd-DOC was linked to nutrient concentration, and to DOM concentration and composition (Fig. 3.5, Table 3.1). The influence of TN (and TP) on Bd-DOC may be threefold: 1) it may be related to increased primary production and thus to the production of an autochthonous Bd-DOC component (Descy et al., 2002;Demarty and Prairie, 2009); 2) it may be related to the stimulating effect of nutrients on DOC degradation rates (Wickland et al., 2012;Guillemette et al., 2013); 3) it may be related to DOM stoichiometry (Sun et al., 1997;Fellman et al., 2009). Chlorophyll *a* concentration, however, was unrelated to Bd-DOC, and although we did not determine organic N, our measurements show that the sum of ammonium, nitrates and nitrites represented on average 8% of TN, and never more than 50%. These results thus suggest that most of the N in our systems was in the form of DON and contained within the DOM itself along with DOC. The same is probably true for phosphorus, although we do not have measurements of inorganic P to support this contention. It would seem that the inclusion of N as a predictor of Bd-DOC is mostly (although not exclusively) reflecting intrinsic DOM properties, i.-e. the stoichiometry and therefore quality of the DOM that was originally loaded from land. This potential effect of DOM quality was reflected in absorbance and fluorescence analyses, as protein-like C6 was the only DOM optical property that was related to Bd-DOC, consistent with previous studies (Guillemette and del Giorgio, 2011;Fellman et al., 2008). The percent contribution of C6 to total fluorescence was further strongly and positively related to the a250:a365 ratio, and negatively to $SUVA_{254}$ (Fig. 3.5), consistent with previously reported relationships of those absorbance properties with microbial processes such as bacterial production and growth efficiency (Berggren et al., 2008).

The patterns in Pd-DOC, on the other hand, were exclusively explained by DOM optical properties (Table 3.1). Extrinsic chemical factors are known to drive the photochemical degradation of DOC (Porcal et al., 2014), and Pd-DOC was indeed significantly correlated with pH ($r^2 = 0.13$, $p < 0.001$, $n = 391$) and iron concentration ($r^2 = 0.35$, $p < 0.001$, $n = 216$). These variables, however, were not significant when included in multiple linear regression models containing DOM concentration or composition, and CDOM entirely accounted for the concentration-effect of FDOM (Table 3.1), suggesting that color integrates several key biochemical properties which collectively determine photochemical reactivity. The connection of Pd-DOC with CDOM or terrestrial influence in general is intuitive, as land-derived DOM is typically associated to highly photo-reactive material with high humic and lignin contents (Spencer et al., 2009b;Hernes et al., 2009;Stubbins et al., 2010). The average loss of DOC in our incubations was 13%, whereas on average 41% of CDOM was lost during the same experiments. This supports the widely accepted notion that colored DOM is preferentially removed by photochemical oxidation (Graneli et al., 1996;Weyhenmeyer et al., 2012), and more importantly, suggests that specific DOM pools (as shown by fluorescence components) contribute more than others to the photochemical losses of DOC (Lu et al., 2013): the degradability of the various fluorescence components (Fig. 6) mostly reflects the degree to which they absorb light in the UVA region (Fig. 3.4). These results thus suggest a strong top-down control of DOM composition by photochemical processes, which is reflected in the large-scale patterns of DOM composition across boreal freshwater ecosystems. Certain fluorescence components were extremely photosensitive (Fig. 3.6); in particular, component C3 was typically completely degraded by light within 24h (Fig.

3.6). The ambient waters differ from experimental conditions in terms of the light climate, but these results nonetheless suggest that there are substantial losses of these fluorescence components in natural environment, and clearly indicate that the photochemical loss rates of C3 are much faster than those of other components. This implies that there must be a constant replenishment of this very reactive DOM across continental watersheds in order to maintain the observed concentrations, such that the contribution of this highly photosensitive DOM (e.g. C3) to aquatic biogeochemical processes is probably greater than what is suggested by its ambient concentrations alone.

3.7.3 Linking DOM optical properties to degradability patterns

Previous work has shown that the links between the patterns of DOC consumption and the dynamics of specific DOM pools identified on the basis of fluorescence are much more complex than what is generally recognized, because most of these components appear to be both consumed and produced by biotic and abiotic processes across diverse aquatic environments (Guillemette and del Giorgio, 2012;Romera-Castillo et al., 2011;Kothawala et al., 2013b). In this regard, Fig. 3.6 shows a consistent behaviour of the various fluorescence components in response to irradiation across lakes, rivers and wetlands with very different environmental properties. It also shows that concentrations of humic/fulvic component C4 systematically increased after exposure to sunlight, yet this component co-varies positively and significantly with Pd-DOC ($r^2 = 0.30$, $p < 0.001$). Photosensitive component C3 (Fig. 3.5) also co-varies positively with Pd-DOC (Table 1), but clearly the mechanism underlying both relationships is completely different.

Component C4 has an emission spectrum comparable to that of very photoreactive C3, but the excitation spectrum shifts towards shorter wavelengths (Fig. 3.4), suggesting that the former may be a photoproduct of the latter. Given its excitation spectrum (Fig. 3.4), however, it is unlikely that component C4 is unreactive to irradiation; ; Figure 6 most likely reflects the net balance of co-occurring photochemical production and degradation processes rather than true reactivity, suggesting that DOC that is potentially photo-reactive may be produced autochthonously in aquatic ecosystems via photochemical processes. Likewise, it has been shown that photo-reactive components such as component C3 reported here are also systematically produced by microbial processes during controlled incubations (Guillemette and del Giorgio, 2012). To add complexity to this framework, not only may biologically labile DOC be produced from the photochemical alteration of terrestrially derived DOC (Bertilsson et al., 1999;Cory et al., 2013), but it can also be rendered more recalcitrant to microbial degradation upon exposure to solar radiation (Tranvik and Bertilsson, 2001). It is difficult to quantify those interactions, in particular the biotic (Guillemette and del Giorgio, 2012) and abiotic (Fig. 3.6) production of Pd-DOC, but those different results nonetheless highlight the multiple processes, on land and in the water, which fuel the aquatic pools of both Bd-DOC and Pd-DOC. Linking DOC degradability measurements with DOM optical properties allows to uncover some of those interactions between production and removal processes, which may not be detected purely based on the characterization of the DOM found in ambient waters.

In the present study we have identified specific fluorescent DOM components associated to either the biological or photochemical degradability of the ambient DOC pool across hundreds of lakes, rivers and wetlands (Table 3.1, Figs. 3.3, 3.5). Our own work in this regard (Stubbins et al., submitted) suggests that these fluorescent components involve not only the molecules responsible for the fluorescence properties, but also that they tend to co-vary with a host of other, non-fluorescent compounds. The molecules responsible for the actual fluorescence of these components may be acting both as substrates, and perhaps more importantly, as tracers of a variety of non-fluorescent pools that share similar sources and sinks, and which may themselves be the main substrates of these microbial reactions.

In this regard, the very strong photochemical degradability of component C3 (Fig. 3.5), combined with published evidence of consistent losses of a comparable component over a gradient of land cover and water retention time in the landscape (Kothawala et al., 2013b;Lu et al., 2013), suggest that it is indeed acting as a substrate for photochemical degradation, and that C3 is a causal driver of Pd-DOC in freshwater environments. Our measurements, however, cannot confirm whether component C6 is mostly driving Bd-DOC as a substrate for microbial processes or acting as a tracer of co-varying bio-labile molecules. Regardless, our results indicate that Bd-DOC and Pd-DOC pools may be adequately tracked by specific DOM properties across a large diversity of freshwater environments, presumably because optical measurements allow to target meaningful DOM pools comprising different molecules which share common production, importation, and removal processes.

3.7.4 Land as a source of both biologically and photo-chemically degradable DOC

Although it may appear intuitive that both Bd-DOC and Pd-DOC increase with overall DOC, the coupling between the concentrations of Bd-DOC and Pd-DOC implies that they share at least some basic sinks, or more likely, sources, in boreal watersheds. The biological and photochemical processes responsible for the removal of DOC from those boreal freshwaters are driven by different extrinsic variables and target different DOM pools (Table 3.1, Fig. 3.6), and the biological and photochemical degradability of DOC, expressed as the fraction of DOC that is biologically or photo-chemically degradable in standardized conditions, are completely decoupled (Fig. 3.3a). The collective evidence discussed above thus rather suggests that Bd-DOC and Pd-DOC partly share land as a common origin, and the relatively weak coupling between both DOC pools suggest that the relative contribution of land-derived DOC to Bd-DOC largely differs across systems.

In this regard, autochthonous processes such as phytoplankton and macrophyte primary production are known to generate fresh, protein-like DOM in freshwaters (Demarty and Prairie, 2009;Lapierre and Frenette, 2009), and more importantly, may supply the Bd-DOC pool independently of terrestrial sources. This appears to be the case in several systems studied here, as the coupling between Pd-DOC and Bd-DOC was weaker in lakes (Fig. 3.3b), and the amount of bio-labile DOM, expressed in the patterns of component C6, was completely independent from CDOM in the lower portion of the CDOM gradient (Fig. 3.7) where most lakes and some large rivers were found. A comparable pattern has been reported in Swedish lakes (Kothawala et al., 2013b) where the equivalent protein-like FDOM component appeared to be relatively invariable across gradients of lake DOC and water retention time. Contrary to this study, however, we observed a stronger relationship between C6 and CDOM as CDOM increased (Fig. 3.7), such that highly colored systems (mostly streams and wetlands) contained much higher concentrations of component C6. The inclusion of rivers ranging from Strahler order 1 to 6, and of a diversity of wetlands, greatly expands the range of terrestrial influence relative to what can be observed based on lakes alone, and may explain the differences between our two studies. This may be a combination of low macrophyte cover and algal biomass in these typically oligotrophic boreal systems, the inhibition of autochthonous processes by CDOM-induced light limitation (Karlsson et al., 2009), and perhaps more importantly, the high rate of supply of terrestrial labile DOC in highly colored systems (Berggren et al., 2010a).

There would thus appear to be a baseline of autochthonous Bd-DOC that is always present in those aquatic environments and varies more or less randomly across gradients of CDOM in response to simultaneously increasing nutrients (Lapierre and del Giorgio, 2012) and light limitation (Karlsson et al., 2009). This baseline may be reflected in the significant intercept of the relationship between Bd-DOC and Pd-DOC (Fig. 3.3b), which would suggest that in systems with very low terrestrial influence and almost no Pd-DOC, there is still a significant pool of Bd-DOC that must be locally produced. Autochthonous sources may be the main driver of Bd-DOC across narrow CDOM gradients, as previously reported (Kritzberg et al., 2004;Guillemette et al., 2013;McCallister and del Giorgio, 2008), but the land-derived Bd-DOC might be the one pool which varies consistently across gradients of terrestrial influence and may thus better explain the patterns in DOC degradability across continental watersheds. These patterns collectively suggest that terrestrially derived Bd-DOC increases proportionately faster than or independently from autochthonous Bd-DOC along a gradient of increasing CDOM, such that land becomes an important, and even the main source of Bd-DOC as terrestrial influence increases. This in turn may explain why bio-labile component C6 (and the molecules it tracks) may actually accumulate and reach high concentrations in wetlands and rivers with very high terrestrial influence, whereas in lakes it is typically decoupled from CDOM (Fig. 3.7), as well as from DOC concentrations and water retention time (Kothawala et al., 2013b), since in the latter systems production, importation and removal may be closer to steady-state.

Our results highlight the apparent links that tie terrestrial influence, water retention time and DOC freshness with DOC composition and degradability across boreal freshwaters. In a previous study we had shown that the concentrations of both Bd-DOC and Pd-DOC tended to increase with CDOM content (Lapierre et al., 2013), resulting in increases in CO_2

flux. This result also suggested an additive dynamic of DOC degradability along a gradient of terrestrial influence, and here we show that the role of land as a major source of both biologically and photo-chemically degradable DOC to boreal aquatic networks results in a pattern of co-variation between these two key pools of carbon across boreal aquatic networks, despite fundamental contrasts in terms of their composition and regulation. The potential of terrestrially derived organic carbon to contribute to ecological and biogeochemical processes in boreal freshwaters is thus apparently not limited by its degradability, at least in environments with high terrestrial influence where this carbon has been freshly imported.

CHAPITRE IV

INCREASES IN TERRESTRIALLY DERIVED CARBON STIMULATE ORGANIC CARBON PROCESSING AND CO2 EMISSIONS IN BOREAL AQUATIC ECOSYSTEMS

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N.B. References cited in this chapter are presented at the end of the thesis.

4.1 ABSTRACT

The concentrations of terrestrially-derived dissolved organic carbon have been increasing throughout northern aquatic ecosystems in recent decades, but whether these shifts impact aquatic carbon emissions at the continental scale depends on the potential for this terrestrial carbon to be converted into carbon dioxide. Here, via the analysis of hundreds of boreal lakes, rivers and wetlands in Canada, we show that, contrary to conventional assumptions, the proportion of biologically degradable dissolved organic carbon remains constant and the photochemical degradability increases with terrestrial influence. Thus, degradation potential increases with increasing amounts of terrestrial carbon. Our results provide empirical evidence of a strong causal link between dissolved organic carbon concentrations and aquatic fluxes of carbon dioxide, mediated by the degradation of land-derived organic carbon in aquatic ecosystems. Future shifts in the patterns of terrestrial dissolved organic carbon in inland waters thus have the potential to significantly increase aquatic carbon emissions across northern landscapes.

4.2 INTRODUCTION

Emissions of carbon dioxide (CO_2) from inland waters to the atmosphere are now recognized as significant relative to other components of the Earth carbon system (Battin *et al.*, 2009 ; Canadell *et al.*, 2007 ; Cole *et al.*, 2007 ; Tranvik *et al.*, 2009). These emissions are fueled by land-derived carbon (Battin *et al.*, 2008 ; Butman et Raymond, 2011 ; Cole *et al.*, 2007), and one of the pathways leading to widespread aquatic CO_2 supersaturation involves the transport of dissolved organic carbon (DOC) from land to continental waters and its subsequent degradation within the aquatic network. There is now mounting evidence that shifts in climate and other environmental factors are driving increasing aquatic concentrations of terrestrially-derived DOC in many landscapes of the world (Larsen, Andersen et Hessen, 2011b ; Monteith *et al.*, 2007 ; Schuur *et al.*, 2009), in what has been termed the "browning"(Roulet et Moore, 2006) of inland waters. Whereas the magnitude and regulation of the browning phenomenon are the focus of intense research and debate (Chapman *et al.*, 2010 ; Clark *et al.*, 2010 ; Erlandsson *et al.*, 2008 ; Freeman *et al.*, 2001 ; Monteith *et al.*, 2007 ; Schindler *et al.*, 1996 ; Zhang *et al.*, 2010), the potential implications of such a shift in terrestrial carbon (C) concentrations for the functioning of the receiving aquatic systems have been less explored, particularly in terms of the impacts on aquatic CO_2 emissions.

In this context, understanding the mechanistic underpinnings of the links between terrestrial DOC and aquatic CO_2 becomes critical to our ability to predict the potential impact of current and projected shifts in the delivery of this terrestrial carbon on global aquatic CO_2 emissions (Billings *et al.*, 2012). DOC and CO_2 concentrations are indeed positively related across temperate and boreal lakes (Jonsson, Karlsson et Jansson, 2003 ; Lapierre et del Giorgio, 2012 ; Roehm, Prairie et del Giorgio, 2009 ; Sobek, Tranvik et Cole, 2005), but the mechanisms underlying this relationship are still debated (Lapierre et del Giorgio, 2012). Should the positive relationship between CO_2 and DOC be mostly driven by the co-variation between the loading of terrestrial DOC and that of soil-derived CO_2, then the use of this relationship to understand and predict the effects of increasing DOC on surface water CO_2 dynamics is questionable. If, on the other hand, the relationship between DOC and CO_2 is to a large extent driven by the actual degradation of terrestrially-derived DOC into CO_2 within aquatic systems, then this relationship has a causal underpinning and can be used to predict future scenarios involving changes in the concentrations of terrestrial DOC in continental waters.

Understanding the potential for the degradation of terrestrially-derived DOC is therefore an essential to establish the link between DOC and CO_2 dynamics. It has long been recognized that terrestrial DOC is susceptible to photochemical degradation in the water (Graneli, Lindell et Tranvik, 1996), but it has traditionally been assumed that this DOC is generally recalcitrant to biological degradation (Bianchi, 2011 ; Hedges, Clark et Cowie, 1988 ; Holmes *et al.*, 2008), and therefore that the contribution of this latter pathway to aquatic CO_2 production is modest. This view is rapidly changing (Bianchi, 2011 ; Holmes *et al.*, 2008), and a growing volume of evidence indicates that terrestrial DOC may be readily degraded by biological processes in aquatic environments, such as the Amazon basin (Ward *et al.*, 2013) and the Arctic (Cory *et al.*, 2013 ; Schuur *et al.*, 2009), temperate (Guillemette, McCallister et del Giorgio, 2013 ; McCallister et del Giorgio, 2008) and boreal (Algesten *et al.*, 2004 ; Spencer *et al.*, 2008) biomes. Boreal biomes contain the highest density of freshwater on earth, yet this evidence for biological DOC degradation is scattered and based on isolated components of the continental aquatic network. As a result, the overall susceptibility of DOC to photochemical and biological degradation, and how this susceptibility varies over gradients of increasing terrestrial influence and at scales relevant for continental C budgets, has not been well established (Berggren, Lapierre et del Giorgio, 2012 ; Dubois, Lee et Veizer, 2010 ; Humborg *et al.*, 2010 ; Lapierre et del Giorgio, 2012 ; Lauerwald *et al.*, 2013).

Here we explicitly address the mechanistic underpinnings of the relationship between aquatic CO_2 and DOC, and in particular, we explore the connections between the photochemical and biological degradability of DOC, and surface water CO_2 dynamics in boreal aquatic networks. We base this work on simultaneous measurements of biological and photochemical DOC degradability, as well as ambient CO_2 concentrations and fluxes, in hundreds of lakes, wetlands and rivers across the northern boreal landscapes of Québec (Canada), spanning a very large gradient of both DOC and terrestrial influence. We first assess how these two facets of DOC degradability vary along a gradient of increasing terrestrial influence (using chromophoric dissolved organic matter (CDOM) as a proxy, see

Supplementary Note 4.7.1), and then explore to what extent DOC degradability mediates the relationship between terrestrial DOC and aquatic CO_2 concentrations and fluxes.

4.3 RESULTS

4.3.1 Environmental gradients covered

The conditions covered in this study encompass much of the range in environmental conditions reported in the literature for northern freshwaters (Supplementary Table S4.1). In particular, surface water concentrations of DOC ranged from 2.1 to 123.9 mg L^{-1} (median = 9.4 mg L^{-1}) across all sites, and CDOM ranged from 0.13 to 30 m^{-1} (median = 4.4 m^{-1}, absorption coefficient measured at 440 nm in Naperian units); both were strongly, positively correlated ($r^2 = 0.60$, Supplementary Figure S4.1), suggesting that much of the variability in ambient DOC concentrations is driven by differences in the loading of terrestrial DOC. The vast majority of ecosystems was supersaturated in CO_2 (average partial pressure of CO_2 (pCO_2) was 754, 3,396 and 5,896 µatm for lakes, rivers and wetlands, respectively), and thus emitted CO_2 to the atmosphere (average CO_2 flux was 450, 1,459 and 960 mg C m^{-2} d^{-1} for lakes, rivers and wetlands, respectively).

4.3.2 DOC degradability patterns

In order to reconstruct the links between terrestrial DOC and aquatic CO_2 fluxes, we first assessed the patterns in DOC degradability, based on measurements of the amount of DOC lost to biological and photochemical processes under standardized conditions (see Methods). There were positive relationships between the amounts of both biologically (Bd-DOC) and photo-chemically (Pd-DOC) degradable DOC and CDOM concentrations across lakes, wetlands and rivers (Fig. 4.1). Although it could be *a priori* expected that higher amounts of degradable DOC would result from increasing overall amounts of dissolved organic carbon, it is the nature of the relationships reported here that is of particular interest. The slope of the type II regression (see Methods) between Bd-DOC and CDOM (Fig. 4.1a; log-slope = 1.15, 95% CI = 0.97- 1.35, $p < 0.001$) indicates that across the whole gradient of systems studied, the DOC pool in the brownest systems with the highest terrestrial influence was as biologically degradable (in terms of the proportion that can be removed) as the DOC pool in clearer waters. In systems with higher terrestrial influence, DOC was in fact proportionately more photo-chemically degradable (Fig. 4.1b; log-slope = 1.54, 95% CI = 1.40-1.68, $p < 0.001$). As a result, the percentage of Bd-DOC shows no significant

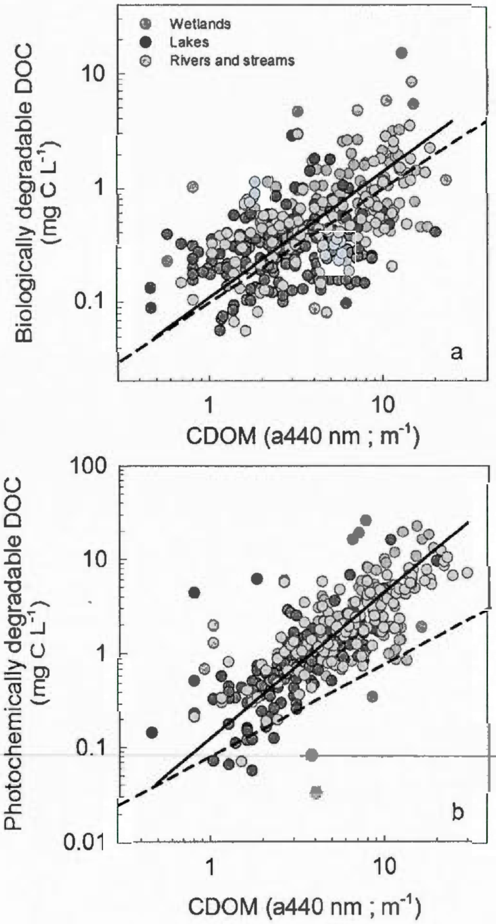

Figure 4.1. Concentrations of degradable DOC across gradients of terrestrial influence.

Concentrations of biologically (Bd-DOC) and photochemically (Pd-DOC) degradable DOC increase as a function of ambient CDOM for natural water samples from a wide range of aquatic systems in the boreal and temperate landscapes of Québec, Canada. a: Log(Bd-DOC) = 1.15 Log(CDOM) (95% confidence interval = 0.97-1.35)- 1.00, $p < 0.0001$, n = 345, $r^2 = 0.30$. b: Log(Pd-DOC) = 1.54 Log(CDOM)(95% confidence interval = 1.40-1.68) – 0.90, $p < 0.0001$, n = 359, $r^2 = 0.59$. The dashed lines represent a slope of 1, i.-e. a proportional increase in degradable DOC as CDOM increases.

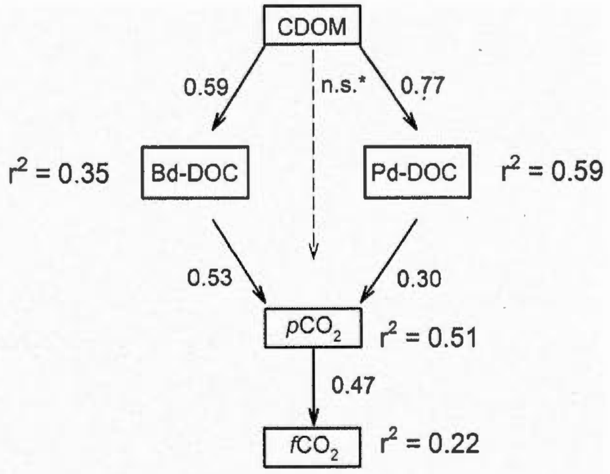

Figure 4.2. Linking terrestrially-derived DOC to aquatic fluxes of CO_2.

Structural equation model linking changes in aquatic CDOM to changes in CO_2 fluxes to the atmosphere. Arrows denote directional links between two variables, and the coefficients represent the rate at which a response variable varies as a function of a given change in its predictor, based on centered and standardized data (see Methods). All paths are significant at $p < 0.001$. The dashed arrow denotes a non-significant (n.s.*) path that was not included in the final model presented here; it is included only for presentation purposes in order to emphasize the absence of a significant direct link between CDOM and pCO_2 or CO_2 flux. pCO_2 represents excess pCO_2. Degradation-mediated CDOM indirect effect coefficient on fCO_2 is 0.25. n = 216. $\chi^2 = 5.20$, p = 0.39, df = 5 relationship with CDOM ($p = 0.82$), but the percentage of Pd-DOC increases significantly with CDOM ($r^2 = 0.30$, $p < 0.0001$, Supplementary Figure S4.2).

4.3.3 Linking DOC processing to CO_2 dynamics

Stable or increasing DOC degradability over gradients of terrestrial influence suggest that increasing CDOM should lead to enhanced conversion of DOC to CO_2 in aquatic ecosystems, and thus to higher concentrations and fluxes of CO_2. There was indeed a positive relationship between ambient pCO_2 and CDOM across all our systems (Supplementary Figure S4.3), but whether or not this pattern may be directly attributed to the conversion of DOC to CO_2 within those systems cannot be determined by this simple relationship. Alternative mechanisms unrelated to direct DOC degradation, including the co-variation in the loading of soil-derived DOC and CO_2 to aquatic systems, could also explain this relationship. To explicitly address these different scenarios, we further explored the causal links that may exist between terrestrially-derived DOC, DOC degradability, and excess aquatic CO_2 concentrations and flux (fCO_2, in mg C m^{-2} d^{-1}) using structural equation modeling (SEM)(Shipley, 2002). In addition to empirically determining the existence of a link between CDOM and fCO_2, this approach allows to determine the pathways by which CDOM is most likely influencing CO_2. We tested several alternative structures linking CDOM to CO_2 for all the sampled sites (see Supplementary Figure S4.4 for key examples), and the only statistically significant structure is one where CDOM-related increases in both Bd-DOC and Pd-DOC positively influence aquatic pCO_2, and subsequently aquatic fCO_2 (Fig. 4.2a). The two paths leading from CDOM to fCO_2 were highly significant, suggesting that both biological and photochemical processing of DOC contribute significantly to the observed CO_2 dynamics. Note that this structure did not contain a significant direct link between CDOM and pCO_2, the latter reflecting variables that influence pCO_2 and that may co-vary with CDOM, such as soil-derived CO_2. Interestingly, although there was a significant positive relationship between pCO_2 and DOC across all systems ($r^2 = 0.28$, $p < 0.001$), there were no significant structures linking DOC, DOC degradability and CO_2 (Supplementary Figure S4.4), thus suggesting that it is the degradation of the terrestrial component of DOC (CDOM) that is more directly influencing aquatic CO_2 dynamics.

4.3.4 The effect of physical forcing

While Fig. 4.2 suggests an important role of DOC processing for aquatic CO_2 dynamics, it also shows that at this scale, the regulation of CO_2 dynamics is not homogenous across all systems. Roughly half of the variation in pCO_2 was explained by factors other than DOC degradation, and, considering that fluxes are a direct function of concentration, the relationship between excess pCO_2 and fCO_2 was unexpectedly weak ($r^2 = 0.22$). Physical forcing, however, strongly mediates the pCO_2 vs fCO_2 relationship, with low-turbulence (expressed by the gas exchange coefficient, k_{CO_2} in m d^{-1}) sites sustaining higher average CO_2 concentrations for a given CO_2 production or input rate, than systems that typically have higher turbulence (Vachon, Prairie et Cole, 2010). In this regard, there was a clear bi-modal distribution of the empirically determined k_{CO2} around a median of 1 m d^{-1} across all sampled sites (Fig. 4.3a), and the regression of fCO_2 against pCO_2 drastically improved when sites with k_{CO2} over and below 1 m d^{-1} were considered separately (Fig. 4.3b). This suggests that, at the expense of the generality of the relationship presented in Fig. 4.2, separating sites into more homogenous groups with regards to physical structure provides a more robust quantification of the impact of changing terrestrial DOC concentrations on aquatic CO_2 fluxes.

4.3.5 Quantifying the effect of CDOM on CO_2 fluxes

Based on the above results, we repeated the SEM analysis separately for these two subgroups of sites that were split based on their k_{CO_2} (sites below and above 1 m d^{-1}, Fig. 4.4). The structures that emerged as significant for each separate group generally resembled that obtained for the ensemble of data shown in Fig. 4.2, but there were some differences in the resulting links and parameters with implications for the prediction of aquatic CO_2 emissions. As mentioned above, there was no significant direct link between CDOM and pCO_2 when all the systems are considered (Fig. 4.2), suggesting that the effect of CDOM on pCO_2 at the whole-network scale is predominantly degradation-mediated. This direct link became significant, however, when high- and low- k_{CO2} systems were analyzed separately, implying that a fraction of the CDOM effect was not due to DOC degradation when more homogenous groups of sites were considered. Moreover, the path connecting Pd-DOC and pCO_2 was non-significant in low-turbulence systems (Fig. 4.4a). As a result, most of the overall CDOM effect on fCO_2 (0.39, Fig. 4.4b) was mediated by Bd-DOC and Pd-DOC (combined coefficient = 0.30, Fig. 4b) for high k_{CO2} systems (mostly lakes and fast-flowing rivers), while roughly half (coefficient = 0.20, Fig. 4.4a) of the overall CDOM effect on fCO$_2$ (coefficient = 0.37) was not mediated by either Bd-DOC or Pd-DOC for low k_{CO2} systems (mostly wetlands and slow-flowing rivers). These coefficients can then be used to estimate how CO$_2$ fluxes respond to increases in CDOM, and together, the different SEM analyses thus provide insights on the links that exist between terrestrial influence and CO$_2$ emissions in aquatic ecosystems, in particular, on the role that DOC processing plays in that framework.

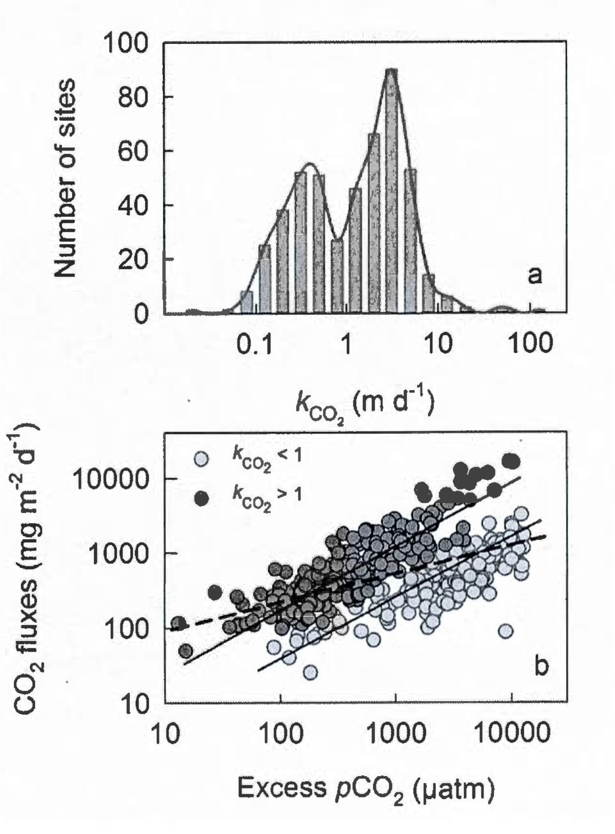

Figure 4.3 Relationship between concentrations and fluxes of CO_2.

a) Frequency distribution of the measured diffusive k_{CO2} across the sampled sites. Note the bi-modal distribution around k_{CO2} = 1 m d^{-1}. b) Regression of CO_2 fluxes to the atmosphere as a function of surface water CO_2 excess partial pressure for systems with k_{CO2} over and below 1. Analysis of co-variance reveals different intercepts ($p < 0.001$), but similar slopes ($p = 0.08$) for both groups. $k_{CO2} > 1$: Log(fCO_2) = 0.73 (± 0.03) Log(excess CO_2) – 0.77 (± 0.08), n = 247, $p < 0.0001$, $r^2 = 0.74$. $k_{CO2} < 1$: Log(fCO_2) = 0.73 (± 0.03)Log(excess CO_2) – 0.26 (± 0.13), n = 172, $p < 0.0001$, $r^2 = 0.68$. Dashed line illustrates the inadequacy of an overall fit in the absence of grouping: Log(fCO_2) = 0.36 (± 0.03)Log(excess CO_2) + 1.67 (± 0.09), n = 419, $p < 0.001$, $r^2 = 0.27$. Note that sample size differs here compared to Figs 2 and 4, hence the different coefficients of determination between pCO_2 and fCO_2.

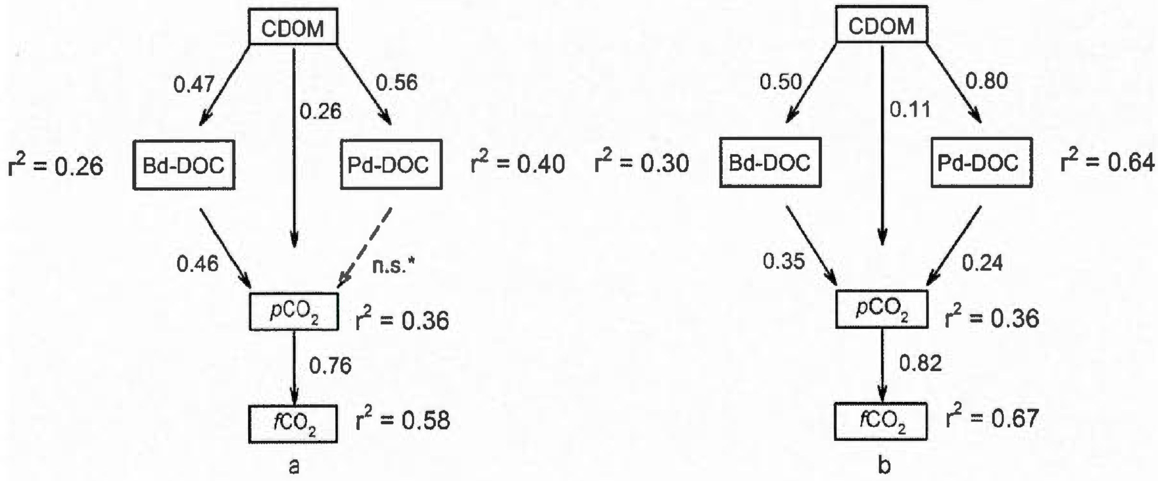

Figure 4.4 The pathways linking CDOM to CO_2 fluxes in high and low turbulence systems.

Structural equation models linking changes in aquatic CDOM to changes in CO_2 fluxes to the atmosphere for the two subsets of sites separated on the basis of k_{CO2} and therefore of average turbulence. Arrows denote directional links between two variables, and the coefficients represent the rate at which a response variable varies as a function of a given change in its predictor, based on centered and standardized data (see Methods). All paths are significant at $p < 0.001$. The dashed arrow denotes a non-significant (n.s.*) path that was not included in the final model presented here; it is included only for presentation purposes in order to emphasize the absence of a significant direct link between Pd-DOC and pCO_2 in low-turbulence systems. pCO_2 represents excess pCO_2. a: Low turbulence systems ($k_{CO_2} < 1$ m d^{-1}). CDOM indirect effect coefficient on fCO_2 is 0.37, degradation-mediated CDOM indirect effect on fCO_2 is 0.17. n = 102. $\chi^2 = 5.07$, p = 0.41, df = 5 . b : High turbulence systems ($k_{CO_2} > 1$ m d^{-1}). CDOM indirect effect coefficient on fCO_2 is 0.39, degradation-mediated CDOM indirect effect on fCO_2 is 0.30. n =114. $\chi^2 = 5.45$, p = 0.24, df = 4

4.4 DISCUSSION

Collectively, our results highlight the importance of terrestrially-derived DOC in fueling both Bd-DOC and Pd-DOC pools across a wide range of aquatic environments. The variability shown in Fig. 4.1 suggests that such patterns may have been masked in previous studies conducted at smaller scales or across narrower environmental gradients, where autochthonous DOC may have emerged as a more important driver of overall DOC degradability. At the scale of the present study, however, increasing terrestrial influence (as reflected in CDOM) clearly implies higher absolute and relative potentials for DOC to be degraded across lakes, rivers and wetlands. Although those patterns are based on potential degradation rates under standardized conditions, they unambiguously show that both the total amount and the proportion of DOC that can potentially be converted to CO_2 tend to increase with terrestrial influence, and as a corollary, it would be expected that surface water CO_2 concentrations should increase as a function of CDOM.

The SEM analyses (Figs. 4.2, 4.4) demonstrate that there is a link from CDOM to CO_2 fluxes that is mediated by the degradation of DOC when very large gradients are considered, such that increasing concentrations and subsequent degradation of terrestrial DOC in aquatic ecosystems should indeed result in rising CO_2 emissions. These results, however, do not imply that colored DOC itself is the only pool being degraded, but rather that systems with high CDOM concentrations are associated with a higher absolute potential for conversion of dissolved organic carbon, both colored and uncolored, into CO_2 in surface waters. They do not imply either that DOC degradation is the only factor influencing aquatic CO_2 dynamics in these northern regions. For example, recent inter-regional assessments have highlighted the importance of terrestrial inorganic C inputs in shaping aquatic CO_2 dynamics (Butman et Raymond, 2011 ; Humborg *et al.*, 2010 ; McDonald *et al.*, 2013). Likewise, studies that have targeted specific components of the aquatic network, such as low DOC lakes (Maberly *et al.*, 2012) or headwater streams (Wallin *et al.*, 2013), have also highlighted the importance of soil CO_2 inputs. There is no actual contradiction between these various studies and the results we present here: The direct influence of terrestrial DOC is superimposed onto a background of CO_2 dynamics driven by external inputs of CO_2. This background is always present but varies both regionally and also locally between different types of aquatic systems (Lapierre et del Giorgio, 2012 ; McDonald *et al.*, 2013), determined by variations in the relative proportion of DOC versus CO_2 delivered from land to the inland water network.

The large heterogeneity that exists among the studied systems was at least partly captured by the SEM analyses performed on subsets of sites sharing comparable patterns in gas exchange coefficient (Fig. 4.4).When more homogenous sets of systems, in terms of physical structure, were analyzed, factors other than DOC degradation emerged as modulating the effect of CDOM on CO_2 concentrations and fluxes. We can only speculate on the causes underlying the differences in pathways linking CDOM to CO_2 in high k_{CO2} *versus* low k_{CO2} systems. It is possible that physical structure integrates other environmental factors which may modulate the impact of CDOM on CO_2 dynamics, such as area and depth (Vachon et Prairie, 2013), which may in turn be related to residence time, exposure to sunlight, or the relative importance of groundwater inputs in regulating CO_2. Regardless of the actual processes, the different SEM analyses converge to essentially the same conclusion, which remains adequate whether the entire dataset or more homogenous subsets of sites are considered: The effect of terrestrially-derived DOC on CO_2 evasion is not entirely, but significantly driven by DOC processing in continental watersheds.

Our results provide a mechanistic underpinning to previous studies that had arrived to similar conclusions concerning the role of DOC but based on regional C mass balances (Humborg *et al.*, 2010), and also provide a process-based framework underlying the regional relationships that have been observed between DOC concentrations and aquatic CO_2 fluxes (Jonsson, Karlsson et Jansson, 2003 ; Lapierre et del Giorgio, 2012 ; Roehm, Prairie et del Giorgio, 2009). We show that DOC degradation strongly mediates this relationship, across rivers ranging from stream order 0 to 6, lakes ranging in size and morphometry from a few hectares to several thousands of square kilometers, and wetlands and ponds that also vary greatly in position and features, within a heterogeneous boreal landscape covering roughly 900,000 km^2. Our results may not necessarily apply to some specific aquatic components or portions of the landscape, but rather provide an integrated perspective of the role of DOC processing in sustaining aquatic CO_2 concentrations and evasion in continental watersheds.

The SEM analyses further allow a first-order quantification of the potential effect of shifts in terrestrial DOC concentrations on aquatic $f\text{CO}_2$. Although the long-term DOC trends are highly variable in time and across landscapes (Chapman *et al.*, 2010 ; Clark *et al.*, 2010 ; Erlandsson *et al.*, 2008 ; Zhang *et al.*, 2010), DOC concentrations have consistently increased across temperate and boreal regions over the past 20 years (Monteith *et al.*, 2007). More specifically, in our own study area, DOC concentrations have increased between 20 and 50% since 1990 (Couture, Houle et Gagnon, 2012), whereas CDOM has increased by up to 155% within the same period in some European landscapes (Chapman *et al.*, 2010). The coefficients provided by the SEMs (Fig. 4.4) suggest that for every percent increase in CDOM there should be a 0.17 and 0.30 percent increase in CO_2 evasion from low and high k_{CO2} systems, respectively, due to enhanced DOC processing in those systems. Our results imply that as a consequence, aquatic CO_2 fluxes may have been increasing in northern Québec and elsewhere across northern temperate and boreal landscapes over the past decades, conceivably from 10% to up to 50% where terrestrial DOC concentrations have increased the most. There are, to our knowledge, no long-term data sets on aquatic CO_2 that can be used to test this hypothesis, which we suggest should be incorporated into future long-term research programs.

Our results further suggest that aquatic CO_2 emissions will keep increasing as a direct function of increasing terrestrially-derived DOC concentrations in aquatic ecosystems. Considering the major contribution of the aquatic networks in these northern, water-rich landscapes to the global continental aquatic C emissions (Canadell *et al.*, 2007 ; Cole *et al.*, 2007 ; Tranvik *et al.*, 2009) (ca. 1.5 Pg y^{-1}), these potential shifts could significantly alter the fine balance that exists between freshwater CO_2 emissions and the estimated continental (2.8 Pg C y^{-1}) and oceanic carbon sinks (2.2 Pg C y^{-1}) (Canadell *et al.*, 2007). Although more focused measurements should be undertaken to adequately quantify the magnitude of the enhanced aquatic CO_2 emissions at continental or global scales, the scenario that we propose here undoubtedly involves the mobilization and degradation of terrestrial organic C which, contrary to historical assumptions, appears to be highly reactive in freshwaters but would otherwise experience much slower degradation in more stable environments such as soil or oceanic refuges (Bianchi *et al.*, 2013 ; Cole *et al.*, 2007 ; Ekschmitt *et al.*, 2005). The absence of evidence for generalized long-term declines in discharge, and the positive relationships that have been reported between long-term trends in discharge and DOC concentrations in landscapes where browning is happening (Clark *et al.*, 2010 ; Erlandsson *et al.*, 2008 ; Evans *et al.*, 2006), suggest that greater amounts of DOC are circulating in inland waters today compared to a few decades ago, yet no increase in the export of DOC from continents to the oceans have been observed so far in regions where browning is happening (Räike *et al.*, 2012). These observations are consistent with our findings that this additional carbon is readily processed and converted to CO_2 as it enters the aquatic networks, which may further enhance the erosion of the terrestrial C (Davidson et Janssens, 2006 ; Dorrepaal *et al.*, 2009 ; Gudasz *et al.*, 2010) sink beyond a direct effect of increasing global temperatures.

4.5 METHODS

4.5.1 Study area and sampling

Over the course of eight years, we sampled lakes, streams, rivers and wetlands (mostly beaver ponds) located in seven temperate and boreal regions of Québec, eastern Canada (44-53 °N, 70-80 °W, Supplementary Figure S4.5). Sites were sampled from late May to early October and a subset of sites was sampled up to three times in a given year.

A more detailed description of the regional features can be found in Lapierre and del Giorgio (2012). In short, these regions cover a total area of approximately 900,000 km^2 and are characterized by a wide range of geography, climate and dominant plant cover: mean annual temperature ranges from 4.9 °C in the Laurentians to -2.0 °C in the Eastmain region, and mean annual precipitations ranges from 695 mm y^{-1} in the Eastmain to 1150 mm y^{-1} in the Eastern Townships regions. Dominant vegetation ranges from deciduous forest in the Eastern Townships and Laurentians regions to mixed deciduous and conifer forest in the Abitibi and Chicoutimi regions; the James Bay, Chibougamau and Eastmain regions are characterized by spruce-moss forest. Topography is generally flat and lakes and rivers are typically shallow and turbid in the low-altitude (typically 200-300 m elevation) Abitibi and James Bay regions, which are located in the Abitibi clay belt. Water discharge was very low in rivers and streams in the latter region, whereas it was the highest in the most elevated and steepest (200-900 m elevation) Laurentians and Chicoutimi regions.

Sampling took place from 2003 to 2005 in Eastern Townships, and from 2009 to 2011 in the remaining regions. The Eastern Townships sites were sampled in June, July and August each year, the Eastmain sites were sampled twice from early June to early July 2009, the Laurentians sites were sampled once between mid-june and mid-august 2010, and three sampling campaigns were performed during the ice-free period for the remaining regions in 2010 and 2011. For these latter regions, the first campaign occurred from late May to early June, the second campaign from mid-July to mid-August, and the third campaign from late September to early October. A subset of sites were sampled at each campaign, and the remaining ones were sampled only once during mid-summer. For this analysis we have used the indiviudal sampling points, without any averaging. Because of various logistical constraints, not all variables could be measured at every site all the time, which explains the different number of observations presented for the main variables. In addition, DOC photochemical degradability was not measured for the Eastern Townships sites.

Water was sampled at 0.5 m from the surface from the deepest measured point of lakes and near the shore of streams, rivers and wetlands. Ambient $p\mathrm{CO}_2$ was measured in situ using an EGM-4 infrared gas analyzer (PP-systems, Boston, MA, USA), after equilibration by pumping water through a Liqui-Cel Mini Module (Charlotte, NC, USA) contactor membrane (for lakes), or by headspace equilibrium (rivers, streams and wetlands). Excess $p\mathrm{CO}_2$ was calculated by subtracting ambient atmospheric $p\mathrm{CO}_2$ at the corresponding sites. CO_2 flux, and the associated diffuse gas exchange coefficients for CO_2 (k_{CO2}), were measured for every site on the basis of changes in $p\mathrm{CO}_2$ with time in floating chambers (Vachon, Prairie et Cole, 2010). The chamber was connected in closed loop to an EGM-4 infrared gas analyzer (PP-systems), $p\mathrm{CO}_2$ in the chamber was measured every minute for 10 minutes and accumulation rate was calculated by linear regression.

4.5.2 Chemical and optical analyses

Colored dissolved organic matter (CDOM) was determined spectrophotometrically in 0.45-µm filtered natural water samples. We measured absorbance at 440 nm with a UV-visible Ultrospec 2100 spectrometer (Biochrom, Cambridge, UK) using a 2-cm quartz cuvette, and corrected by subtracting nanopure water blanks. The absorption coefficient (a440, in m^{-1}) was reported in Naperian units by dividing the optical absorbance at 440 nm by the path length in meters and multiplying by 2.303 (Cuthbert et del Giorgio, 1992).

Concentrations of DOC from filtered (0.45 µm) water samples were measured in duplicate (taken from a unique vial) on an OI-1010 TIC-TOC Analyzer (OI Analytical, College Station, TX, USA). Total phosphorous (TP, Supplementary Table S1) was analyzed spectrophotometrically using the standard molybdenum blue method after persulfate digestion (Cattaneo et Prairie, 1995), and Chl *a* samples (Supplementary Table S1) were analyzed spectrophotometrically following filtration on Whatman (GF/F) filters and hot ethanol (90 %) extraction (Marker et Nusch, 1980). Filters were sonicated prior to extraction.

The surface and catchment areas of the lakes we sampled were determined using the ArcView 3.2 and ArcGIS v.9 software applied on the DEM derived from (1:50000) maps.

4.5.3 DOC degradability

The DOC degradation data presented here reflect the potential for DOC to be mineralized under standardized conditions, and not to actual degradation rates under ambient conditions. Our approach aimed at removing or minimizing site-specific features such as local temperature and light exposure and thus to ensure that the resulting DOC degradability was comparable across the entire spectrum of sites.

Biological degradation experiments were carried out in the dark at a fixed incubation time (14 days) and temperature (20°C), and the data presented in Fig. 4.1a thus correspond to the amount of biologically degradable DOC over a period of 14 days. We filtered 1.5 liters of ambient water through 2.7 µm pore-size GF/F filters (Whatman, Maidstone, UK) for biological degradation experiments in order to preserve most bacteria and avoid re-inoculation (Guillemette et del Giorgio, 2011). We used the same pool of water for photochemical degradation experiments to minimize the differences in manipulations and thus maximize the comparability of both properties over the large range of samples. Two 500-ml sub-samples were used as replicates for biological degradation experiments and dispensed in acid-washed glass bottles (500 ml). Figure 4.1a presents the average of both replicates. The remainder of the water was used for photochemical degradation experiments, which were carried out in a solar simulator (Qsun XE1-BC, Qlab, FL, USA) under a standard light dose (0.68 W m^{-2} at 340 nm, spectrum representative of natural sunlight) over a fixed incubation time (24 h) and temperature (24 °C). The data presented in Fig. 4.1b thus correspond to the amount of photo-chemically degradable DOC in 1 day at the maximum sustainable light intensity from the solar simulator; considering diel light cycles and the natural light intensity at the studied latitudes, this would roughly correspond to six days of natural light exposure in the sampled regions.

Irradiated samples were contained in 40 ml glass tubes, and thus the data presented would correspond to loss rates in the first centimeters of the water column. Roughly 80 % of the light between 360 and 700 nm passes through the glass, decreasing linearly to reach 10 %

at 315 nm; no light below 300 nm went through. The measured loss rates are thus conservative compared to what would have been obtained with quartz tubes, but still represent a level of exposure representative of the first centimeters of the water column. Given the very strong light intensity and the small size of the vials, the light dose within the vials was high and the loss rates due to photochemical degradation were high, thus a 24 h period was sufficient to obtain reliable estimates of DOC losses. We assumed that all bacteria were killed by the very high UV dose. Even if that were not the case, the DOC loss rates due to photochemical degradation were systematically at least an order of magnitude higher than those measured in the biological degradation experiments (when compared on a d^{-1} basis), implying that if bacteria did survive they could not contribute importantly to the measured loss rates. DOC concentrations were measured within one month after incubation.

These standardized biological and photochemical degradation rates could potentially be extrapolated to ambient waters by adjusting them for in situ temperature, light exposure and water retention time, among other factors, but this is not the focus of this study. Here we rather concentrate on the comparative analysis of this standardized DOC degradability across sites.

4.5.4 Statistical analyses

Data were log-transformed to attain normality and homoscedasticity. Single regressions were performed using JMP software version 7.0 (SAS Institute, NC, USA). We used major axis (MA; type II) regressions to obtain a representative slope for the regression between two log-transformed variables containing measurement errors in Fig. 4.1. We performed structural equation modeling (SEM) to identify the sequences of presumed causal relationships that may exist (Shipley, 2002) between CDOM, the amounts of biologically and photo-chemically degradable DOC, ambient DOC, excess $p\mathrm{CO}_2$ and $f\mathrm{CO}_2$, using EQS 6.1 (Multivariate Sofware, CA, USA). This analysis tests the significance of individual paths between variables as well as that of the structure as a whole. Similar to most analyses, a path with $p < 0.05$ is typically considered significant. Regarding the overall model, however, a value of $p > 0.05$ means that the proposed structure effectively captures the variability in the modeled variables and the directional links between them, whereas $p < 0.05$ would imply a significant difference between the observed and the modeled data[38].

The coefficients provided by the SEM for the links between two variables (noted beside the arrows in Figs.4.2 and 4.4) are conceptually analogous to the slope of the linear regression between those variables, but the computation differs from MA regressions, thus the coefficients provided by the different types of analyses cannot be directly compared. Furthermore, the log-transformed data have been centered and scaled for the SEM analyses, such that different coefficients within a given structure can be directly compared. A higher coefficient between two variables denotes a stronger link than between two variables linked by a lower coefficient. Further details on the SEM analyses are provided in the Supplementary Note 4.7.2.

4.6 CONCLUDING NOTES

4.6.1 Acknowledgements

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4.6.2 Author contributions

J.-F.L. and P.d. G. designed the study; all authors contributed to the manuscript structure; J.-F. L. and F.G. processed and analyzed the data; J.-F. L. and P. d. G. wrote the manuscript; all authors commented on the manuscript.

4.6.3 Competing Financial Interests

The authors declare no competing financial interests.

4.7 SUPPLEMENTARY NOTES

4.7.1 Using CDOM as a proxy of terrestrially-derived DOC

In this study we use CDOM concentration as a proxy of terrestrial influence, more particularly, of terrestrially-derived DOC concentrations. It should be pointed out that CDOM and terrestrial DOC are not strictly equivalent, since DOC absorbance can vary not only as a function of terrestrial DOC concentration but also locally as a function of factors that influence the specific absorbance of DOC, such as changes in pH or iron concentration (Heikkinen, 1990 ; Pace *et al.*, 2012 ; Weishaar *et al.*, 2003). However, over broad regional scales, there is a consistently and often strong proportional relationship between CDOM and total DOC (Pace et Cole, 2002), especially in oligotrophic regions where DOC is almost exclusively from terrestrial origin (Jonsson, Karlsson et Jansson, 2003), indicating that CDOM essentially tracks bulk terrestrial DOC. The coupling between DOC and CDOM, however, becomes weaker as residence time and productivity increase (Pace et Cole, 2002), when in-situ processes tend to mask catchment properties in determining the concentration of different sources of DOC (Köhler *et al.*, 2013), thus when terrestrial DOC is cumulatively degraded and autochthonous sources of DOC represent a greater portion of the DOC pool.

In this regard, local concentrations of CDOM are the result of the loadings of terrestrial DOC and the cumulative losses along the aquatic continuum. Not all terrestrial DOC is colored, and some labile, uncolored fraction may lost faster than the bulk CDOM (Berggren *et al.*, 2010a ; Fellman *et al.*, 2008), hence actual terrestrial influence in some systems may be higher than what is suggested by CDOM alone. Nonetheless, across large spatial and environmental gradients such as those covered in this study, local specificity will not mask the strong landscape patterns, and we can safely assume that CDOM tracks terrestrial influence adequately, although not perfectly, considering the questions addressed. Although clearly desirable, more detailed molecular or isotopic analyses could not realistically be performed to determine precisely the exact concentration of terrestrial DOC for this large dataset, and the relationship between CDOM and DOC for all the sampled sites (Supplementary Figure S4.1) shows that indeed DOC is much less colored in some environments with presumably high concentrations of autochthonous DOC, especially productive lakes and wetlands, and thus using DOC in those sites would not provide an accurate evaluation of the terrestrial fraction. Hence we used CDOM not as a measure of the exact concentration of terrestrial DOC in aquatic ecosystems, but rather as a quantitative proxy of terrestrial influence which we use to assess DOC degradability under scenarios of changing delivery of terrestrial organic carbon to aquatic ecosystems.

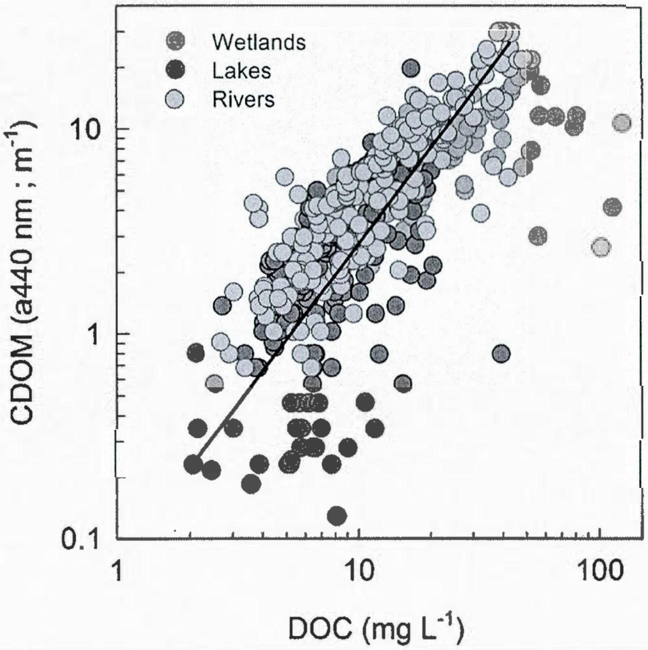
4.7.2 Structural Equation Modeling (SEM)

We used structural equation modeling to test how well a series of potential causal and directional links between measured variables predicts the actual variability in the observed data (Shipley, 2002). SEM analyses test, separately, the significance of the individual paths as well as that of the structure as a whole. A statistically significant model thus does not warrant significance for the individual paths, and the overall model may still not be statistically significant even if all the individual paths are significant if, for example, information is highly redundant within the structure or explained variation in a predicted variable is not transmitted downstream in the structure.

Latent variables can further be used to test the potential effect of an unmeasured, theoretical variables potentially underlying other measured properties. For example, if "Terrestrial inputs of CO_2" were a latent, underlying variable influencing DOC, CDOM and pCO_2 simultaneously in the sampled systems, there would have been a structure in the data captured by this "latent" variable, which would have significantly explained pCO_2. Supplementary Figure S4.4 presents alternative plausible structures that we tested, one of which incorporated this latent variable, yet none of these combinations adequately captured the structure in the measured data when all the sites were considered together.

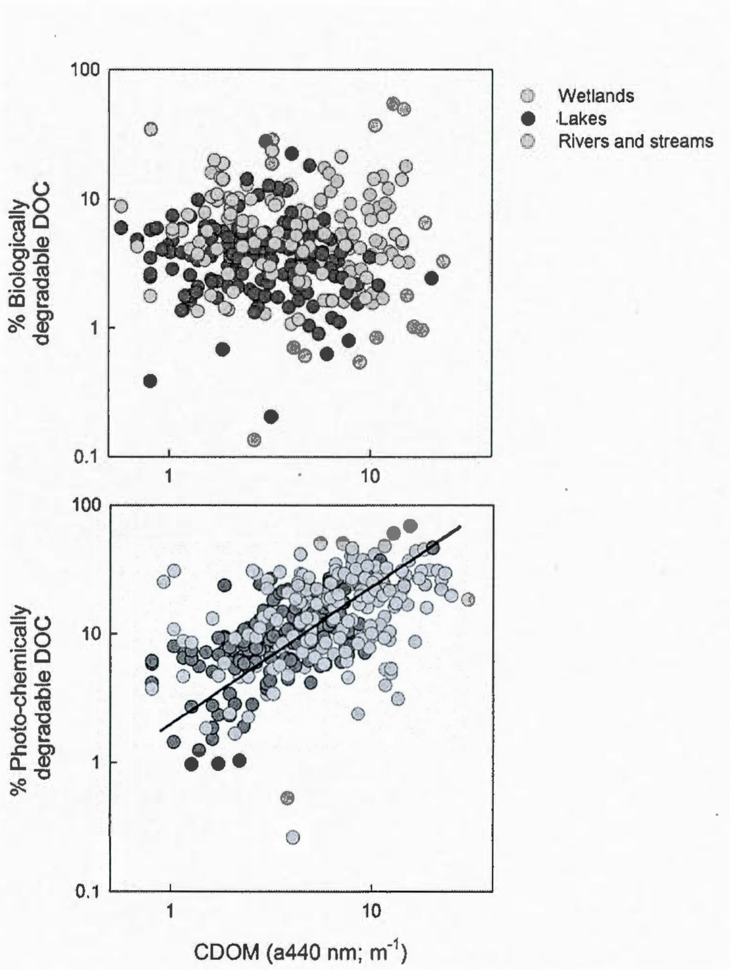
The parameters provided by the SEM further allow to estimate the change in a response variable as a function of changes in the upstream variables. This is done by multiplying the coefficients along a path, and adding the coefficients when paths converge to a specific variable. For example, we multiplied the coefficients along the Bd-DOC pathway ($0.59 * 0.53 = 0.31$) and the Pd-DOC pathway ($0.77 * 0.30 = 0.23$) of Fig. 2. The sum of those coefficients may then be multiplied by the coefficient linking pCO_2 to fCO_2 ($0.54 * 0.47 = 0.25$) to obtain the total effect of CDOM on fCO_2.

It would also be possible to do the same calculation to estimate the contribution of each pathway; in the above case, since a direct link between CDOM and $p\mathrm{CO}_2$ is not significant, the entire effect of CDOM on $f\mathrm{CO}_2$ appears to be degradation-mediated. In Fig. 4.4, part of the variation in $f\mathrm{CO}_2$ was not explained by Bd-DOC and Pd-DOC, and we thus calculated the overall effect of CDOM on $f\mathrm{CO}_2$ as well the part of that variation that was degradation-mediated based on the above explanations.



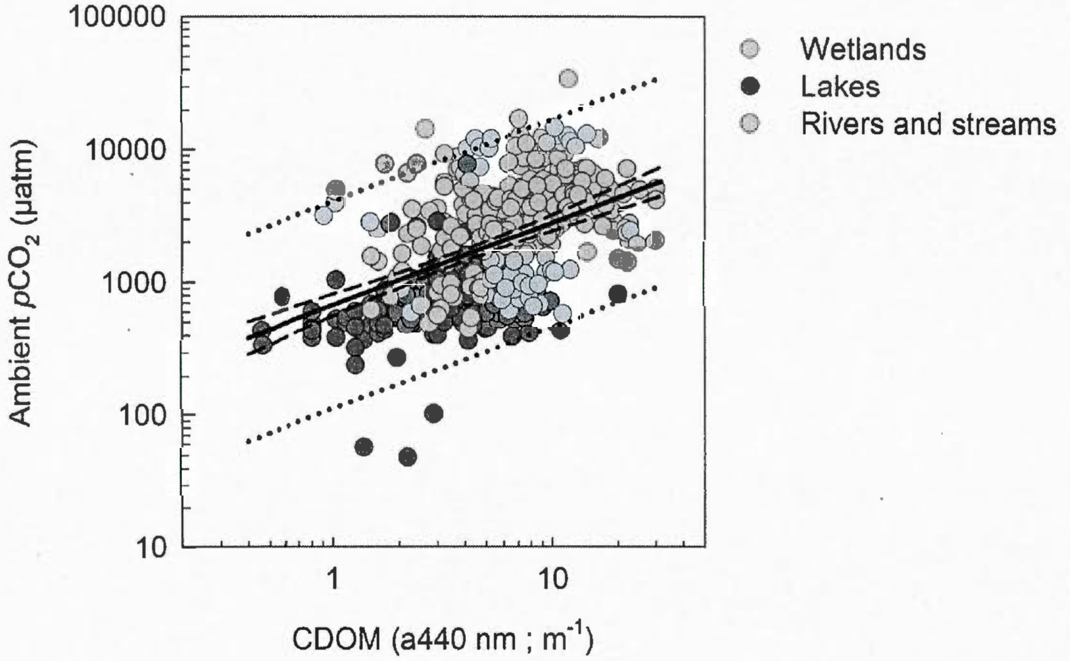
Supplementary Figure S4.1 CDOM content as a function of total DOC concentrations.

CDOM concentrations as a function of DOC concentrations across boreal lakes, rivers and wetlands. Log(CDOM) = 1.15Log(DOC) (95% confidence interval = 1.07-1.23) - 0.59. Type II regression was performed.



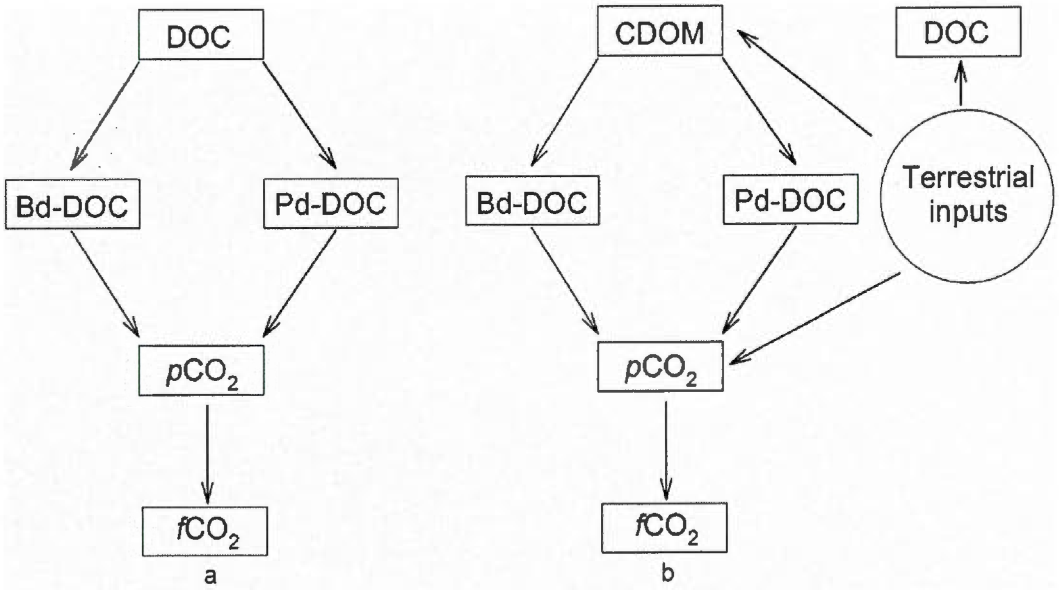
Supplementary Figure S4.2 Patterns of DOC degradability across gradients of terrestrial influence.

Percentage of biologically (Bd-DOC) and photochemically (Pd-DOC) degradable DOC as a function of ambient CDOM for natural water samples from a wide range of aquatic systems in the boreal and temperate landscapes of Québec, Canada. Panel a: regression not significant ($p = 0.81$, $n = 314$, $r^2 = 0.00$).Panel b: Log(% Pd-DOC) = 1.07 Log(CDOM) (95% confidence interval = 0.91-1.27) – 0.34, $p < 0.0001$, $n = 358$, $r^2 = 0.30$). Type II regressions were performed.



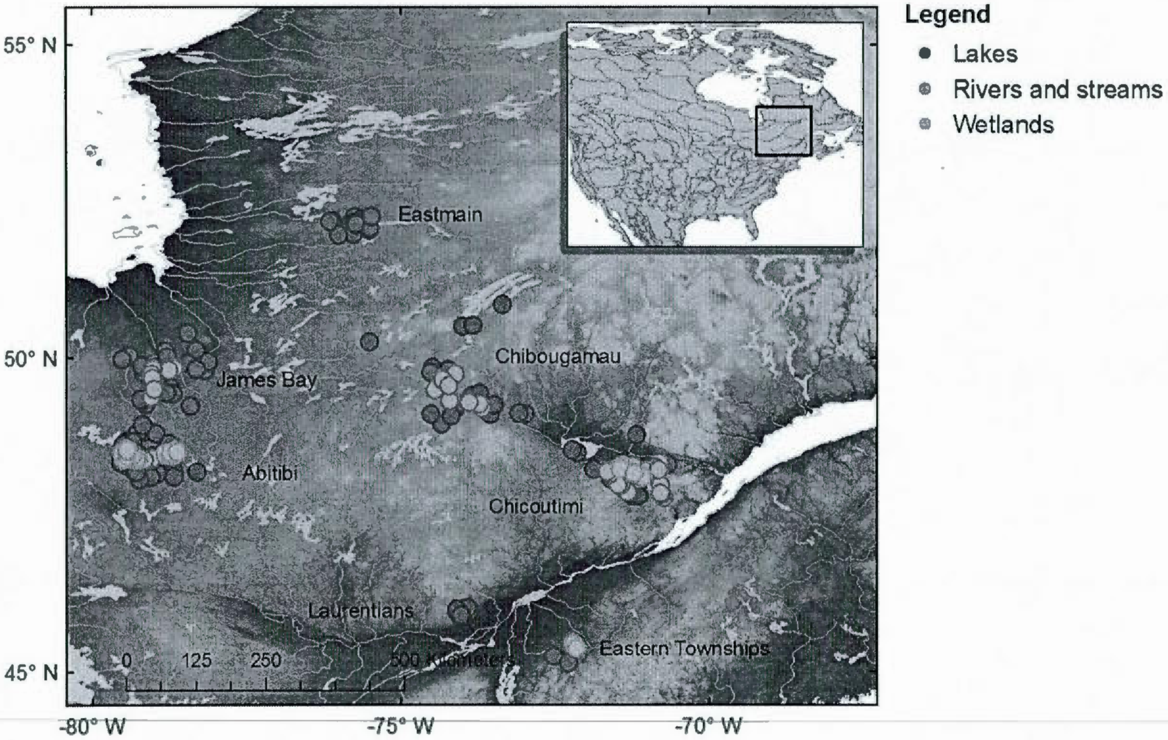
Supplementary Figure S4.3 Aquatic CO_2 concentrations as a function of CDOM.

The least squares regression equation is Log(pCO_2) = 0.62 (± 0.06) Log(CDOM) + 2.83 (± 0.04), $p < 0.0001$, $n = 485$, $r^2 = 0.26$). Dashed lines represent the 95% confidence interval around the fit, and dotted lines represent the 95% confidence interval for individual predictions.



Supplementary Figure S4.4 Alternative pathways potentially explaining aquatic fluxes of CO_2.

Arrows denote directional causal links between two variables. Measured variables are represented inside rectangles whereas a latent variable (inferred, but not measured, see Supplementary Note 2) is represented inside a circle. There were statistically significant differences between the proposed models and the structure in the data (based on p values), indicating that the models did not capture adequately the directional links between the variables; the individual coefficients are thus not shown.a: $\chi^2 = 13.52$, $p = 0.009$, df = 5. b: $\chi^2 = 56.18$, $p < 0.0001$, df = 6



Supplementary Figure S4.5 Map of the study area.

Sampling sites were distributed across seven temperate and boreal regions of Québec, Canada. Nearby sites appear under-represented due to dots overlap, especially in the Eastern Townships and Laurentians regions.

CONCLUSION

5.1 Principales contributions

Un thème commun de cette thèse a été de placer, sur des gradients communs, des connaissances auparavant éparpillées dans la littérature quant au role que le carbone organique dissous (COD) joue sur les émissions de CO_2 par les écosystèmes aquatiques. Nous nous sommes rapprochés comme rarement auparavant de l'interface terre-eau pour un travail de recherche considéré comme aquatique, tout en continuant à explorer les patrons et les mécanismes dans les milieux lacustres et riverains plus traditionnels. Il en résulte des gradients environnementaux à toutes fins pratiques jamais explorés auparavant dans une même étude empirique, qui ont permis de grandement raffiner et souvent d'unifier des connaissances apparamment contradictoires sur le cycle du carbone aquatique, et sur le role que celui-ci joue sur le cycle du carbone continental à l'échelle du paysage.

Plus particulièrement, les points clés suivants ressortent des différents chapitres:

1) La combinaison des propriétés du climat et du paysage avec la concentration et la composition du COD et des nutriments résulte en de forts patrons spatiaux au niveau du métabolisme des lacs, lequel varie principalement à l'échelle régionale. La mobilisation de COD et de nutriments du milieu terrestre vers les eaux continentales apparaît comme un processus clé qui permet de relier climat, paysage terrestre et métabolisme aquatique à l'échelle régionale, où l'effet direct du climat n'est peut-être pas pleinement exprimé.

2) Vraisemblablement en réponse aux patrons observés dans le premier chapitre, il y a une forte régionalité dans la relation qui existe entre COD et CO_2 dans les lacs du biome boréal nord-américain et européen, modulée surtout par la topographie du paysage et les moyennes régionales en nutriments; l'équilibre entre COD et phosphore total est un prédicteur clé. Ces résultats suggèrent un double rôle du COD en tant que i) indicateur des

importations de CO_2 et de nutriments depuis le milieu terrestre et ii) substrat organique pour la production de CO_2 à l'intérieur de l'environnement aquatique. Ces deux rôles sont apparamment modulés par les propriétés régionales du paysage et de la composition du COD.

3) Il y a un lien fort entre composition et potentiel de dégradation du COD, et le milieu terrestre semble injecter une grande quantité de COD frais qui est à la fois biologiquement et photochimiquement dégradable; cet effet est surtout observé dans les rivières et les milieux humides avec une forte influence terrestre. Dans les écosystèmes aquatiques retrouvés à l'échelle du paysage boréal québécois, il y a donc un couplage significatif entre les concentrations en COD biologiquement et photochimiquement dégradable, même si ces derniers diffèrent largement en termes de composition et de régulation.

4) Le dernier chapitre intègre les éléments clés des chapitres précédent. Il démontre d'abord, de façon empirique, une augmentation graduelle de la dégradabilité biologique et photochimique du COD sur un gradient d'influence terrestre, puis un effet causal fort du COD en tant que substrat de dégradation pour la production et l'émission de CO_2 dans les eaux continentales. Des pressions environnementales largement répandues telles que les changements climatiques et le "brunissement" (augmentation à long terme du contenu en COD coloré) des eaux intérieures résultent donc, et devraient continuer à résulter dans le futur, en des augmentations significatives des de CO_2 des écosystèmes aquatiques vers l'atmosphère dans l'ensemble du biome boréal.

5.2 Principales nouveautés et implications

L'ampleur de l'étude empirique réalisée, en termes de gradients environnementaux couverts et de la combinaison de patrons en milieu naturel et d'expériences en milieu contrôlé, ont permis de mettre en lumière des aspects inattendu du rôle du COD d'origine terrestre sur le fonctionnement des écosystèmes aquatiques. Les principaux résultats établissent non seulement un lien fort entre les propriétés du paysage terrestre et le fonctionnement des écosystèmes aquatiques, mais démontrent aussi l'existence de patrons régionaux prévisibles au niveau du COD et des processus aquatiques impliqués dans le cycle du carbone à travers un paysage boréal couvrant plus de 1 million de kilomètres carrés. Les liens entre le paysage terrestre et le CO_2 aquatique ont rarement été étudié à cette échelle, et lorsque ce fut le cas, les mécanismes sous-jacents ainsi que la variabilité associée aux patrons régionaux du climat et du paysage n'ont jamais été aussi explicitement analysés. Cette thèse dresse donc un portrait sans précédent des interactions complexes ayant lieu entre le climat, le paysage terrestre et le fonctionnement des écosystèmes aquatiques boréaux.

D'un côté plus mécanistique, il a aussi été démontré que le COD terrestre a une dégradabilité plus forte que communément assumée dans les eaux continentales. Ce changement de vue peut peut être attribué à l'intégration d'une très large gamme d'écosystèmes aquatiques sur un gradient commun d'influence terrestre, et en particulier, à l'inclusion de rivières et de milieux humides fortement connectés avec le milieu terrestre environnant. Contrairement aux idées généralement acceptées, c'est dans ces milieux qu'on retrouve les plus grandes quantités, et aussi les plus grandes proportions, de COD biologiquement et photochimiquement dégradable, et de façon générale c'est donc dans les milieux les plus colorés qu'on retrouve aussi les plus fortes concentrations et émissions de CO_2. Ces résultats mettent en lumière un rôle souvent négligé de la dégradation du COD comme source majeure de CO_2 dans les rivières, milieux humides, mais aussi dans les lacs fortement connectés à leur bassin versant. De même, ces résultats augmentent l'emphase sur le rôle des rivières et des milieux humides non seulement en tant qu'émetteurs, mais aussi de processeurs carbone d'origine terrestre, lequel rôle était traditionnellement associé aux lacs et aux réservoirs.

Finalement, nous avons décortiqué la complexité inhérente aux différents patrons et mécanismes qui relient le paysage terrestre au CO_2 aquatique, et identifié le COD en tant que variable clé qui intègre l'influence du paysage et exerce un contrôle majeur sur les processus écologiques et biogéochimiques aquatiques. La couleur que le COD donne aux eaux continentales permet donc rapidement d'estimer la force de l'influence terrestre ainsi que l'importance des processus de dégradation de carbone organique résultant en la production et l'émission de CO_2. Si cette thèse seule ne permet pas de clore le débat sur les sources de CO_2 en milieu aquatique, elle y contribue significativement en faisant la démonstration que la dégradation du COD représente une source majeure à l'échelle du paysage, qui s'ajoute aux sources locales associées à la respiration dans les sédiments ou dans les sols avoisinants. Nous avons développé des relations mécanistiques simples, basées sur la couleur de l'eau, qui pourront servir à estimer et à extrapoler le potentiel et les taux de dégradation du COD dans les eaux de surface, de même que les concentrations et les flux de CO_2 pour diverses catégories d'écosystèmes aquatiques à travers le biome boréal au Québec et ailleurs dans le monde. Basés sur ces relations, nous concluons que des pressions environnementales actuelles telles que les changements climatiques et le brunissement des eaux intérieures résultent en un retour accéléré de carbone terrestre vers l'atmosphère, via la portion aquatique du paysage boréal. Des recherches futures seront nécessaires afin de bien quantifier l'impact net de nos résultats en fonction d'autres aspects du cycle du carbone qui peuvent aussi être affectés, peut-être différemment, par les mêmes pressions environnemntales. Néanmoins, les patrons observés ici ont la capacité d'altérer significativement le cycle aquatique du carbone à travers le biome boréal, avec des conséquences potentielles sur le cycle global du carbone.

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