UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES

EN ASSOCIATION AVEC

UNIVERSITÉ DU QUÉBEC À MONTRÉAL

MODÉLISATION ET SIMULATION DE LA DYNAMIQUE DE LA MATIÈRE ORGANIQUE DISSOUTE EN MILIEU FLUVIAL

THÈSE PRÉSENTÉE
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Logic will get you from A to B.
Imagination will take you ***anywhere****.*
– Albert Einstein

AVANT-PROPOS

Les chapitres I, II et II de cette thèse sont présentés sous forme d'articles scientifiques. Je confirme avoir travaillé en tant que premier auteur sur tous les chapitres que contient cette thèse. Les données ayant servi à la réalisation de cette recherche proviennent du professeur Jean-Jacques Frenette.

Le premier chapitre de cette thèse a été accepté dans le journal *Ecological Applications* (***Massicotte, P.***, *Frenette, J.J., 2011. Spatial connectivity in a large river system: resolving the sources and fate of dissolved organic matter. Ecological Applications 21(7) 2600-2617.*)

Le second chapitre (*Hydrodynamic modeling of a fluvial lake: evidences of multi-scale spatial heterogeneity shaped by the complex bed morphology and the tributary network*) est actuellement en cours de révision dans la revue *Journal of Hydrology*.

Le troisième chapitre (*Mechanistic modeling of DOC dynamic: understanding interactions between kinetics processes and mass transport in large river*) est actuellement en cours de révision dans la revue *Ecosystems*.

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RÉSUMÉ

Le réservoir de matière organique dissoute (MOD) dans les écosystèmes aquatiques constitue l'une des plus grandes sources de carbone sur Terre et joue un rôle important dans le cycle biogéochimique du carbone. De plus, la MOD influence considérablement l'écologie des systèmes aquatiques en étant la source principale d'énergie des bactéries hétérotrophes situées à la base de la chaine alimentaire. Le cycle biogéochimique de la MOD dans les grands fleuves est cependant mal connu en raison notamment du caractère dynamique et hétérogène qui caractérise l'hydrologie et la morphologie de tels systèmes. La connectivité spatiale, l'hétérogénéité environnementale et le régime hydrodynamique combinés à un ensemble complexe de processus de production et de transformation du carbone sont les principaux facteurs influençant la dynamique de la MOD.

Cette thèse doctorale, par le biais de la modélisation, propose d'étudier la dynamique de production et de transformation de la MOD dans le fleuve Saint-Laurent (FSL). Les objectifs principaux de cette thèse sont : (I) d'identifier les rôles de l'hétérogénéité environnementale et de la connectivité spatiale dans la dynamique de la MOD d'un système fluvial hétérogène présentant d'importantes discontinuités spatiales, environnementales et hydrodynamiques; (II) d'évaluer l'impact du régime hydrodynamique dans le transport de la MOD au sein du lac Saint-Pierre (lac fluvial du FSL) et (III) de modéliser l'influence de ces discontinuités dans le cycle biogéochimique de la MOD par le développement d'un modèle mécanistique.

Les résultats indiquent que la matière organique dissoute dans les grands fleuves présente un patron spatial fortement influencé par le régime hydrodynamique et le réseau de tributaire à l'origine de la formation de masses d'eau leur conférant des propriétés physiques, chimiques et biologiques distinctes. En accord avec les hypothèses, la connectivité hydrologique observée dans le FSL influence davantage la distribution spatiale de la MOD humique d'origine terrestre que celle de la MOD produite *in situ*. Cela peut être expliqué par le fait que la MOD terrestre est essentiellement introduite dans le FSL par le biais des tributaires qui sont par définition structurés géographiquement. La nature réfractaire de la MOD humique favorise donc son accumulation entre les différentes sections du FSL puisqu'elle est moins utilisée qu'elle n'est produite. D'autre part, la MOD protéinique produite *in situ*, et de nature plus labile, est plus efficacement utilisée par les microorganismes hétérotrophes. Cette MOD est cependant plus rapidement utilisée qu'elle n'est

produite et sa distribution le long du FSL ne présente donc pas de patron d'accumulation particulier.

Pour la première fois, nous présentons un modèle mécanistique portant sur la cinétique du cycle biogéochimique du carbone organique dissous (COD, principal constituant de la MOD) dans un lac fluvial. Ce modèle mécanistique est ensuite couplé à un modèle hydrodynamique de haute résolution spatiale. Les principaux résultats démontrent que le patron spatial des acides humiques est fortement contrôlé par les processus hydrologiques alors que le COD de type protéinique est plus étroitement lié à des processus biologiques tels que la production primaire et la consommation bactérienne.

INTRODUCTION GÉNÉRALE

La matière organique dissoute dans les milieux aquatiques

Le réservoir de matière organique dissoute (MOD) dans les écosystèmes aquatiques est l'une des plus grandes sources de carbone sur Terre et joue un rôle important dans le cycle biogéochimique du carbone (Stedmon 2004, Battin et al. 2009). Plus de 97 % du carbone organique existe sous forme de MOD (Benner 2002) et influence considérablement le fonctionnement des écosystèmes aquatiques, comparable en importance au rôle joué par les nutriments (Prairie 2008).

En plus d'exercer une influence déterminante dans les budgets globaux du carbone, la MOD est également importante à des échelles spatiales réduites de par ses propriétés physiques, chimiques et biologiques. Dans de nombreux systèmes, la MOD joue un rôle de médiateur de la quantité et de la qualité de lumière présente dans la colonne d'eau ce qui entraine des conséquences à la fois positives et négatives sur les organismes aquatiques. Par exemple, la fraction chromophorique de la MOD (CDOM) constitue un écran naturel contre le rayonnement UV pouvant être nuisible pour les organismes aquatiques (Morris and Hargreaves 1997, Zhang et al. 2007, Boily et al. 2011). Inversement, lorsque présente en concentration élevée, la MOD peut limiter la pénétration de la lumière disponible pour la photosynthèse (PAR) et donc influencer la distribution spatiale, la composition taxonomique et la productivité des algues phytoplanctoniques et des macrophytes (Kirk 1994, Wetzel 2001). La MOD est également une source d'énergie et de nutriments pour les bactéries hétérotrophes (Mladenov et al. 2007) et influe sur la composition des communautés microbiennes aquatiques (Findlay and Sinsabaugh 2003, Kritzberg et al. 2006b). L'efficacité avec laquelle les bactéries transforment ce substrat en biomasse dépend de l'origine (source) et l'état diagénétique de la MOD, qui à leur tour déterminent sa composition chimique (Meili 1992, Benner 2003, Hood et al. 2005, Bade et al. 2007, Wickland et al. 2007).

Composition et sources de la MOD

D'un point de vue physique, la matière organique dans les milieux aquatiques est généralement caractérisée en deux fractions selon la taille des molécules qui la compose. Une définition opérationnelle généralement adoptée consiste à départager le dissous (MOD) du particulaire (MOP) à l'aide d'un filtre GF/F (*Glass Fiber Filter*) en fibre de verre variant entre 0.2 et 0.7 µm. Sur le plan chimique, le réservoir de MOD est un ensemble complexe où plus de 1500 composés chimiques ont été identifiés à l'aide de la spectrométrie de masse (Seitzinger et al. 2005) dont seulement 4 à 11 % sont identifiables à l'aide d'analyses moléculaires (Benner 2002). De ce fait, en raison de sa nature complexe et hétérogène, il est actuellement impossible de décrire complètement la structure chimique de chaque composante moléculaire de la MOD dans les milieux aquatiques.

Néanmoins, il est convenu que le réservoir de MOD se compose de deux grands groupes discriminés son leur origine et leur poids moléculaire (Coble et al. 1990, Coble 1996, McKnight et al. 2001, Stedmon 2004). La première classe de MOD est la fraction d'origine terrestre. Cette MOD provient essentiellement de la dissolution de matière organique du sol, de l'érosion, du drainage des zones forestières et agricoles ainsi que des eaux usées. Elle est principalement composée d'acides humiques et fulviques (Harvey et al. 1983, Benner 2002) de poids moléculaire relativement élevé (> 1 kDa, (Stedmon 2004, Duan et al. 2007)). La seconde classe de MOD provient surtout de la production primaire *in situ* par les macrophytes (Demarty and Prairie 2009, Lapierre and Frenette 2009) et le phytoplancton (Romera-Castillo et al. 2010, Pinardi et al. 2011). Cette matière organique est composée principalement d'acides fulviques, de protéines, d'acides aminés et de sucres neutres (Benner 2002) de faible poids moléculaire (< 1 kDa; (Stedmon 2004, Duan et al. 2007)). D'autres processus tels que la lyse virale ou le *sloppy feeding* (libération de composés organiques lors de la rupture des cellules au cours du broutage zooplanctonique) peuvent également être à l'origine de matière organique d'origine aquatique, quoique leurs contributions soient faibles en termes de quantité (Jumars et al. 1989, Gobler et al. 1997, Nagata 2000) en eau douce notamment en raison de la capacité limitée d'ingestion des prédateurs (Nagata 2000). La taille réduite des molécules composant la classe de MOD d'origine aquatique facilite leur assimilation par les bactéries hétérotrophes, car leur métabolisation requiert un effort de transformation enzymatique moindre que pour les composés humiques d'origine terrestre de haut poids moléculaire (Amon and Benner 1996).

Cinétique de la matière organique dissoute

Au sein des écosystèmes aquatiques, le réservoir de matière organique est continuellement altéré par un ensemble de processus qui en modifient les propriétés physiques et chimiques. Dans les systèmes lotiques, la dynamique globale des composés chimiques est dictée par deux classes de processus : la cinétique et le transport (Chapra 1997). En ce qui concerne la MOD, les processus cinétiques importants impliqués dans son cycle biogéochimique comprennent : (I) la production par les organismes photosynthétiques (Descy et al. 2002, Kritzberg et al. 2005, Lapierre and Frenette 2009), (II) la photodégradation (Benner and Ziegler 1999, Amado et al. 2006, Zhang et al. 2009), (III) la production et la respiration microbienne (Cole et al. 2006, Kritzberg et al. 2006b, Berggren et al. 2010) et (IV) la sédimentation et la floculation (Sholkovitz 1976, von Wachenfeldt and Tranvik 2008).

Production primaire

Les producteurs primaires (phytoplancton, macrophytes) libèrent via divers processus, tels que l'excrétion et l'exsudation, des quantités importantes de MOD dans les écosystèmes d'eau douce (Demarty and Prairie 2009). La MOD ainsi libérée peut représenter jusqu'à près de 50 % de la production primaire totale (Nagata 2000, Christian and Anderson 2002), pouvant cependant varier d'un écosystème à l'autre (Connolly et al. 1992). La sénescence des organismes photosynthétiques (principalement les macrophytes) est également une autre source de production importante de MOD (Lapierre and Frenette 2009).

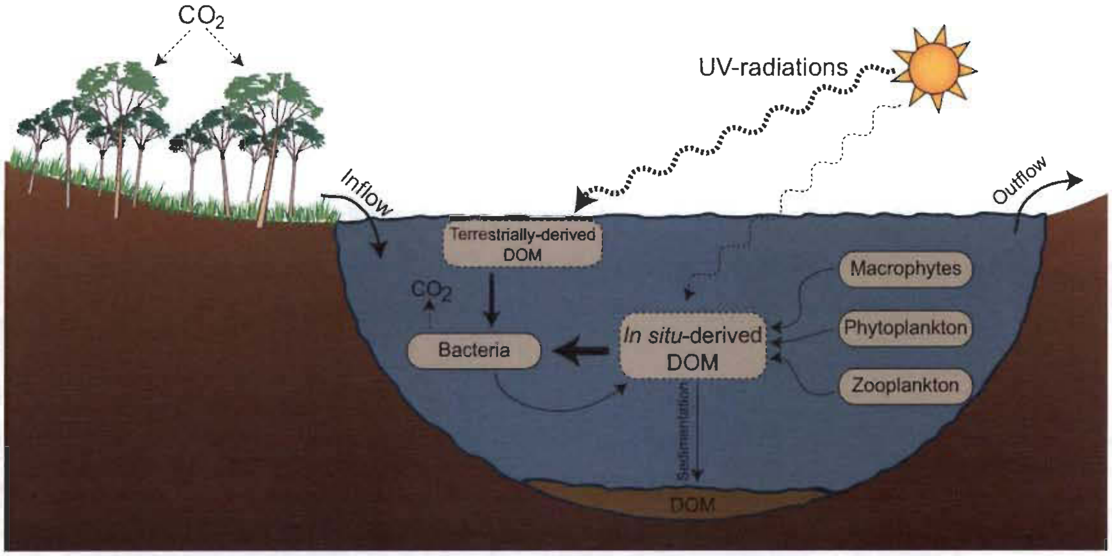

Figure 1 : Schématisation du cycle biogéochimique de la matière organique dissoute (MOD) dans les écosystèmes aquatiques. La taille du trait des flèches indique l'importance relative des flux entre les divers compartiments.

Métabolisme bactérien

Les bactéries sont un médiateur important de la qualité et de la quantité de la MOD dans les systèmes aquatiques. En fonction de la qualité du substrat, les bactéries assimilent plus ou moins efficacement la MOD. Ainsi, l'assimilation bactérienne de composés de haut poids moléculaire implique un coût énergétique important de par la mobilisation des processus enzymatiques requis, ce qui se traduit par une importante respiration bactérienne et une faible efficacité de croissance bactérienne (BGE). Inversement, lorsque le réservoir de MOD est composé de molécules facilement assimilables (acides aminées, molécules de faible poids moléculaire) les bactéries utilisent plus efficacement le substrat pour la production favorisant ainsi une BGE plus élevée. Des études récentes en laboratoire démontrent d'ailleurs clairement des taux de consommation beaucoup plus élevés de la matière de type protéinique issue de la production primaire *in situ* en comparaison avec la matière humique d'origine terrestre (Cole et al. 1988, Reche et al. 1996, Carrillo et al. 2002).

Photodégradation

La photodégradation de la MOD est le processus par lequel le rayonnement solaire (particulièrement les UVA et UVB) altère la structure physique et chimique ainsi que les propriétés optiques des substances humiques (Bertilsson and Tranvik 2000). Malgré le nombre grandissant d'études portant spécifiquement sur la photodégradation de la MOD, il n'existe aucun consensus quant aux répercussions biologiques de ce mécanisme notamment sur le métabolisme bactérien (Tableau 1 dans Benner and Ziegler (1999)). L'un des effets reconnus de la photodegradation de la MOD sur les communautés subaquatiques est l'accroissement de la production bactérienne (Bano et al. 1998, Anesio et al. 2005, Amado et al. 2006). Il a ainsi été démontré que suite à une exposition au rayonnement UV, les molécules de grand poids moléculaire, constituant majoritaire de la MOD d'origine terrestre, sont scindées en molécules de plus petites tailles favorisant ainsi leur assimilation par les bactéries et stimulant la BGE (Anesio et al. 2005). D'autres études ont cependant rapporté une diminution de la BGE suivant l'exposition de la MOD au rayonnement UV (Tranvik and Bertilsson 2001, Smith and Benner 2005).

Problématiques et mise en contexte

Simultanément, les processus précédemment décrits déterminent la qualité et la quantité du réservoir de MOD transitant dans les systèmes aquatiques (Fig. 1). De plus, en réponse à la structure chimique de la MOD, les processus de production et de transformation n'ont pas la même influence sur chacune des classes de MOD. Par exemple, la nature fortement aromatique de la MOD de type humique favorise l'absorbance des rayons UV ce qui induit une photodégradation plus efficace que sur les composés faiblement aromatiques tels que ceux issus des organismes photosynthétiques (Mostofa et al. 2007). Ces processus sont donc intimement liés aux conditions environnementales présentes dans l'écosystème qui déterminent l'ampleur de chaque mécanisme sur le cycle biogéochimique du réservoir de MOD. En revanche, les processus hydrodynamiques déterminent le temps de séjour de cette matière dans les écosystèmes aquatiques et donc le temps d'opération des différents processus cinétiques sur la MOD.

Compte tenu du rôle important de la MOD dans les écosystèmes aquatiques, l'étude de la matière organique dissoute (ou du carbone organique dissous (COD) constituant principal de la MOD) a connu un intérêt quasi exponentiel (essentiellement en milieux marins) durant les dernières décennies, tel qu'illustré à la Fig. 1 par Prairie (2008). Si la dynamique de la MOD est très étudiée en milieux lacustre et océanique, il en est tout autre dans les systèmes fluviaux. Cela est particulièrement vrai pour les grands fleuves qui sont pourtant connus pour véhiculer des quantités importantes de matière organique terrestre dans les océans

(0.4×10^{15} gC an^{-1}) (Hedges et al. 1997) et être des sources considérables de substrat labile de type protéinique (Bianchi et al. 2004, Duan et al. 2007). Bien que les grands fleuves aient été longtemps considérés comme de simples vecteurs de matière organique vers les océans, les quantités et la diversité de la MOD qui y transigent suggèrent toutefois qu'ils jouent un rôle prédominant sur le cycle biogéochimique de la MOD. Ainsi, nous pouvons présumer que toute modification, à quelque échelle spatiale ou temporelle que ce soit, affectant le réservoir de COD est susceptible d'avoir un impact important sur les flux de carbone au sein de l'écosystème aquatique (c.-à-d. la balance entre la production primaire et la respiration hétérotrophe). Cette hypothèse s'intègre à une littérature croissante qui tend à démontrer que les fleuves et les grandes rivières sont de moins en moins considérés comme de simples vecteurs de transport, mais plutôt comme des acteurs importants dans le cycle biogéochimique de la MOD (Findlay 2005, Cole et al. 2007, del Giorgio and Pace 2008, Spencer et al. 2009). Cependant, nos connaissances de la dynamique et du rôle biogéochimique de la MOD dans les écosystèmes d'eau douce sont faibles (Fellman et al. 2010). Par conséquent, comprendre comment la MOD est produite, transformée et transite dans ces systèmes est d'une importance capitale pour les biologistes et les écologistes (Cole et al. 2007).

Tel que discuté dans les paragraphes précédents, le cycle biogéochimique de la matière organique dissoute dans les écosystèmes aquatiques forme un système complexe où les différents processus de production et de transformation opèrent simultanément. De plus, les discontinuités environnementales dans les écosystèmes fluviaux engendrées par les masses d'eau provenant d'un bassin versant hétérogène influencent spatialement l'amplitude avec laquelle chacun des processus opère dans le cycle biogéochimique global de la MOD. Par ailleurs, la complexité bathymétrique des grands fleuves, combiné à un important réseau de tributaires, contribue à créer un régime hydrodynamique hétérogène. Cette situation est à l'origine de discontinuités hydrauliques et favorise la formation de masses d'eau distinctes en termes caractéristiques physiques et chimiques (Frenette et al. 2003, Frenette et al. 2006) et de temps de résidence. Ultimement, ce contexte hydrodynamique particulier détermine la durée d'action des différents processus de production et de transformation impliqués dans la dynamique de la MOD lors de son transit dans les systèmes fluviaux vers les océans. Le régime hydrodynamique de ces systèmes détermine également le degré de connectivité entre les habitats. Cette connectivité asymétrique détermine donc ultimement l'ampleur des échanges longitudinaux (amont-aval) et latéraux (terrestre-aquatique) qui ont lieu dans les systèmes où l'hydrologie est à la base de la distribution spatiale de la matière.

À cet égard, le fleuve Saint-Laurent (FSL) et son principal lac fluvial, le lac Saint-Pierre (LSP), sont des modèles appropriés (c.-à-d. des systèmes représentatifs des grands fleuves) pour étudier la dynamique de la matière organique dissoute (Fig. 1). Le FSL est le second plus grand fleuve en termes de débit de l'Amérique du Nord (Allan and Castillo 2007). Parmi les 167 plus grands fleuves du monde, le FSL se situe au 19e et 20^{e} rang respectivement en termes d'aire de drainage et de débit[1]. Le FSL forme un système complexe composé d'une mosaïque hétérogène de zones hydrogéomorphologiques (succession de tronçons et lacs fluviaux) avec une forte connectivité longitudinale et latérale dont les structures physiographiques changent dans le temps et dans l'espace (Morin et al. 2003). Un total de 21 tributaires (débit > 7 m^{3} s^{-1}) s'écoulent à travers un bassin versant de 1 600 000 km^{2}, où l'utilisation des terres est dominée par un haut degré d'urbanisation à proximité de Montréal tandis que l'agriculture, des pâturages, des forêts et des zones humides constituent les habitats de la section avale (Frenette et al. 2006, Vis et al. 2007). Ce réseau complexe de tributaires conduits à la formation de plusieurs masses d'eau s'écoulant parallèlement (souvent sur de longues distances) avec des propriétés physiques et biogéochimiques distinctes (Frenette et al. 2012). Cette hétérogénéité est

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[1] *http://en.wikipedia.org/wiki/List_of_rivers_by_length*

susceptible d'affecter les propriétés biogéochimiques de la MOD ainsi que l'ampleur des processus impliqués dans son cycle de vie en créant des discontinuités hydrodynamiques et environnementales entre les différents habitats, qui ultimement, influencent la quantité et la qualité de la MOD qui transite vers l'océan.

L'échantillonnage pour ce projet a été réalisé entre le 8 et le 15 août 2006 sur le navire de recherche le *Lampsilis* (Fig. 2). Plus précisément, le plan échantillonnage a permis de suivre le déplacement des masses d'eau du LSP depuis leur source à la sortie des Grands Lacs près de Cornwall jusqu'à leur mélange avec l'eau salée de l'océan Atlantique dans la zone de transition estuarienne près de l'Isle-aux-Coudres (≈ 450 km). L'envergure de l'étendue du plan d'échantillonnage est certainement un des caractères uniques de ce projet de recherche qui au meilleur de nos connaissances n'a jamais été reproduit dans aucun autre grand fleuve au niveau de l'étude de la MOD et du COD.

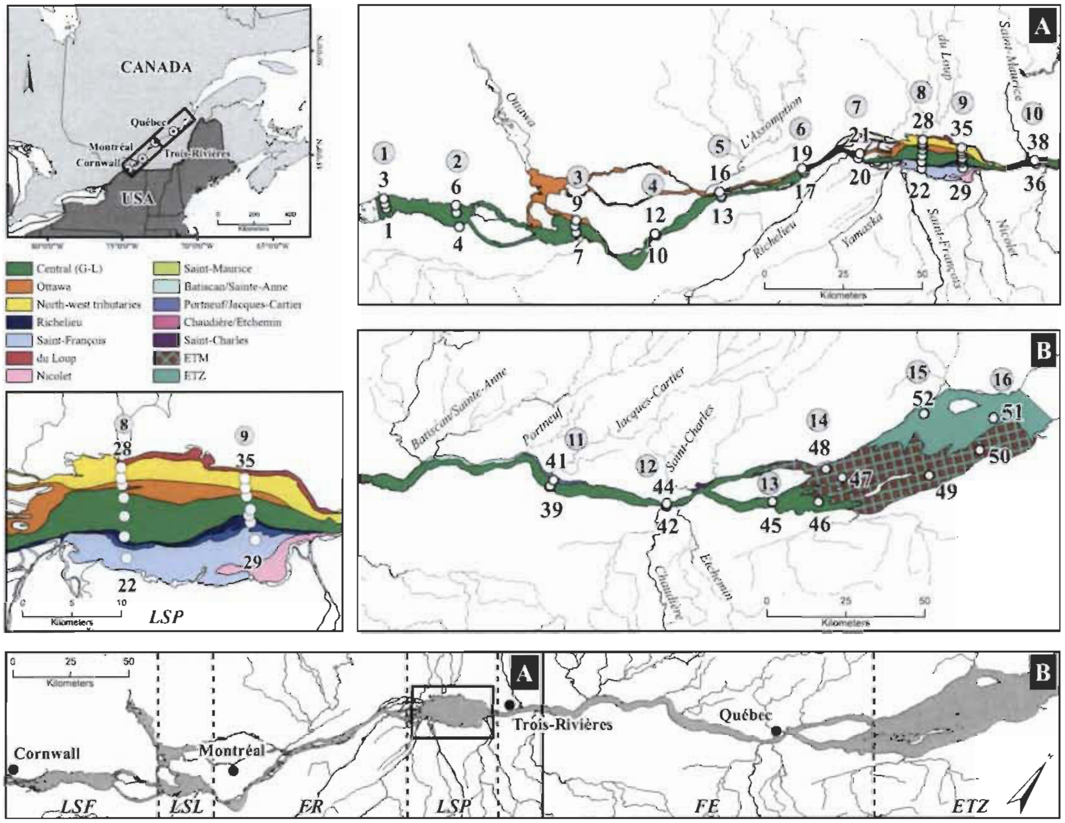

Figure 2 : Plan d'échantillonnage réalisé pour la période du 8 au 15 août 2006 et distribution des masses d'eau dans le fleuve Saint-Laurent (FSL). Vingt-trois (23) tributaires se déversent continuellement dans les différentes zones du FSL sur une distance de 450 km. LSF = lac Saint-François, LSL = lac Saint-Louis, FR = tronçon fluvial, LSP = lac Saint-Pierre, FE = estuaire fluvial, ETZ = zone de transition estuarienne (mélange d'eau douce et d'eau salée). Les masses d'eau générées par les tributaires drainent un bassin versant très hétérogène. Les habitats ainsi créés présentent de fortes variations physiques et chimiques susceptibles d'influencer localement la production et la transformation de la MOD et du COD. Les chiffres dans les cercles représentent les radiales (1 à 16) tandis que les autres chiffres correspondent aux stations d'échantillonnage. Figure tirée de Frenette et al. (2012).

De récents développements dans les domaines de la statistique et de la spectrométrie permettent maintenant de mieux caractériser le réservoir de MOD (Bro 1997, McKnight et al. 2001, Stedmon et al. 2003, Bertolosh and Pepinosh 2011).

Combinées à des analyses de décomposition spectrale, les propriétés optiques (absorbance et fluorescence; largement déterminées par les caractéristiques chimiques) de la MOD peuvent être facilement utilisées comme traceurs pour caractériser les changements quantitatifs et qualitatifs du réservoir de MOD (Stedmon and Markager 2005b) lors de sa transition dans le système aquatique. Ceci offre des perspectives intéressantes notamment pour étudier les effets de la MOD dans les systèmes fluviaux (tel que le FSL et le LSP) et comment ceux-ci contribuent au cycle biogéochimique de cette matière. En ce sens, plusieurs études empiriques ont permis de mettre en évidence divers acteurs impliqués dans la dynamique de la MOD. Cependant, l'hétérogénéité des systèmes fluviaux, combinée à la nature complexe de la dynamique de la MOD, fait en sorte qu'il est actuellement difficile de saisir toutes les subtilités relatives au cycle biogéochimique de la MOD en milieu fluvial. Afin de décortiquer cette boîte noire qu'est la MOD, de plus en plus d'efforts sont et doivent être mis en œuvre afin d'aborder la dynamique globale de la MOD en petits compartiments (Fellman et al. 2010). D'ailleurs, cette réalité a même été comparée à la version scientifique de *Humpty Dumpty* (Prairie 2008) dont les morceaux n'ont pu être recollés après être tombés de son muret. Ainsi, bien que toutes les informations acquises sur ces compartiments constituent d'importantes connaissances en soi, il est maintenant nécessaire qu'elles soient testées au niveau des écosystèmes, où leurs véritables contributions au cycle global de la MOD pourront être légitimement évaluées (Prairie 2008).

Les études qui intègrent ces aspects d'hétérogénéité environnementale et de discontinuités hydrodynamiques dans les écosystèmes fluviaux et des conséquences au niveau de la dynamique de la MOD sont au meilleur de nos connaissances inexistantes. Dès lors, des études portant sur le cycle biogéochimique de la MOD orientées sur les processus écosystémiques sont nécessaires dans les grands fleuves pour bien comprendre leur rôle dans la budgétisation globale de la MOD. Dans ce contexte, de nouvelles approches doivent être utilisées pour bien saisir la portée des interactions liées à la dynamique de la MOD. Parmi celles-ci, la modélisation numérique offre une perspective intéressante puisqu'elle permet d'étudier la MOD en termes de processus et de mécanismes à la base de sa dynamique. De ce contexte particulier émergent certaines questions. Par exemple, (I) quels sont les effets de la connectivité hydrologique sur les patrons spatiaux de la MOD, (II) selon certains scénarios environnementaux bien précis, quels sont les impacts à court et moyen termes sur la distribution spatiale de la MOD et (III) quelle est la contribution de chacune des masses d'eau dans la budgétisation de la MOD dans le LSP?

Objectifs de la thèse

Puisque la dynamique de la matière organique dissoute joue un rôle prépondérant dans les grands écosystèmes fluviaux et que sa dynamique est mal connue, les objectifs principaux de cette thèse sont : (I) d'identifier les rôles de l'hétérogénéité environnementale et de la connectivité spatiale sur la dynamique de la MOD dans un système fluvial hétérogène caractérisé par d'importantes discontinuités spatiales, environnementales et hydrodynamiques; (II) d'évaluer le rôle du régime hydrodynamique sur le transport de la MOD dans le LSP et (III) de déterminer l'influence de ces discontinuités en développant un modèle mécanistique intégrant les processus-clés impliqués dans le cycle biogéochimique de la MOD. Spécifiquement, chacun de ces trois objectifs a fait l'objet d'un chapitre de cette thèse doctorale.

L'objectif général du chapitre I vise à déterminer comment l'hétérogénéité environnementale et la connectivité spatiale influencent le cycle biogéochimique de la MOD dans le fleuve Saint-Laurent. Dans ce contexte, les objectifs spécifiques de cette étude sont : 1) de caractériser le réservoir de MOD dans le FSL à l'aide de la spectrométrie et de techniques de décomposition spectrale, 2) d'étudier comment la connectivité spatiale entre les sites d'échantillonnage influence la distribution des différentes formes de MOD au sein des masses d'eau du FSL et 3) de donner un aperçu sur les principaux facteurs de régulation impliqués dans le cycle biogéochimique des deux grandes classes de MOD dans un système fluvial hétérogène.

L'objectif global du chapitre II consiste à étudier comment la bathymétrie atypique qui caractérise les lacs fluviaux tels que LSP conditionne le déplacement des masses d'eau et donc le déplacement des particules passives tel que la MOD. Pour apporter un meilleur aperçu sur la dynamique des flux de carbone qui prévaut dans ces systèmes complexes et hétérogènes, nous avons développé un modèle hydrodynamique de haute résolution spatiale pour le LSP lequel a été étalonné avec des vitesses de courants mesurées en utilisant un courantomètre à effet Doppler (*Acoustic Doppler Current Profiler* ou ADCP). Dans ce contexte, les objectifs spécifiques de cette étude sont de : (1) développer un modèle hydrodynamique de haute résolution spatiale pour le LSP en y intégrant la géomorphologie complexe et le réseau de tributaires et (2) mettre en évidence l'importance de la structure fluviale sur le temps de transition des masses d'eau dans un environnement hétérogène. Les résultats peuvent ainsi être généralisés à d'autres grands lacs fluviaux afin de déterminer leur régime hydrodynamique à petite échelle spatiale.

L'objectif global du chapitre III est de modéliser explicitement la dynamique du COD dans les grands systèmes fluviaux qui sont habituellement considérés comme de simples vecteurs de transport du carbone et de mettre en évidence le rôle précis de chacun des mécanismes impliqués dans le cycle biogéochimique du COD. Dans ce contexte, les objectifs de ce chapitre sont : (1) de développer un modèle mécanistique suivant une approche de réacteurs parfaitement mélangés successivement liés « *feed-forward system* » afin de comprendre le rôle et l'amplitude des différents processus en utilisant un modèle basé sur les deux principales classes de COD dans le LSP, (2) de déterminer le rôle du régime hydrodynamique en terme de temps de séjour sur le cycle biogéochimique du COD, et ce, dans un système aquatique présentant de fortes discontinuités hydrodynamiques.

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CHAPITRE I

SPATIAL CONNECTIVITY IN A LARGE RIVER SYSTEM: RESOLVING THE SOURCES AND FATE OF DISSOLVED ORGANIC MATTER

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Résumé

Les grands fleuves sont généralement des systèmes hétérogènes et productifs recevant d'importants apports de matière organique dissoute (MOD) en provenance des milieux terrestres et aquatiques. Ces apports sont susceptibles de jouer un rôle important dans le cycle biogéochimique de la MOD transitant vers les océans. Le gradient spatial asymétrique déterminé par le régime hydrodynamique et l'hétérogénéité environnementale contribuent au cycle biogéochimique de la MOD s'écoulant vers l'aval. Cependant, les effets relatifs de la connectivité spatiale et de l'hétérogénéité environnementale sur le cycle biogéochimique de la MOD sont encore mal compris. Par exemple, puisque les variables environnementales reflètent l'hétérogénéité spatiale, la variation expliquée par les variables environnementales et spatiales peut être redondante. Nous avons utilisé le fleuve Saint-Laurent (FSL) en tant que système représentatif des grands fleuves du monde, pour résoudre les influences relatives de l'hétérogénéité environnementale et de la connectivité spatiale sur la dynamique de la MOD. Des matrices tridimensionnelles de fluorescence combinées à l'analyse parallèle des facteurs (PARAFAC) ont été utilisées pour caractériser le réservoir de MOD dans le FSL. Sept fluorophores ont été modélisés, dont deux qui ont été identifiés comme étant d'origine terrestre et trois d'origine algale. Nous avons mesuré un ensemble de variables environnementales connues pour intervenir dans le cycle biogéochimique de la MOD. De plus, l'analyse asymétrique des vecteurs propres (AEM) a permis de prendre en compte la connectivité spatiale du système. La combinaison des modèles spatiaux et environnementaux a permis d'expliquer 85 % de la variation de la MOD. La connectivité spatiale s'est avérée être un moteur important de la dynamique de la MOD, puisqu'une fraction importante de l'hétérogénéité environnementale était attribuable au gradient asymétrique spatial. Le long de l'axe longitudinal, nous avons noté une augmentation rapide du carbone organique dissous (COD), principalement contrôlée par les apports terrestres de MOD en provenance des affluents. Le partitionnement de variation a démontré que la MOD de type protéinique fraîchement produite était le substrat préférentiel pour les bactéries hétérotrophes en croissance rapide, tandis que l'abondance de MOD de type humique était plus corrélée au coefficient d'atténuation des rayons UVA.

Mots-clés : Modélisation asymétrique des vecteurs propres, bactéries, CDOM, connectivité, EEM, fluorescence, fleuve, PARAFAC, analyse parallèle des facteurs, tributaires.

Abstract

Large rivers are generally heterogeneous and productive systems that receive important inputs of dissolved organic matter (DOM) from terrestrial and in situ sources. They are thus likely to play a significant role in the biogeochemical cycling of the DOM flowing to the oceans. The asymmetric spatial gradient driven by directional flow and environmental heterogeneity contributes to the fate of DOM flowing downstream. Yet, the relative effects of spatial connectivity and environmental heterogeneity on DOM dynamics are poorly understood. For example, since environmental variables show spatial heterogeneity, the variation explained by environmental and spatial variables may be redundant. We used the St. Lawrence River (SLR) as a representative large river to resolve the unique influences of environmental heterogeneity and spatial connectivity on DOM dynamics. We used three-dimensional fluorescence matrices combined with parallel factor analysis (PARAFAC) to characterize the DOM pool in the SLR. Seven fluorophores were modeled, of which two were identified to be of terrestrial origin and three from algal exudates. We measured a set of environmental variables that are known to drive the fate of DOM in aquatic systems. Additionally, we used asymmetric eigenvector map (AEM) modeling to take spatial connectivity into account. The combination of spatial and environmental models explained 85% of the DOM variation. We show that spatial connectivity is an important driver of DOM dynamics, as a large fraction of environmental heterogeneity was attributable to the asymmetric spatial gradient. Along the longitudinal axis, we noted a rapid increase in dissolved organic carbon (DOC), mostly controlled by terrestrial input of DOM originating from the tributaries. Variance partitioning demonstrated that freshly produced protein-like DOM was found to be the preferential substrate for heterotrophic bacteria undergoing rapid proliferation, while humic-like DOM was more correlated to the diffuse attenuation coefficient of UVA radiation.

Key words: Asymmetric Eigenvector Map modeling; bacteria; CDOM; connectivity; EEM; fluorescence; large river; PARAFAC; parallel factor analysis; tributaries.

Introduction

Dissolved organic matter (DOM) plays important roles in aquatic ecosystems. For example, the chromophoric fraction of the DOM (CDOM) constitutes a natural screen protecting aquatic organisms against UV radiation (Morris and Hargreaves 1997, Zhang et al. 2007). DOM is also the main source of metabolic substrates for heterotrophic bacteria and influences the composition of aquatic microbial communities (Findlay and Sinsabaugh 2003, Kritzberg et al. 2006b). The efficiency with which bacteria transform this substrate into biomass depends on the source of the DOM, which in turn determines the chemical composition of the DOM.

In aquatic ecosystems, the DOM pool can be derived from terrestrial sources external to the aquatic system and from sources within the aquatic system (Hood et al. 2005). Protein-like material is generally considered the labile fraction, since its low molecular weight (<1 kDa) allows effective uptake by heterotrophic bacteria (Stedmon 2004, Berggren et al. 2010). Protein-like DOM originates essentially from extracellular release by photosynthetic organisms such as macrophytes and phytoplankton within the water body (Findlay and Sinsabaugh 2003). Humic-like material is usually the fraction derived from the terrestrial ecosystem and introduced in the aquatic environment by advective transport of surface and ground waters (Findlay and Sinsabaugh 2003). Terrestrial DOM is primarily composed of humic and fulvic acids of high molecular weight (>1 kDa), thought to be more resistant to bacterial degradation due to the cleavage effort needed to separate molecules into smaller fractions (Amon and Benner 1996).

It has been shown that bacterial activity is correlated with bacterial production and chlorophyll *a* (Chl *a*) (Kritzberg et al. 2005, Bouvier et al. 2007, Stenuite et al. 2009), presumably in response to the quality of the substrate fulfilling the bacterial demand. Conversely, consumption of dissolved humic-like substances, which in many streams and lakes are derived from the surrounding terrestrial ecosystems (Cole et al. 2006), is mostly channeled through microbial respiration (Farjalla et al. 2009). Thus the composition of DOM is likely to influence the metabolic activity of aquatic ecosystems (i.e. the balance between primary production and heterotrophic respiration), since it directly affects the rate at which the whole ecosystem processes carbon and, consequently, the carbon transfer at higher trophic levels (Grey et al. 2001, Daniel et al. 2005, Jansson et al. 2007).

In addition to bacterial degradation, the chemical properties of both fractions of DOM are continually altered by abiotic processes such as photomineralization (Stedmon et al. 2007, Spencer et al. 2009, Zhang et al. 2009), sedimentation and flocculation (von Wachenfeldt and Tranvik 2008). Therefore, the magnitude at which these mechanisms operate will depend upon the environmental conditions present in the aquatic ecosystem and the composition of the DOM bulk.

Many studies focusing on DOM dynamics have been carried out in marine environments (Coble 1996, Stedmon et al. 2003, Murphy et al. 2008), lakes (Cole et al. 2006, Kritzberg et al. 2006a, Ask et al. 2009) and small rivers (Hood et al. 2005). Despite increasing interest (Lapierre and Frenette 2009, Spencer et al. 2009, Yamashita et al. 2010), little is known about DOM biogeochemical cycling in large river systems, which have been viewed for decades as simple vectors transporting the DOM from inland waters to the oceans. However, on a temporal and spatial scale, several studies have highlighted the importance of large rivers as active contributors to the composition, transformation and processing of DOM and to its subsequent lability and reactivity (Bianchi et al. 2004, Frenette et al. 2006, Duan et al. 2007, Spencer et al. 2009, Yamashita et al. 2010). However, these studies mostly focused on a few processes, which did not allow simultaneous consideration of most of the known processes of gains and losses involved in DOM dynamics. Additionally, only a few studies (e.g. Duan et al. 2007) have investigated the role of large rivers on a large spatial scale.

The metabolic responses of lakes and streams are a common metric used to integrate the impact of environmental change across a broad range of landscapes. Because large rivers are at the lowest points in the landscape, they represent the most integrative signal of environmental changes such as nutrient or organic carbon cycling (Williamson et al. 2008). A general characteristic of large rivers is that they are dominated by areas of intensive agriculture, which have been reported to have important implications for global carbon cycling (Wilson and Xenopoulos 2009) and whole-lake metabolism, which is directly influenced by the relative balance of external loading of nutrients and dissolved organic carbon (Hanson et al. 2003). As a consequence of their large catchment size, large rivers are known to convey substantial amounts (0.4 Gt C yr^{-1}) of terrestrial organic matter to the oceans (Hedges et al. 1997) and can also be important sources of protein-like material (Bianchi et al. 2004, Duan et al. 2007). Therefore, we can hypothesize that transformations in terms of quality or quantity of even a small fraction of any of those pools can have significant impacts on the metabolic balance of river ecosystems. Additionally, large rivers are generally characterized by high numbers of tributaries, often with heterogeneous biophysical characteristics that are connected at different spatial scales. Yet, due to the lack of appropriate statistical methods and global studies of large river ecosystems, there are currently gaps in the understanding of spatial connectivity among contrasting environments and the consequent impacts on DOM processing, beginning at the source and continuing down the river to the marine intrusion.

In this regard, the St. Lawrence River (SLR) is an appropriate model (i.e. a representative large river system) to resolve the sources and fate of DOM in such integrated systems. The SLR is the second-largest river (in term of discharge) in

North America (Allan and Castillo 2007). Based on the 167 largest world rivers, the SLR is 19th and 20th, respectively, in terms of drainage area and average discharge rate (World Resources Institute: http://www.wri.org). The SLR forms a complex system composed of a mosaic of heterogeneous hydrogeomorphic zones with strong longitudinal and lateral connectivity. A total of 21 tributaries (discharge rates > $7\ m^3\ s^{-1}$) flow through a watershed covering $1\ 600\ 000\ km^2$, where land use is dominated by a high degree of urbanization near Montreal and areas of agriculture, pastures, forests and wetlands in the mid and lower reaches of the stream system (Frenette et al. 2006, Vis et al. 2007). This leads to the formation of several parallel water masses with distinct physical and biogeochemical properties. This hydrological heterogeneity is likely to affect the biogeochemical properties of DOM as well as the magnitude of the processes involved in DOM biogeochemical cycling. This will ultimately influence the quantity and quality of DOM flowing downstream.

More and more effort is currently being devoted to breaking down the various influences on DOC and studying them in isolation, while combining information acquired about those compartments could lead to a substantial gain in knowledge about global biogeochemical cycling of DOC (Prairie 2008). So it is now necessary to study DOM dynamics at an ecosystem level to identify how environmental heterogeneity and spatial connectivity are influencing DOM processing in a large river system from its source to its discharge in the estuary.

Traditionally, absorbance of CDOM (*a*CDOM) has been used as a qualitative tracer of DOM in diverse aquatic environments. However, this approach is best suited for colored DOM associated with terrestrial sources, and is likely to underestimate protein-like DOM, which is less colored (Meili 1992). Recently, developments in fluorescence measurements have allowed rapid and more detailed characterization of fluorescent DOM (FDOM) (Fellman et al. 2010) as a proxy that covaries closely with total DOM. Moreover, 3D excitation-emission fluorescence matrices (EEM) combined with parallel factor analysis (PARAFAC) have been used to trace the quantitative and qualitative changes of the DOM pool (Stedmon et al. 2003). Briefly, the technique allows the decomposition of complex fluorescence signals into a set of trilinear terms and a residual array (Bro 1997). Furthermore, the fluorescence signals are decomposed into the different underlying groups of fluorophores present and thereafter can be used to trace the dynamics of these groups in natural environments in terms of quantity and quality. Additionally, improvements in statistical methods for spatial analysis have been made to help to understand how the asymmetric environmental gradients, such as those found in large rivers, influence the distribution of response variables. We further used the asymmetric eigenvector map (AEM) analysis (Blanchet et al. 2008b) to assess the impact of spatial connectivity on the dynamics of DOM. This approach provides a framework to formally describe the longitudinal and lateral connectivity observed in the SLR.

Since little is known about the composition and fate of DOM in large heterogeneous fluvial systems, it is of interest to investigate how environmental heterogeneity and spatial connectivity are influencing DOM processing in the SLR. In that context, the main objectives of this study were: 1) to characterize the DOM pool from the SLR, 2) to investigate how spatial connectivity among sampling sites influences the distribution of the various forms of DOM within the SLR water masses and 3) to provide insights on the key factors regulating DOM biogeochemical cycling in a complex fluvial system.

Materials and methods

Study site: the St. Lawrence River

The St. Lawrence River (SLR) is one of the largest rivers of North America and forms a complex hydrographical system connecting Lake Ontario to the Atlantic Ocean. The main tributaries of the SLR form several water masses, each with its own distinct physical and chemical characteristics, which flow side by side, sometimes for long distances, before mixing. Water residence time, abundance of submerged plants (macrophytes), underwater light characteristics, mean water column depth and concentration of DOC contribute to increasing the contrast between the green water from Lake Ontario, which flows rapidly into the main channel, and water from the tributaries, which flows slowly along the shore (Martin et al. 2005, Frenette et al. 2006). Additionally, the hydrological regime of the SLR plays a central role in its functioning, especially in terms of the relative importance of humic-like and protein-like DOM production. For example, within fluvial Lake St. Pierre, springtime flooding increases lake surface area by more than 40%, representing an additional 100 km^2 of floodplain and thereby greatly increasing the aquatic/terrestrial contact zone (Vincent and Dodson 1999). Between Cornwall and Quebec City, the mean discharge rises from 7 543 $m^3 s^{-1}$ to 12 309 $m^3 s^{-1}$.

Sampling cruise

Sampling was carried out aboard the RV *Lampsilis* from the Université du Québec à Trois-Rivières from August 8th to August 15th of 2006. A total of 44 samples distributed along 13 transects were collected from Cornwall to the estuarine transition zone along a 375 km transect (Fig. 1). Transects were positioned perpendicularly to the main east-to-west axis of the SLR. Locations of stations within each transect were determined in order to study the lateral heterogeneity of the SLR's water masses. Water samples were collected using an 8 L GO-FLO water sampler

(Model 1080; General Oceanics) at 0.5 m below the surface. Temperature vertical profiles were obtained using a multiprobe depth profiler (6600 EDS-M, Yellow Spring Instruments).

Chlorophyll a (Chl a)

Duplicate subsamples of water were filtrated on 25 mm diameter, 0.7 µm pore size GFF filters (Millipore) immediately after collection and kept frozen until analysis. Filters were sonicated in cold 90% acetone and extraction continued for 24 hours in the dark at 4°C. After centrifugation, concentrations of Chl *a* were measured on a Turner Designs fluorometer (model 10-005R) before and after acidification (Parsons et al. 1984).

Phosphorus analyses

Samples for soluble reactive phosphorus (SRP) were filtrated on 45 mm diameter, 0.7 µm pore size GFF filters (Millipore) and kept frozen until analysis. SRP was analyzed using the acid molybdate technique (APHA 1998).

DOC measurements

As a quantitative measure of the total DOM, dissolved organic carbon (DOC) was measured as follows. At each sampling site, 200 mL of water was filtered through a 45 mm diameter, 0.2 µm nominal poresize polycarbonate membrane (Isopore, Millipore). Membranes were prerinsed with 100 mL of MilliQ water to remove potential impurities. The filtrate was stored in acid-washed borosilicate bottles and kept in the dark at 4°C until analysis. DOC concentrations were determined with a total organic carbon analyzer (OI Analytical, TOC-1010) by sodium persulfate digestion.

aCDOM measurements

CDOM absorbance was measured with a Shimadzu UV-2401PC UV–Vis spectrophotometer using a 1 cm quartz cell between 190 and 900 nm. Absorption coefficients were then calculated according to equation 1 (Kirk 1994).

$$a(\lambda)=\frac{2.303A(\lambda)}{L} \tag{1}$$

Where $a(\lambda)$ is the absorption coefficient (m^{-1}) at wavelength λ, A the absorbance measured at wavelength λ and L the path length of the optical cell in meters (0.01m). To ensure that absorbance was following a continuous inverse exponential distribution, absorption spectra were modeled according to equation 2.

$$a_{(\lambda)} = a_{(\lambda 0)} e^{-S\left(a_{(\lambda_0)}-a_{(\lambda)}\right)} + K \tag{2}$$

Where $a_{(\lambda 0)}$ and $a_{(\lambda)}$ are the absorption coefficients (m^{-1}) at reference wavelength $\lambda = 375$ nm and at defined wavelength $\lambda 0$ respectively, K a background scattering constant and S the spectral slope that describes the approximate exponential decline in absorption with increasing wavelength. Samples that were poorly fitted by the non-linear regression ($R^2 < 0.90$) or where the spectral slope was too high ($S > 0.03$ nm^{-1}, (Siegel et al. 2002)) were removed from subsequent analysis.

It has been reported that humic substances are characterized as being yellow to dark in color (Aiken et al. 1985, McKnight and Aiken 1998), so terrestrial DOC concentrations were estimated by calculating the DOC/*a*CDOM$_{(340)}$ ratio, which is an indicator of the color intensity of the measured DOC. The DOC/*a*CDOM$_{(340)}$ ratio is similar to the well-known specific ultraviolet absorbance (SUAV) which has been reported to be a good indicator of the aromaticity and biodegradability of DOC

(Weishaar et al. 2003, Bade et al. 2007, Fellman et al. 2008). Moreover, terrestrial DOC concentrations (mgC L^{-1}) were calculated as follows.

$$[DOC]_{\text{terrestrial}} = \frac{\varphi}{\left(\dfrac{DOC}{aCDOM_{(340)}}\right)} \times DOC \qquad (3)$$

This can be rewritten as:

$$[\text{DOC}]_{\text{terrestrial}} = \varphi \times aCDOM_{(340)} \qquad (4)$$

Where $\varphi = 0.3078$ and represents the minimum DOC/*a*CDOM$_{(340)}$ ratio found in our dataset over five *Lampsilis* cruises ($n = 199$) on the SLR and was assumed to represent the ratio of an exclusively terrestrial DOC pool (optical terrestrial end-member). *a*CDOM$_{(340)}$ (m^{-1}) is the calculated absorption coefficient at 340 nm.

DOM fluorescence

Three-dimensional excitation-emission fluorescence matrices (EEMs) of DOM were measured on a Varian Eclipse fluorescence spectrophotometer for each sample over excitation wavelengths between 220 and 450 nm (5 nm increments) and emission wavelengths between 230 and 600 nm (2 nm increments). Due to the low signal-to-noise ratio, EEMs were cut below 230 nm in excitation to remove regions that contained limited information.

EEMs pre-processing

Scans were first corrected against a water blank to remove most of the first and second order of Raman scattering. Then, scans were standardized to Raman's units (normalized to the integral of the Raman signal between 390 nm and 410 nm in emission at a fixed excitation of 350 nm) with a Milli-Q water sample run the same day as the samples, as suggested in Lawaetz and Stedmon (2009). To account for reabsorption of the light emitted by fluorophores in the water, absorbance spectra were used for correction of both primary and secondary inner filtering effects in the EEMs according to equation 5 (Ohno 2002).

$$I_0 = \frac{I}{\left(10^{-b(A_{ex}+A_{em})}\right)} \tag{5}$$

Where I_0 is the fluorescence in the absence of self-absorption and I is the measured fluorescence intensity (both in Raman's units, R.U.), b is half the cuvette path length (0.5 cm) for excitation and emission absorbance, A_{ex} the absorbance at the *ex* wavelength and A_{em} the absorbance at the *em* wavelength. EEMs were subsequently corrected for instrument biases using an excitation correction spectrum derived from a concentrated solution of rhodamine B and an emission correction spectrum obtained using a ground quartz diffuser as recommended by the manufacturer. The remaining first-order Rayleigh scattering was removed by the insertion of missing values (*NaN*) in a 20 nm diagonal band where excitation is equal to the emission wavelength.

PARAFAC modeling

It has been pointed out that a large number of samples (EEMs) were generally required to obtain a dataset with a range of sources of diverse chemical quality in order to adequately decompose the fluorescence signal of DOM (Stedmon and Markager 2005a, Stedmon and Bro 2008, Fellman et al. 2009c). Therefore, in addition to the 44 EEMs used in the present study, excitation-emission matrices of 1056 DOM samples ($n = 1100$) from diverse aquatic systems covering a wide range of environments (see Table 1) were modeled by parallel factor analysis (PARAFAC) to increase the variability of DOM fluorescence signatures and therefore help detect components that could have been present in insufficient quantity to detect in our environment. To reduce the dominance of high-fluorescence-intensity signals from lateral water and wetlands, the EEMs were first scaled to a unit of variance within the sample mode to construct the calibration model (see Bro (1997) for model specifications). PARAFAC models from two to ten components with constraints of non-negativity in all modes were successively conducted with MATLAB (version R2008b) using DOM Fluorescence Toolbox (1.6) and validated as described in Stedmon and Bro (2008). The parameters obtained from the PARAFAC model were used to calculate an approximation of the abundance of each component, expressed as $F_{\max}$ (in Raman's unit, R.U.), which corresponds to the maximum fluorescence intensity for a particular sample (Lapierre and Frenette 2009).

Underwater light

Downward irradiance was measured at every 0.02 m with a spectroradiometer (HyperPro, Satlantic Instruments) which was slowly lowered through the water column. Light data were corrected automatically for "dark irradiance" values obtained from the shutter darks. These are continuously recorded during the measurements by occulting the input fiber with an optical shutter, typically after every five light samples. Further details are available in the *Prosoft* software user manual (Satlantic, Document SAT-DN-00228-Rev. C). As a main photolytic agent, the underwater UVA light intensity was calculated by integrating the light energy, measured between 350 and 400 nanometers (due to limitations of the instrument) according to equation 6 (Kirk 1994).

$$\text{UVA}=\frac{1}{hc}\int_{350}^{400}\lambda E_d(\lambda,z)\,d\lambda \tag{6}$$

Where h is Planck's constant, used to describe the size of quanta (6.62 x 10^{-34} J s), c the constant speed of light (299 792 458 m s^{-1}) and $E_d\ (\lambda,z)$ the measured irradiance at wavelength λ at depth z (μW cm^{-2} nm^{-1}). The diffuse attenuation coefficients for UVA light, $K_{d\,(UVA)}$ (m^{-1}), were calculated by linear regression of the natural logarithm of UVA irradiances versus depth.

Bacterial abundance

The abundance of bacterial cells with high nucleic acid content (HNA) and low nucleic acid content (LNA) were enumerated by flow cytometry according to the protocol described in Belzile (2008). Briefly, the technique consists of staining the bacterial nucleic acid and then measuring the fluorescence intensity. Due to their higher DNA and RNA content per cell, the HNA bacteria display higher fluorescence intensity than LNA bacteria. This distinction allows determination of the abundance of bacteria in each group.

Water mass distribution

The water mass distribution map (Fig. 1) used to build the AEM directional graph (Fig. 2) and to determine the relative position of the sampling sites to each water mass was based on the analysis of Landsat-5 Enhanced Thematic Mapper (ETM) satellite images of the SLR taken on August 16 and 26, 2006, using the approach described in Frenette et al. (2006). Briefly, inland waters were differentiated according to their spectral properties, which are mainly determined by chromophoric dissolved organic matter (CDOM) and suspended particulate inorganic matter (SPIM). Optical satellite sensors allow the characterization of CDOM and SPIM, since they have different spectral responses. The green band (520–600 nm) is particularly sensitive to absorption by CDOM, while the red band (630–690 nm) shows the reflection characteristics of SPIM. Based on a similarity matrix of the per-pixel red-to-green surface reflection ratio, a clustering analysis, processed by an unsupervised clustering algorithm (ISODATA/PCI-Geomatica 10), was used to identify the specific lateral limits of each water mass. Stations that were positioned close to the junction of two water masses were validated with their bio-optical properties to ensure their exact localization. Inspection of the SLR and major tributaries showed little variation in flows and water levels between the satellite image acquisition date and the dates of the sampling campaign, supporting the assumption of the relative stability of water masses during this period.

Asymmetric Eigenvector Maps (AEM) modeling

The explanatory spatial variables (eigenfunctions) used to model the lateral and longitudinal distributions of DOM components were generated by asymmetric eigenvector maps (AEM) analysis (Blanchet et al. 2008b). The term "explanatory" refers to all variables used initially to generate a subset of variables that best explained the spatial variability of the dependent variables. The AEM directional graph of the river network (Fig. 2) was based on the empirical assumption of lateral mixing determined by associations between sampling sites according to the spatial water mass distribution map presented in Fig. 1. Weights were given to the edges based on the concave-up ($f = 1/d^2$) distance function (Dray et al. 2006). The distances between sites (d) were calculated using the site coordinates measured with a GPS system installed aboard the *Lampsilis*. Moran's I coefficients, which measure the degree of correlation among neighboring observations in a pattern (Boots and Getis 1988), were calculated for each eigenfunction produced by the AEM procedure. Only valid eigenvectors ($p < 0.05$) with a positive Moran index ($I > 0$) were kept for subsequent analysis.

Numerical analysis

Numerical analyses were performed using the [R] graphical and statistical computing environment (http://www.r-project.org, version 2.9.2). Before analysis, data were normalized with a Box-Cox transformation (Sakia 1992) for statistical tests that required the assumption of normality. The dataset used for numerical analysis was composed of three subsets. The dependent variables matrix (Y) consisted of F_{max} computed by the PARAFAC analysis. Explanatory spatial variables (X_1) consisted of eigenfunctions generated by the AEM analysis. The second set of explanatory variables (X_2) contained environmental measurements (Temperature, $K_{d\ (UVA)}$, HNA/LNA ratio, SRP and Chl *a*) from the sampling cruise.

We used the *leaps* [R] package to perform an exhaustive search for the best subsets of the environmental variables for predicting each DOM pool in a linear regression, using an efficient branch-and-bound algorithm (i.e. an organized and highly structured search of all possible solutions). However, since the algorithm returns the best model for any size, the results do not depend on a penalty model for model size (i.e. taking into consideration the number of selected variables) (Miller 2002). To counter this problem, we used an information criterion to measure the goodness of fit of each model. Moreover, to select the best models for each subset of predictive variables ($K = 1$, $K = 2$, ..., $K = 5$), the Akaike Information Criterion corrected (AICc) for a small sample size (usually when the number of parameters, K, is relatively large to n ($n/K > 40$)) was used to compare and rank the models (Burnham and Anderson 2002). AICc is based on the principle of parsimony, helping to identify the model that accounts for the most variation with the fewest variables. Such a model selection method requires the calculation of the AICc differences (Δ_i) for all candidate models in the set as:

$$\Delta_i = \mathrm{AICc}_i - {}_{\mathrm{min}}\mathrm{AICc} \tag{7}$$

where ${}_{\mathrm{min}}$AICc is the smallest AICc value within a given set of models (Burnham and Anderson 2002). The larger the Δ_i, the less plausible the model: models with $\Delta_i < 2$ have substantial support, those where $4 < \Delta_i < 7$ have considerably less support, and those with $\Delta_i > 10$ have essentially no support (Burnham and Anderson 2002). For this reason, only models with $\Delta_i < 2$ are presented in this paper.

For a multivariate perspective (i.e. to find variables that best explained both DOM pools), forward selection using redundancy analysis (RDA) was carried out according to the procedure proposed by Blanchet et al. (2008a). Each model was tested by 999 random permutations using the *anova.cca* function of the *vegan* package. Variation partitioning among retained spatial and environmental variables (i.e. % contribution by each predictor in the regression model) was assessed by hierarchical partitioning using the lmg method in the relaimpo R package as described in Groemping (2006). A clustering analysis (to group stations) based on PARAFAC component similarity matrices (using Fmax values), was used to highlight the lateral distribution of DOM. Longitudinal distribution of DOM components included stations that were located in the central water mass at each transect. A piecewise regression was calculated by fitting a bilinear relationship to the DOC longitudinal distribution (i.e. to segment the longitudinal distribution of DOC and identify breakpoints if any) using the R segmented package.

Results

PARAFAC and component identification

The residual and split-half analysis determined that seven distinct fluorescent groups (components) adequately modeled the different DOM profiles in our dataset (Fig. 3, explained variance 99.79%). Considering the large number of EEMs used and the wide range of habitats sampled, identified components are likely to be found in all large river systems. All components have been identified in previous studies (Table 2). Component 1 showed strong absorption (excitation) in the UVB and UVC region and looked similar to a photoproduct that has been found earlier in degradation experiments and has been suggested to originate essentially from UV degradation of terrestrially derived DOM (e.g. Stedmon et al. (2007)). Fluorescence signals of components C2 and C3 corresponded to previously identified fulvic and humic fluorescence of terrestrial origin. Fluorophores C4 and C5 shared similar spectral characteristics with the well-known tryptophan-like fluorescence. However, the emission peak of component C4 presented a blue shift of about 20 nm in comparison with component C5, which leads to the distinction between tryptophan bound to proteins and free dissolved tryptophan (Determann et al. 1998). Absorption and emission spectra of component C6 were closely correlated to those of tyrosine-like fluorescence. Components C4, C5 and C6 have been reported to be present in many different aquatic environments and bear resemblances to protein-like fluorescence associated with biological production of DOM (Bertilsson and Jones 2003). The fluorescence signature of component C7 has been associated with anthropogenic activities such as water pollution by a polycyclic aromatic hydrocarbon (PAH) contaminant frequently found in fuel oils.

Components classification

The seven DOM components identified by the PARAFAC analysis were grouped (summed) into four distinct groups according to their spectral characteristics (Fig. 3) and their relationship to terrestrial DOC concentration (Fig. 4). Fulvic and humic components C2 and C3 had the highest correlation and the steepest slope, indicating they increase rapidly with terrestrial DOC concentration. Therefore they have been included in the humic-like group. Protein-like components C4, C5 and C6 also showed a strong correlation with terrestrial DOC, but the slope of the linear regression clearly indicated an increase in fluorescence occurring at a much lower rate. Consequently, they were grouped and associated with in situ DOM biological production. The regression model for component 7 had the smallest slope of the three linear models and hence forms its own group. The regression model including an interaction term between DOC and component groups showed that the values of the slopes were significantly different ($R^2 = 0.95$, $F_{5,426} = 1758$, $p < 0.0001$). Component 1 was found to have a different behavior, which was better modeled by a second-order equation indicating a more "exponential" accumulation of this fluorophore as terrestrial DOC increased. This component has also been identified in both terrestrial and in situ sources (see the principal component analysis and discussion in Lapierre and Frenette (2009)).

Lateral distribution

The analysis of the sum of squares by the number of clusters extracted determined that stations were best classified into three clusters (data not shown) and represents changes in DOC concentrations that are apparently large across the width of the river. The first cluster included stations sampled in confluence zones, the second cluster had stations located in the central water mass and the third cluster had stations positioned in lateral mixing zones (Fig. 5). The average DOC reached its maximum concentration in the lateral water masses directly associated with tributaries (cluster 1), being about three times as high as in Great Lakes water (cluster 2) and twice the average concentration of mixing zones (cluster 3). ANOVA followed by an *a posteriori* Tukey-Kramer test showed significant differences in the average DOC concentration among the three clusters (box-plot Fig. 5, $R^2 = 0.77$, $F_{2,41} = 69.13$, $p < 0.0001$). Humic-like and protein-like DOM components achieved maximum abundance in the near-shore zones (Fig. 5). The ratio of component 2 to 3 had about the same value (≈1.7) in the three clusters ($F_{2,41} = 3.03$, $p = 0.06$). The C1-to-C2 ratio was similar in the Great Lakes and mixing zones clusters (≈0.5) but was significantly different in the tributaries' cluster ($p < 0.001$), where C1 was the dominant fluorophore. Tryptophan-like components (C4 and C5) presented the same ratio in the three clusters (≈0.43), whereas the tyrosine-like component (C6) had a higher relative abundance in cluster 2 only. The relative abundance of the protein-like fraction was about 15% in cluster 1 and 18% in cluster 3. It reached its maximum in the Great Lakes cluster, with 26%.

Longitudinal distribution

The piecewise regression model showed that the longitudinal distribution of DOC in the central water mass followed two different trends (Fig. 6A, $t_{slope1} = 1.924$, $t_{slope2} = 4.473$, df = 8). Between transects 1 and 6, DOC increased at a rate of 0.002862 mg C L^{-1} km^{-1}. After transect 6, i.e. just before Lake Saint-Pierre (LSP), DOC started to accumulate about 2.5 times as fast, at 0.007217 mg C L^{-1} km^{-1}. Maximum increases of DOC occurred in LSP, which receives inputs from the main tributaries of the SLR. Moreover, DOC increased approximately 20% between transects 6 and 9 and 42% at the exit of LSP between transect 10 and 12. Net losses of DOC were observed between transects 3 and 6, 9 and 10, and 12 and 13. Overall, DOC was about 2.5 times as high as at downstream sites, indicating a net accumulation between transects 1 and 13.

The fluorescence signature of the DOM pool in the upstream part of the SLR was relatively homogenous and became gradually terrestrially dominated where the contribution of humic-like components reached 77% at downstream sites (Fig. 6B). The fluorescence signal of terrestrially derived DOM followed the same trend as the DOC and increased approximately five times as fast as protein-like DOM, which remained relatively stable despite a slight increase from upstream to downstream. The breaking point identified in the DOC longitudinal distribution was not significant for any of the DOM groups.

Spatial and environmental models

AEM analysis produced a total of 41 eigenvectors, of which 13 had a significant Moran's I coefficient ($p < 0.05$). Furthermore, of those 13 eigenfunctions, five had a positive spatial autocorrelation index ($I > 0$). Among them, the forward selection procedure pointed out that two eigenfunctions best modeled the lateral and longitudinal distribution of the humic-like and protein-like DOM components, at 37% and 30% respectively (Table 4).

All environmental models presented high coefficients of determination ($0.8079 \leq$ Adj. $R^2 \leq 0.8488$, Table 5). Univariate selection of environmental variables determined that subset sizes of environmental variables from 3 to 5 predictors were best suited to model both DOM pools (Table 5). Models A, B and C were found to be equivalent ($\Delta_i < 2$) in predicting humic-like DOM fluorescence, while models D and E were shown to be good candidates for predicting protein-like DOM components. Terrestrially derived DOM models A, B and C include temperature, $K_{d(UVA)}$ and HNA/LNA and differ in terms of SRP and Chl *a*. Protein-like models (D, E) had temperature, HNA/LNA and $K_{d(UVA)}$ as common variables and differed in Chl *a*. In both cases, because of the very small Δ_i, we can consider all the candidate models to be equivalent, meaning that all variables included in each model provide relevant information. Multivariate selection of environmental variables (RDA) determined that the three predictors ($K_{d\ (UVA)}$, temperature and HNA/LNA ratio) were best suited to model both of the DOM pools. Even if Chl *a* and SRP provide relevant information in the prediction of both DOM pools, due to the high predictive power of all models (Table 5) we decided to use conservative models and therefore the smallest set of predictors that were common to both approach ($K_{d\ (UVA)}$, temperature and HNA/LNA ratio) for subsequent analysis.

Assessing the relative importance of spatial and environmental variables in DOM predictability

The combination of spatial and environmental models predicted both DOM fractions at 85% (Fig. 7). Variation partitioning showed that the unique spatial influence in DOM dynamics (i.e. advection only, left circles in Venn diagrams) accounted for only a small fraction of the total explained variance. A large part of the total variance explained by the environmental model was found to be under the influence of upstream environmental conditions (overlapping regions in Venn diagrams). Moreover, 43% ($0.36/0.84\times100$) of the total variance explained by the terrestrial environmental model was attributable to the asymmetric directional connectivity observed in the SLR, compared with 31% ($0.25/0.81\times100$) for protein-like components.

Local environmental conditions (i.e. the environmental conditions not influenced by upstream flow) had more impact on the fate of labile DOM. The relative contributions of each predictor were calculated (Fig. 7C and 7D). The temperature and the HNA/LNA ratio were the variables that best explained the variance of organic matter of aquatic origin, representing 43.5% and 19.9%, respectively. In counterpart, 48.7% of the unique environmental fraction was attributable to the UVA-light attenuation coefficient ($K_{d\ (UVA)}$) in the terrestrially derived DOM model.

Discussion

In the St. Lawrence River, in situ sources from wetlands and massive tributary intrusion continually replenish the DOM pool, thus contributing to environmental heterogeneity. Since DOM differs in quality and quantity among the hydrogeomorphic zones of the SLR, we used this ecosystem as a representative model to resolve the sources and fate of dissolved organic matter in large rivers with respect to the environmental heterogeneity and strong spatial connectivity observed in such systems. Due to their contrasting characteristics, the two principal pools of DOM have been shown to have different behaviors in the SLR, which in turn influence bacterial distribution.

Identification of PARAFAC components

The PARAFAC analysis identified seven components that were present in our dataset. It is likely that there are more fluorophore groups present as a consequence of the complex nature of DOM in aquatic systems and the wide range in sites sampled (Stedmon and Markager 2005a), but they most likely strongly covary in their distribution. Thus, due to the large dataset used (1100 EEMs), most of the potential variability in DOM fluorescence characteristics has been captured (Stedmon and Markager 2005a), and each component represents molecules with similar optical characteristics that share similar chemical characteristics (Sharma and Schulman 1999, Stedmon and Markager 2005a, Fellman et al. 2009a). Therefore, considering the large number of EEMs used and the wide range of habitats sampled (Table 1), the identified components in this study (Table 2, Fig. 3) have been found in many different aquatic ecosystems. This contributes support to the view of large rivers as integrative environments receiving different sources of DOM. Components C2 and C3 were strongly correlated with each other and sensitive to the dynamics of terrestrial DOC. Previous studies have also shown that fluorophores with longer emission wavelengths are highly conjugated and more aromatic in nature (Coble

1996, Stedmon et al. 2003). It is thus likely that those components represent humic and fulvic terrestrially derived DOM. Components C4, C5 and C6 corresponded to in situ, photosynthetically derived DOM found in rivers and marine environments (Table 2). Moreover, leaching experiments carried out on three species of macrophytes in Lake Saint-Pierre during summer 2006 (Lapierre and Frenette 2009) revealed that submerged macrophytes were a net source of protein-like DOM associated with our components C4, C5 and C6 and could consequently represent an important supply of protein-like DOM in shallow, productive environments.

The spatial distribution of DOM components in the St. Lawrence River

del Giorgio (2008) showed that in the absence of new inputs from tributaries, DOC concentration decreased linearly and became more resistant to bacterial degradation as the pool flowed downstream of the Hudson River. However, the SLR continually receives DOM from inflowing tributaries, which leads to a net accumulation of DOC along the longitudinal axis. At the exit of the Great Lakes (the source of the SLR), the fluorescence signal of components C2 to C6 was equally distributed between humic-like and protein-like groups. The signature of organic matter of terrestrial origin became gradually dominant as the central water mass flowed downstream under the influence of tributaries and landscape (Fig. 6). In the absence of experimental evidence, three scenarios were considered in order to investigate the rapid accumulation of terrestrial components and the relative stability of protein-like fluorophores in the main central water mass.

In the first scenario (*i*), the different components are assumed to have the same physical and biological lability (i.e. the same rate of losses). Therefore, the rapid accumulation of the terrestrial fraction could simply be explained by different rates of production. While protein-like DOM is produced directly in situ, the terrestrial DOM originates from the leaching of organic matter that occurs on thousands of km^2 of land. The potential rate of production of terrestrial DOM consequently exceeds the production of protein-like DOM by the algal communities in the SLR. For the second scenario (*ii*), the rates of production of terrestrially derived and photosynthetically derived DOM are supposed to be the same. However, the high bioavailability of protein-like substrate allows an intensive degradation by heterotrophic bacteria, thereby slowing its accumulation between zones. The most plausible scenario (*iii*) combines both previous hypotheses. In that situation, each fraction has different rates of production and degradation. The terrestrial DOM is produced rapidly and is also resistant to degradation, while the protein-like DOM is slowly produced but has a fast turnover. The last scenario is in agreement with the clustering analysis, which showed the high dominance of terrestrial DOM components in the near-shore zones that are continually replenishing the river with DOM originating from the terrestrial environment (Fig. 5). Previous studies have also shown preferential removal of different DOM fractions, particularly protein-like fluorescence (Wickland et al. 2007, Fellman et al. 2009b).

The breaking point found in the longitudinal DOC distribution observed at the entrance to Lake Saint-Pierre can be explained by two factors. One distinguishing feature of fluvial lakes is the general reduction in water velocity as each water mass enters the shallow depths characterized by the presence of extensive beds of macrophytes (Frenette et al. 2006, Vis et al. 2007). Thus, the different residence times in LSP contribute to increasing physical contrasts between lateral and central water masses, which amplify the lateral mixing. Additionally, among the hydrogeomorphic zones of the SLR, LSP represents the most heterogeneous environment (Frenette et al. submitted). LSP is strongly connected with the terrestrial ecosystem through its extensive floodplain and the confluence of seven tributaries (Lapierre and Frenette 2009). These contribute to the formation of up to eight distinct water masses representing an important source of DOC (Frenette et al. 2006) that supplies the green water originating from Great Lakes. Additionally, due to their low mean depth, fluvial lakes (such as LSP) are generally characterized by wetlands, which have been pointed out as important sources of DOC (Fellman et al. 2009b). Although a large fraction of the DOC appears to be controlled by terrestrial input of DOM originating from the watershed (Fig. 5), neither fraction was associated with this bilinear pattern. Rather, both of the DOM pools presented distinct linear rates of augmentation in the central water mass. This is possibly due to a portion of the DOM that includes other fluorophores that behave slightly differently than the DOC.

Impacts of spatial connectivity and environmental conditions on fate of DOM

The fate of DOM in large fluvial systems is determined by a logical combination of lateral and longitudinal connectivity between water masses and environmental conditions that establish the magnitude at which each biogeochemical process induces changes to the DOM pool. Eighty-five percent (85%) of the DOM variance could be simply explained by coupling the spatial and environmental models (Fig. 7). It is well known that spatial distributions of species are influenced by environmental gradients, eventually leading to spatially structured data (Huston 1994). As environmental variables show spatial heterogeneity, the variation explained by environmental and spatial variables may be redundant, as shown by the little improvement in fit gained by adding the spatial model to the environmental model. Therefore, to understand what the contribution of each model was, we removed the confounded portion in order to capture the unique spatial and local environmental effects. Variation partitioning demonstrated that the effects of spatial connectivity and environmental conditions on the dynamics of each DOM group were unequal (Fig. 7). Moreover, a large fraction of the variance of environmental variables controlling the dynamics of DOM was found to be under the influence of the spatial gradient. This important bias can lead to misinterpreting data if the redundant fraction is not removed from both compartments.

Spatial influence

Our results suggest that the complex hydrological connectivity observed in SLR plays a more important role in the dynamics of humic-like DOM. This can be explained by the fact that terrestrially derived DOM, which is essentially introduced into the system by tributaries and floodplains (see Fig. 5), is by definition geographically structured. Additionally, given that terrestrial matter is typically more resistant to degradation, it will tend to accumulate between zones, and a fraction at downstream sites is likely to be supplied by upstream sites. On the other hand, the high lability of protein-like material allows an effective uptake by heterotrophic organisms, which does not promote its accumulation between zones (Fig. 6B) and therefore leads to a less structured pattern in its distribution.

Environmental influence

Conversely, the local environmental conditions (after supressing spatial influence) accounted for more of the dynamics of protein-like DOM. Temperature, among other variables, is a key factor controlling the growth rate of photosynthetic organisms, which represent major sources of protein-like DOM (Bertilsson and Jones 2003) and also control the microbial use of DOM by bacteria (Raymond and Bauer 2000, Duan et al. 2007). It has been pointed out, however, that a certain fraction of the algal exudates could be at the origin of high molecular compounds resistant to bacterial degradation (Aluwihare and Repeta 1999). This could explain why temperature is also related to the dynamic of humic-like DOM.

Photomineralization has been claimed to be a major pathway in the biogeochemical cycle of dissolved organic matter in natural environments (Benner and Ziegler 1999). Moreover, it has been reported that photobleaching had more impact on high-molecular-weight organic compounds (Lou and Xie 2006, Zhang et al. 2009) and produced labile DOM of lower molecular weight that was more prone to microbial degradation (Wetzel et al. 1995, Bano et al. 1998). This statement can be supported by examination of two of our results. First, the diffuse light attenuation coefficient for UVA-light, $K_{d\ (UVA)}$ (which we hypothesize to be a good proxy for photobleaching), explained more of the variation in the terrestrial model. So it is likely that photodegradation is having a huge impact on the removal rate of components C2 and C3 (Fig. 7C and 7D). Second, component C1 was expected to be produced at a quasi-exponential rate by the simultaneous photodegradation of fulvic and humic components C2 and C3 (see Fig. 4), which accumulate rapidly along the longitudinal axis. However, the photoproduct followed a slow linear accumulation (similar to the labile DOM) in the SLR, suggesting a rapid loss (Fig. 6B). The dominance of fluorescence signal of terrestrial origin in lateral water masses (Fig. 5) and higher diffuse attenuation coefficients for UVA light (Table 3) indicates that near-shore zones could be more prone to photodegradation. More specifically, the ratios between C1 and terrestrially derived components in cluster 1 propose that shallow-depth brownwater (humic) zones and their inherently low transport times favor rapid photobleaching of terrestrial DOM. Additionally, recent studies in marine environments did not identify this component, supporting the idea of component C1 being essentially a photoproduct of terrestrially derived DOM (Stedmon et al. 2007). Several other studies, however, have demonstrated that exposure of labile substrate (protein and algal extracts) to solar radiation under macrophyte-dominated environments can result in a reduction in bacterial growth rates (see Table 1 in Benner and Ziegler (1999)). This suggests that exposure of photosynthetically derived DOM to UV may be responsible for the production of biorefractory material. Therefore, since LSP (a typical fluvial lake) has been shown to be a major source of protein-like material (Lapierre and Frenette 2009), photochemical processes occurring in the nearshore zones are expected to be involved in the production as well as in the destruction of biorefractory DOM.

Food quality and bacteria

Large HNA/LNA ratios were generally observed throughout the river, but dominated along the shores (Table 3). This corresponded to a predominance of bacteria undergoing rapid proliferation, presumably in response to a high quality of labile DOM derived from primary producers (Fig. 7D). It has been demonstrated that HNA bacteria dominate phytoplankton-rich waters, while LNA bacteria do so in phytoplankton-poor waters in response to low Chl-*a* biomass (Li et al. 1995, Stenuite et al. 2009). This seems to be applicable here, since the HNA/LNA ratio was correlated with Chl-*a* biomass (Pearson's $r = 0.27$, $p = 0.08$, $n = 44$). Koch et al. (2007) have shown a strong correlation between heterotrophic bacterial production and algal production in large freshwater rivers (see Stenuite et al. (2009) for similar results in lakes). They found that up to 40% of the total bacterial carbon demand was provided by photosynthetically derived DOM during summer. If we assume that bacteria are capable of utilizing 100% of this highly labile DOM (protein-like fraction), bacterial activity should be correlated with the spatial and temporal fluctuations in primary production. Due to the spatial heterogeneity in underwater light conditions and nutrient availability in LSP, rates of primary production have been observed in shoreline and wetland habitats characterized by a high abundance of macrophytes and phytoplankton that are markedly superior to those observed in open water (Vis et al. 2007). Autotrophic productive zones along the shores are thus likely to provide high substrate quality that fuels bacterial communities under rapid development and play a key role in carbon transfer at higher trophic levels.

Our results are also in agreement with Kritzberg et al. (2005), who used steady-state model simulation and found that protein-like DOC was twice as available to bacteria as terrestrial sources of carbon, even in highly heterotrophic aquatic ecosystems. We have no clear evidence that heterotrophic production exceeds that of autotrophs in the SLR. However, large rivers are generally net heterotrophic ecosystems, because terrestrial inputs exceed algal production (del Giorgio and Gasol 1995, del Giorgio et al. 1997). Consequently, terrestrial sources of organic matter are presumed necessary to fulfill bacterial demand. Our results suggest that microbial communities could also play an important role in the cycling of freshly humic-like DOM (Berggren et al. 2007, Berggren et al. 2010) in the SLR (Fig. 7C), especially in the nearshore zones where terrestrial DOM is dominant (Fig. 5).

Ecological implications

Accumulation of DOM in the water bodies represents the largest carbon reservoir. Therefore, transformations of even a small fraction can potentially have a huge impact on the carbon balance budget. In that sense, DOM occupies a central role in the functioning of aquatic ecosystems, especially in large rivers, since they convey substantial amounts of terrestrial organic matter to the oceans (Hedges et al. 1997) and are important sources of protein-like material (Bianchi et al. 2004, Duan et al. 2007).

AEM analysis showed that spatial connectivity in an asymmetrically driven system (i.e. with a prevailing directional hydrodynamic current), such as we find in large rivers, had an important impact on the fate of DOM flowing to the estuary. Spatial connectivity plays a fundamental role in the arrangement of environmental variables that drive the dynamics of DOM. Since the hydrogeographic zones of the SLR differ in physical characteristics (Frenette et al. submitted), they determine how the local environmental conditions govern the magnitude with which major mechanisms induce changes to the DOM flowing at downstream sites.

Altogether, bacterial degradation, photomineralization and spatial connectivity contribute to driving the fate of carbon exported to the ocean and atmosphere. Bacterial consumption of DOC represents the largest flux of carbon in most aquatic ecosystems (Cole 1999). While bacterial production provides a major link between DOC and higher organisms, bacterial respiration simply burns the DOC, which is lost as CO_2 in the atmosphere (del Giorgio and Duarte 2002). The contribution of DOC to lake metabolism is widely recognized (Williamson et al. 1999), and it has been argued that the source and chemical composition of DOC could be a key factor regulating bacterial growth efficiency and consequently influencing the food webs at higher levels (Kritzberg et al. 2005). While our results point toward a predominance of bacteria undergoing rapid development for freshly produced protein-like DOM, photodegradation (approximated with UVA-light attenuation) was the major sink of terrestrially derived DOM, (Fig. 7) which represents an important source of CO_2 (Benner and Ziegler 1999).

In particular, the heterogeneity observed in LSP suggests that this fluvial lake acts as a reactor in the biogeochemical cycling of the DOM in the SLR. For example, the colors of water masses present a transition from brownwater (humic) near the shore toward clear-water in the middle, which will affect the underwater light characteristics (Frenette et al. 2006; Lapierre and Frenette 2008). Thus, lateral variability in photomineralization rates and primary production are likely to affect the contribution of each water mass in the DOM budget of LSP. Additionally, the fact that 70% of stations contained in the mixing zone cluster (Fig. 5) were located downstream of LSP demonstrates that this fluvial lake plays an integrative role in the upstream process and influences the composition of DOM exported toward the Atlantic Ocean.

Because of spatial connectivity and water mass heterogeneity, quantitative and qualitative changes in both DOM fractions during the DOM's transition in the SLR by biogeochemical processes suggest that large rivers represent an active component of the global carbon cycle that deserve attention rather than to be viewed as simple vectors transporting DOM toward oceans. Our findings are consistent with a growing literature that demonstrates that large rivers are not pipes but rather can act as reactors in DOM biogeochemical cycling.

It is clear that the larger number of samples used in this study has considerably increased the variability of DOM fluorescence, as a result of both quantitative and qualitative changes in the pool, and this has in turn increased the resolution of the decomposition of the fluorescence signal (Stedmon and Markager 2005a). The combination of this fine characterization of the DOM and the use of spatial analysis in large heterogeneous fluvial systems offers promising insights toward understanding their roles in the DOM biogeochemical cycling. However, it has been argued that effort should be put into a more empirical limnology oriented toward understanding relations between physical, chemical and biological process controlling the dynamics of DOM (Prairie 2008). New tools are needed to synthesize the roles of the main production and transformation processes on the dynamics of DOM in environments dominated by heterogeneous water masses (Spencer et al. 2009). The complexity of the nonlinear interactions among these processes requires the development of mechanistic mathematical models.

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Table 1. Description of EEMs used in the PARAFAC model.

Location	**Number of EEMs**	**Site description**	**Sampling period**
St. Lawrence River	28	Large river	August 2006
Lake Saint-Pierre	58	Wetlands	May to August 2005
St. Lawrence River	16	Large river	June to September 2008
Lake Saint-Pierre	88	Fluvial lake	June to August 2004
Lake Saint-Pierre	78	Fluvial lake	3 periods in 2006 (macrophyte life cycle) ▪ Maximum abundance : August ▪ Senescence : October ▪ Submerged drifting : November
Lake Saint-Pierre	32	Fluvial lake	Summer 2006
New Zealand	190	Coastal lakes Volcanic lakes River	February to March 2006
Canadian Shield	172	Lake system	Summer 2004
St. Lawrence River	438	Large river	*Lampsilis* cruises ▪ August 2005 ▪ June 2005 ▪ May 2006 ▪ August 2006 ▪ October 2006
Total	**1100**		

Table 2. Characterization of the seven fluorophores identified by PARAFAC analysis and their correspondence with previously identified components. Second maxima are presented in brackets. References: (I) Stedmon et al. (2003); (II) Stedmon and Markager (2005a); (III) Stedmon and Markager (2005b); (IV) Murphy et al. (2006); (V) Murphy et al. (2008); (VI) Lapierre and Frenette (2009); (VII) Ohno and Bro (2006); (VIII) Stedmon et al. (2007). Asterisk (*) represents part of the identified component. Exponent represents the ecosystem type where the components have been found in cited studies: (a) fjord; (b) estuary; (c) lake; (d) ocean; (e) wetland; (f) river.

Component	Excitation maxima (nm)	Emission maxima (nm)	References							
			I	II	III	IV	V	VI	VII	VIII
$1^{a,b,c,d,e,f}$	< 230	430	C1	C1		C9		C1	C2	C6
$2^{a,b,c,d,e,f}$	230 (320)	430	C4	C5	C5	C2	P1	C2*	C2	C1
$3^{a,b,c,d,e,f}$	255 (340)	478	C3	C2	C1	C3	P3	C6*	C1*	C3
$4^{a,b,c,d,e,f}$	< 230 (270)	340	C5*	C7*	C6*	C6	P6/P7	C8*	C4*	C4*
$5^{a,b,c,d,e,f}$	< 230 (290)	358	C5*	C7*	C6*	C7	P6/P7	C8*	C4*	C4*
$6^{a,b,c,d,e,f}$	<230 (275)	310	C5*	C8	C4	C1	P2/P5	C3	C5	C5
$7^{b,c,d,e,f}$	245 (295)	376		C6		C4		C5		

Table 3. Descriptive statistics of sampled variables.

	Total (*n* = 44)		Tributaries (*n* = 7)		Great Lakes (*n* = 20)		Mixing zones (*n* = 17)	
Variables	Mean ± S.D.	Range (min. – max.)	Mean ± S.D.	Range (min. – max.)	Mean ± S.D.	Range (min. – max.)	Mean ± S.D.	Range (min. – max.)
Chl *a* (μg L^{-1})	3.73 ± 6.04	0.87 - 41.79	8.94 ± 14.51	1.84 - 41.79	2.22 ± 1.03	0.87 - 4.84	3.36 ± 1.73	1.45 - 7.01
SRP (mg L^{-1})	9.24 ± 4.78	1.93 - 23.47	13.64 ± 2.53	10.25 - 17.03	5.72 ± 3.68	1.93 - 17.64	11.57 ± 3.61	8.24 - 23.47
Temperature (°C)	23.05 ± 0.97	20.29 - 24.51	21.49 ± 1.14	20.29 - 23.52	23.73 ± 0.53	22.51 - 24.51	22.87 ± 0.41	22.06 - 23.44
HNA/LNA	0.33 ± 0.07	0.17 - 0.56	0.39 ± 0.09	0.29 - 0.56	0.30 ± 0.05	0.17 - 0.45	0.33 ± 0.06	0.23 - 0.45
$K_{d\,(UVA)}$ (m^{-1})	6.14 ± 3.48	0.29 - 12.10	11.03 ± 1.18	9.58 - 12.10	3.16 ± 1.54	1.09 - 5.84	7.54 ± 2.65	0.29 - 12.05

Table 4. Multiple regression model explaining variation in humic-like and protein-like DOM components using spatial variables generated by the asymmetric eigenvector map (AEM) modeling.

Selected spatial variables (X_1)	**Humic-like DOM**		**Protein-like DOM**	
	Adj. R^2	***p*-value**	**Adj. R^2**	***p*-value**
AEM_1, AEM_2	0.3744	< 0.001	0.2962	< 0.0001

Table 5. Results of the environmental model selection based on the Akaike information criterion corrected for small samples (AICc). *K* and RSE are the number of parameters and the residual standard error. Models in bold represent the best model ($\Delta_i = 0$) for each case.

Model	**Selected environmental variables (X_2)**	***K***	**AIC_c**	**Δ_i**	***p-value***	**Adj. R^2**	**RSE**
Humic-like DOM							
A	Temperature + $K_{d(UVA)}$ + HNA/LNA	3	43.07	1.71	< 0.001	0.8359	0.3733
B	**Temperature + $K_{d(UVA)}$ + HNA/LNA + SRP**	**4**	**41.36**	**0.00**	**< 0.001**	**0.8488**	**0.3584**
C	Temperature + $K_{d(UVA)}$ + HNA/LNA + SRP + Chl *a*	5	43.30	1.94	< 0.001	0.8481	0.3592
Protein-like DOM							
D	**Temperature + $K_{d(UVA)}$ + HNA/LNA**	**3**	**11.09**	**0.00**	**< 0.001**	**0.8079**	**0.2528**
E	Temperature + $K_{d(UVA)}$ + HNA/LNA + Chl *a*	4	11.78	0.69	< 0.001	0.8123	0.2499

Figure Legends

Fig. 1. Distribution of sampling sites (1-45) between Cornwall and the estuarine transition zone. Transect numbers (1-13) are indicated in circles. (A) Fluvial section between Cornwall and Lake Saint-Pierre, (B) Lake Saint-Pierre, (C) Fluvial estuary.

Fig. 2. Directional graph representing the asymmetric process of the St. Lawrence River network between Cornwall and estuarine transition zone. Numbers in circles represent sampling sites.

Fig. 3. Spectral properties of the seven fluorophores identified by the PARAFAC analysis. Line plots represent emission (gray lines) and excitation (black lines) loadings for each component. Components are presented in decreasing order of their contribution to the explained variation.

Fig. 4. Maximum fluorescence ($F_{\max}$, in Raman's unit, R.U.) of different groups of components as a function of terrestrial DOC concentration ($n = 144$). Δ indicates the slope of the regression line.

Fig. 5. Clustering based on the seven components (1 to 7) identified by the PARAFAC analysis (vertical bars plot with the standard error – left *Y* axis in Raman's units). The box plot shows the average DOC concentration among the three clusters (right *Y* axis).

Fig. 6. Longitudinal distribution of average DOC (A) and average fluorescence intensity (B) in the central water mass as a function of distance from Cornwall. Vertical lines represent the standard errors (±S.D.). The dashed vertical line corresponds to the break point found by the piecewise regression model at 150 km.

Fig. 7. Variation partitioning between spatial and environmental models for humic-like DOM (A) and protein-like DOM (B). Relative importance of each independent variable for the unique environmental fraction (C and D).

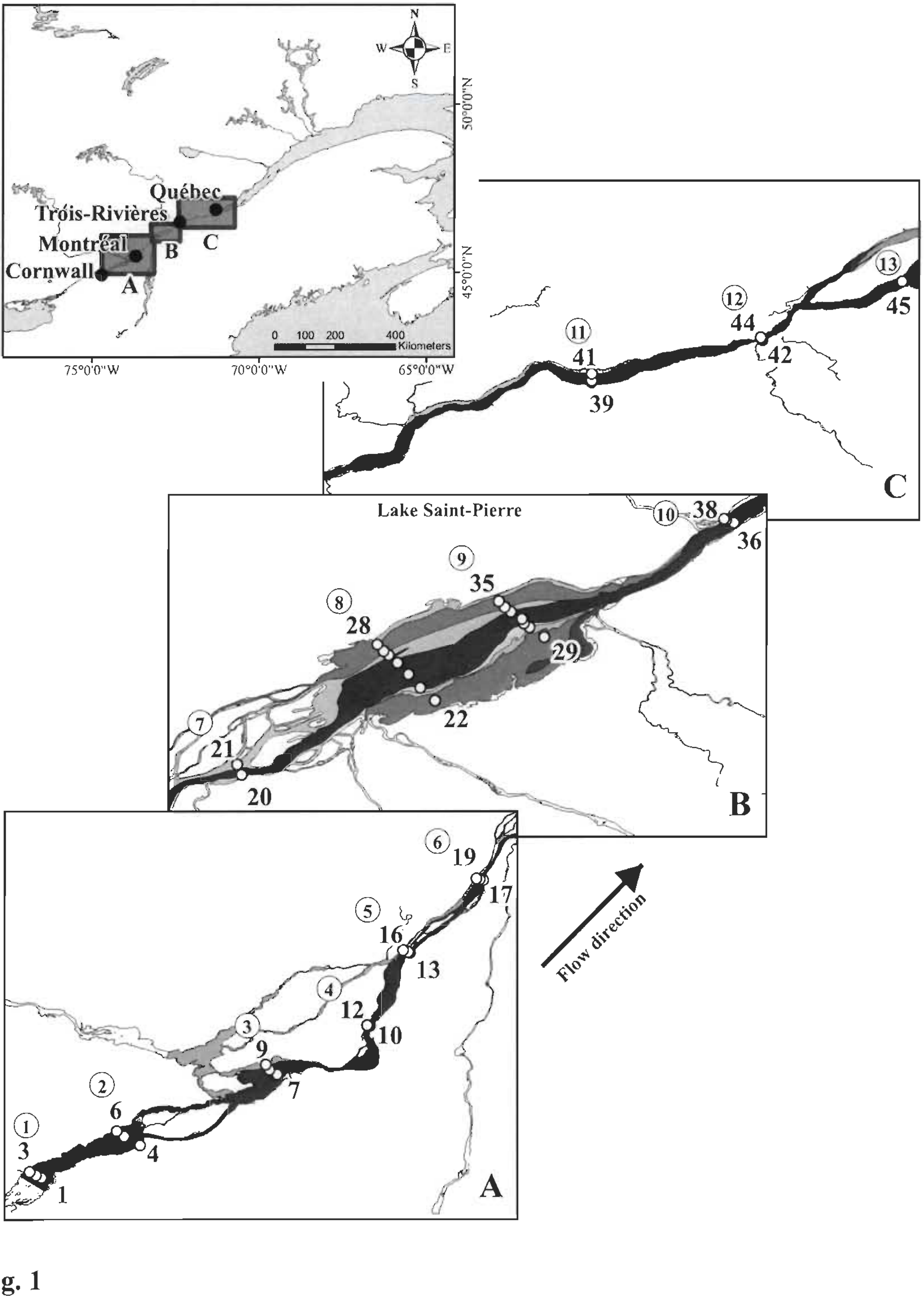

N
W
E
S
50°0'0"N
45°0'0"N
Québec
Trois-Rivières
Montréal
Cornwall
A
B
C
0 100 200 400 Kilometers
75°0'0"W
70°0'0"W
65°0'0"W
⑪
41
39
⑫
44
42
⑬
45
C
Lake Saint-Pierre
⑩
38
36
⑨
35
29
⑧
28
22
⑦
21
20
B
⑥
19
17
⑤
16
13
④
12
10
③
9
7
②
6
4
①
3
1
A
Flow direction

Fig. 1

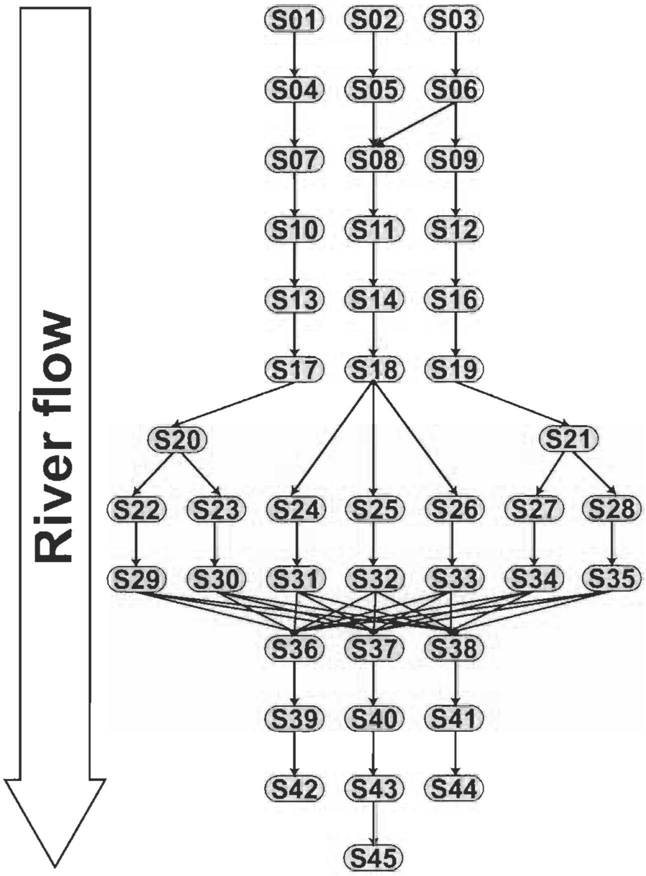

River flow
S01
S02
S03
S04
S05
S06
S07
S08
S09
S10
S11
S12
S13
S14
S16
S17
S18
S19
S20
S21
S22
S23
S24
S25
S26
S27
S28
S29
S30
S31
S32
S33
S34
S35
S36
S37
S38
S39
S40
S41
S42
S43
S44
S45

Fig. 2

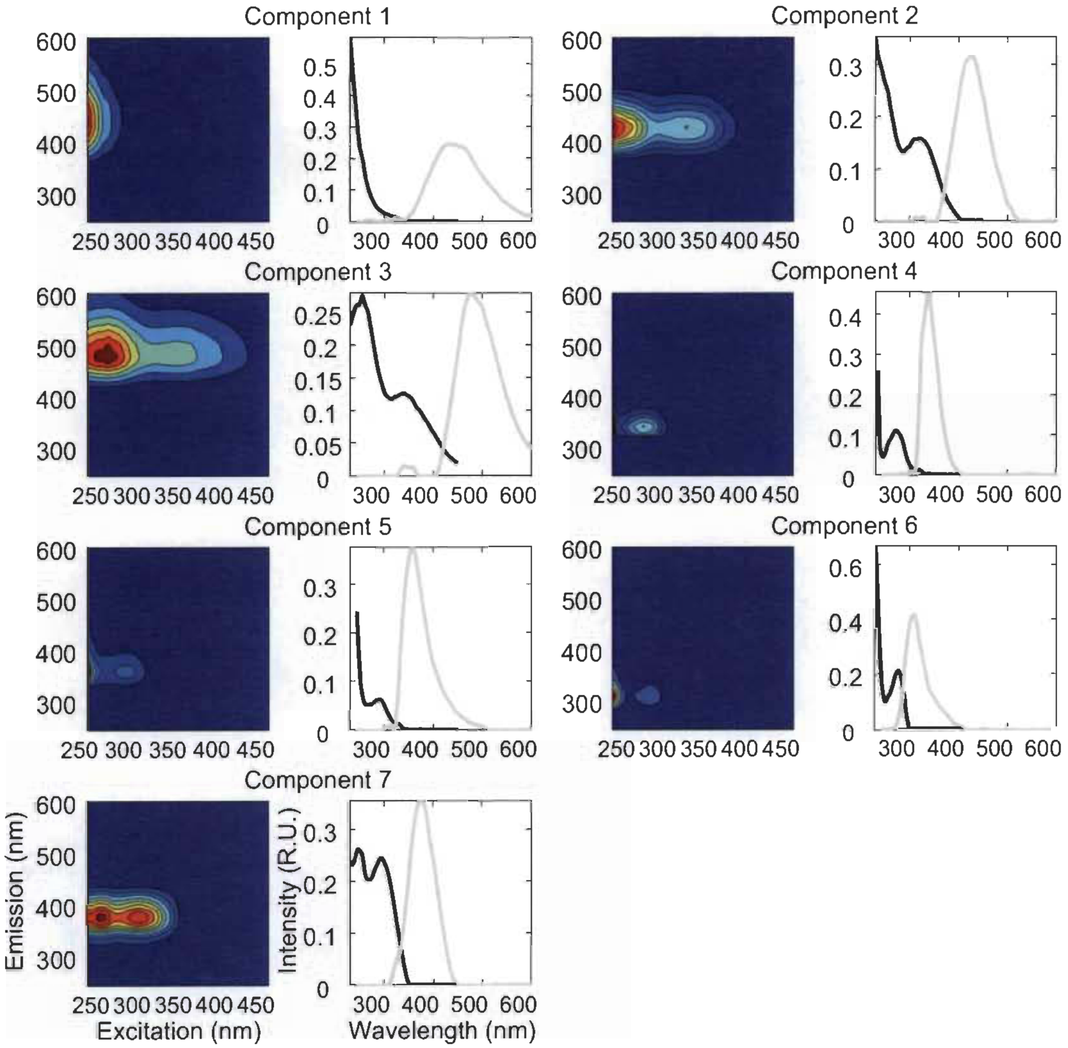
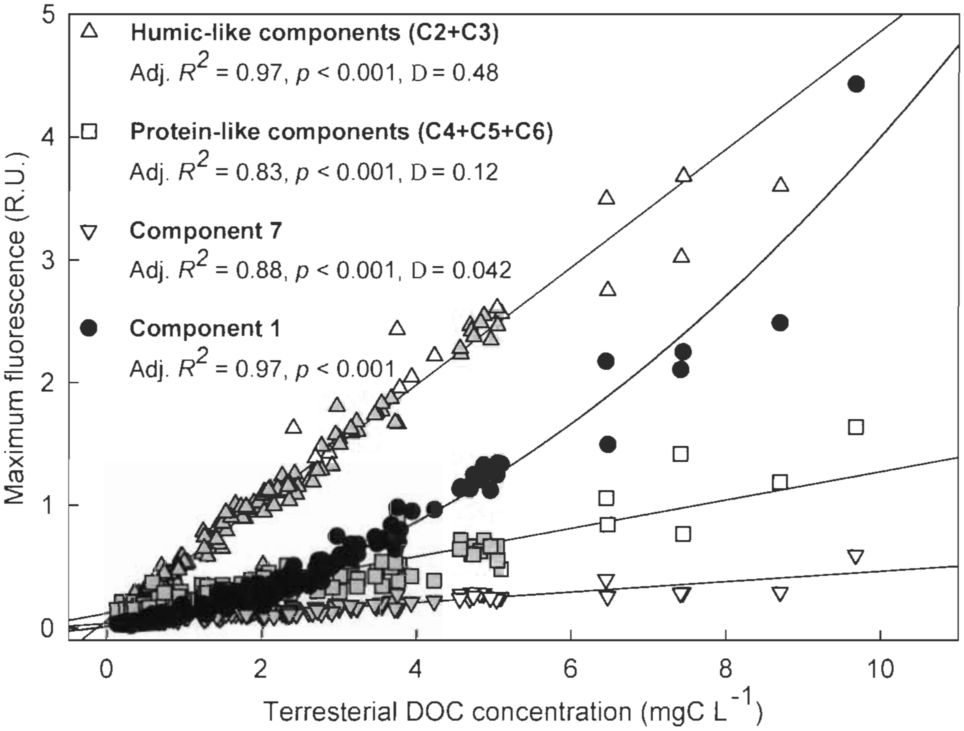

Component 1
Component 2
Component 3
Component 4
Component 5
Component 6
Component 7
600
500
400
300
250 300 350 400 450
0.5
0.4
0.3
0.2
0.1
0.25
0.15
0.05
0.6
0
300 400 500 600
Emission (nm)
Excitation (nm)
Intensity (R.U.)
Wavelength (nm)

Fig. 3



△ Humic-like components (C2+C3)
Adj. R^2 = 0.97, p < 0.001, D = 0.48
□ Protein-like components (C4+C5+C6)
Adj. R^2 = 0.83, p < 0.001, D = 0.12
▽ Component 7
Adj. R^2 = 0.88, p < 0.001, D = 0.042
● Component 1
Adj. R^2 = 0.97, p < 0.001
Maximum fluorescence (R.U.)
0
1
2
3
4
5
0
2
4
6
8
10
Terresterial DOC concentration (mgC L^{-1})

Fig. 4

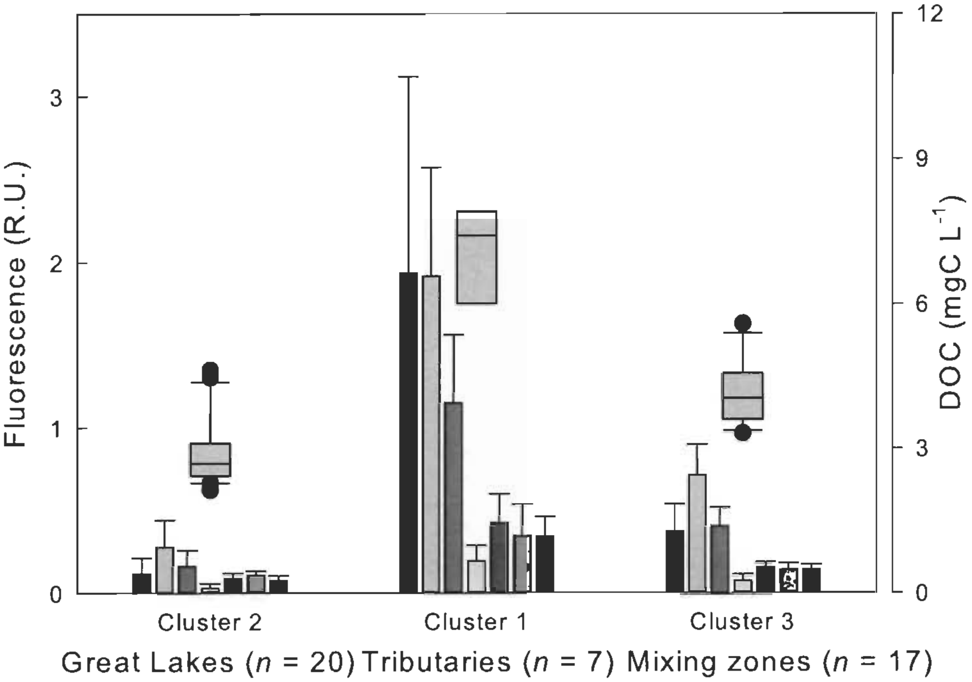

Fluorescence (R.U.)
0
1
2
3
DOC (mgC L^{-1})
0
3
6
9
12
Cluster 2
Cluster 1
Cluster 3
Great Lakes (*n* = 20)
Tributaries (*n* = 7)
Mixing zones (*n* = 17)

Fig. 5

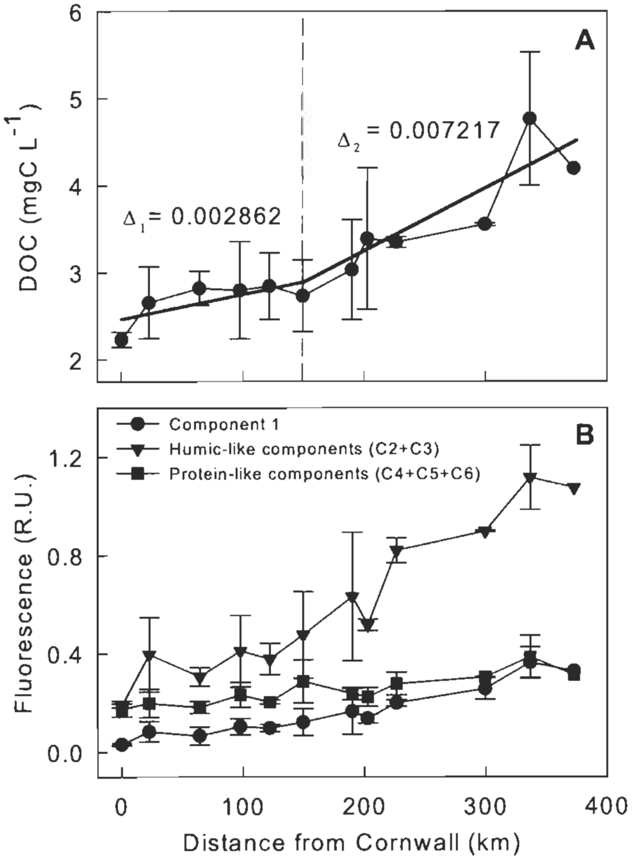

6
5
4
3
2
DOC (mgC L^{-1})
A
Δ_1= 0.002862
Δ_2 = 0.007217
1.2
0.8
0.4
0.0
Fluorescence (R.U.)
B
Component 1
Humic-like components (C2+C3)
Protein-like components (C4+C5+C6)
0
100
200
300
400
Distance from Cornwall (km)

Fig. 6

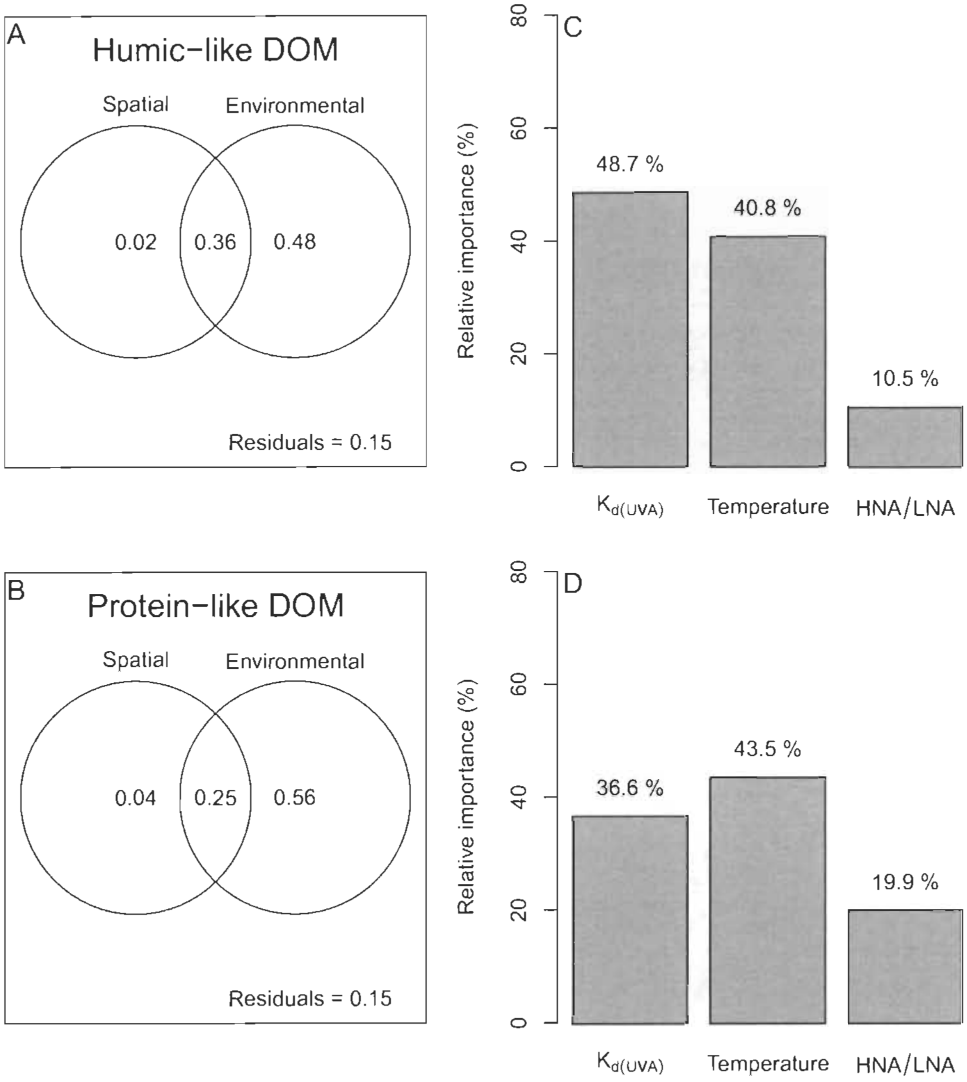

A
Humic−like DOM
Spatial
Environmental
0.02
0.36
0.48
Residuals = 0.15
B
Protein−like DOM
Spatial
Environmental
0.04
0.25
0.56
Residuals = 0.15
C
Relative importance (%)
0
20
40
60
80
48.7 %
40.8 %
10.5 %
$K_{d(UVA)}$
Temperature
HNA/LNA
D
Relative importance (%)
0
20
40
60
80
36.6 %
43.5 %
19.9 %
$K_{d(UVA)}$
Temperature
HNA/LNA

Fig. 7

CHAPITRE II

HYDRODYNAMIC MODELING OF A FLUVIAL LAKE: EVIDENCES OF MULTI-SCALE SPATIAL HETEROGENEITY SHAPED BY THE COMPLEX BED MORPHOLOGY AND THE TRIBUTARY NETWORK

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Résumé

Les courants hydrologiques sont parmi les variables environnementales influençant le plus le fonctionnement des écosystèmes fluviaux considérant leurs impacts sur une variété de processus biologiques. Malgré ce fait, les mécanismes hydrologiques sous-jacents de la connectivité spatiale, à fine et à grande échelle, sont mal compris. Dans les grands systèmes fluviaux, le régime hydrologique est fortement modulé par la morphologie du lit (bathymétrie) et le réseau de tributaires. Dans les environnements aquatiques tels que les lacs fluviaux, le régime hydrodynamique peut être très hétérogène en réponse à la bathymétrie complexe et aux nombreux tributaires se jetant dans le cours d'eau principal. Afin d'apporter une meilleure connaissance de la dynamique des flux de matière opérant dans ces systèmes fluviaux, nous avons développé un modèle hydrodynamique à l'état d'équilibre de haute résolution spatiale) en utilisant les vitesses mesurées par un courantomètre à effet Doppler (*Acoustic Doppler Current Profiler* ou ADCP) dans le lac Saint-Pierre (un lac fluvial typique. Nous démontrons que la topographie complexe du lit et l'importance du réseau de tributaires jouent un rôle important sur le régime hydrodynamique global d'un lac fluvial en modifiant localement les courants d'eau, lesquels influencent à leur tour la biologie et la distribution de la matière vivante et non vivante. Les résultats révèlent que le régime hydrodynamique en place est caractérisé par des zones de vitesse et de temps de résidence contrastés ce qui détermine ensuite le temps de transformation de la matière transitant vers les océans.

Mots-clés : Géomorphologie fluviale, fleuve, temps de résidence, vélocité, masses d'eau

Abstract

Water currents are among the strongest environmental variables driving the functioning of river ecosystems through their impacts on a variety of biological processes and related proximal mechanisms. Despite the importance of water currents in such systems, the fine and broad scale physical mechanisms underlying the spatial connectivity are poorly understood. In large river systems, the hydrologic regime is strongly modulated by the bed morphology and the tributary network. In river environments such as fluvial lakes, hydrodynamic regime can reach high levels of heterogeneity in response to their complex bathymetry and large number of tributaries flowing in. To bring better insights on the flow dynamic which prevails in these systems, we developed a calibrated steady-state hydrodynamic model of high spatial resolution for the lake Saint-Pierre (a typical fluvial lake) based on measured velocity using an *Acoustic Doppler Current Profiler*. We demonstrate that the complex bed topography and the important tributary network found in fluvial lake could play important roles in their global hydrodynamic by locally modulating the water currents which in turn impact the biology and distribution of living and non-living components. Furthermore, the observed hydrodynamic regime was characterized by zones with contrasting velocity and thus residence times which ultimately determine how long the matter is transiting and processed in these systems before being flushed out toward oceans.

Keywords: ADCP, Fluvial geomorphology, Large River, Residence time, Velocity, Water mass

Introduction

Water currents are among the strongest environmental variables driving the functioning of river ecosystems. For example, flow velocity can influence: (1) the structure of benthic macroinvertebrates (Statzner and Higler 1986) and photosynthetic organism in coastal zones (Vincent et al. 1982); (2) occurrence and/or abundance of aquatic plants (Janauer et al. 2010) such as macrophyte (Chambers et al. 1991) and periphyton (Biggs et al. 1999, Trudeau and Rasmussen 2003); (3) plankton community composition and concentrations (Hudon et al. 1996, Twiss et al. 2010); (4) fish larvae distribution (Dettmers et al. 2005); (5) sediments deposition and transport (Haschenburger and Church 1998, Topping et al. 2005); (6) escape behaviors in stream insects (Hoover and Richardson 2010); (7) skeletogenesis of vertebrate (Cloutier et al. 2010) and (8) even transfer of energy through river food webs (Finlay et al. 1999, Allan and Castillo 2007). It has also been recognized that flow regime were greatly influencing phytoplankton biomass and community structure in shallow and lowland rivers (Bahnwart et al. 1998, Leland 2003) by inducing pronounced gradients in environmental conditions. Thus, understanding flow patterns in river environments is of importance because it has many implications on a variety of biological processes and related proximal mechanisms.

Among large river ecotype systems, fluvial lakes are considered to be productive environments playing important roles in the global dynamic of their receiving system (Frenette et al. 2006, Vis et al. 2007, Lapierre and Frenette 2009). Principal characteristics of fluvial lakes are the general shallow water in lateral areas compared to the main channel, small mean water depth, low turbulence, reduction in water velocity, longer residence time and heterogeneous bathymetry (Centre Saint-Laurent 1996, Vincent and Dodson 1999, Frenette et al. 2006). Furthermore, fluvial lakes continually receive matter of the surrounding watershed by many tributaries and are incorporating inflows with distinct abiotic and biotic characteristics which lead to the formation of several parallel water masses with contrasting physical and biogeochemical properties (Frenette et al. 2003, Frenette et al. 2006, Frenette et al. Submited). This hydrodynamic phenomenon is typical of large river ecosystems such as the St. Lawrence, the Parana or the Nile rivers. Such hydrodynamic singularities greatly contribute to increase the heterogeneity in water velocity which results into different pathways and transport times over water masses (Frenette et al. 2006). Because of this and the fact that fluvial lakes are usually the lowest point in the landscape, they are generally considered as sentinels ecotypes (Williamson et al. 2008, Williamson et al. 2009). Consequently, hydrological flow pattern in such system is likely to have a significant role in the biogeochemical cycling of different types of matter transported downstream toward ocean. For example, the high abundance of photosynthetic organisms in fluvial lakes (Vis et al. 2007) have been recognized important source of dissolved organic matter (Demarty and Prairie 2009, Lapierre and Frenette 2009) which in turn is an essential driver of aquatic ecosystems ecology (Prairie 2008). Because this matter (from tributaries and in situ production) is likely to be transported by advection and/or diffusion downstream, and ultimately processed, understanding where (direction) and how long (residence time) it will transit in the system is of considerable interest for biologists and ecologists.

From a statistical point of view, it has been demonstrated that the asymmetrical connectivity in large rivers, driven by the hydrology, has a major role on the distribution of chromophoric dissolved organic matter (Massicotte and Frenette 2011) which has many implications on the structural and functional properties of riverscape ecosystems (Prairie 2008, Frenette et al. 2012). Unfortunately, the fine and broad scale physical mechanisms underlying the observed connectivity are poorly understood.

To overcome this problem, numerical model describing hydrological processes need to be developed. Most of the recent models provided interesting results for streams (Kim et al. 2009), marine and coastal environments (Bellafiore and Umgiesser 2010) and estuaries (Simons et al. 2006, Simons et al. 2010). Because rivers are usually pipe shaped, the flow velocity is relatively simple to predict. However, fluvial lakes present a far more complex geomorphology where the horizontal length scale is much greater than the vertical length scale. Because of this, physical laws governing the movement of flow and displacement of water are different than what we find in more homogeneous aquatic systems such as straight river channels, reservoirs rivers or larger scale environments like oceans. Therefore, in large river systems such as St. Lawrence River (SLR), which constitute a distinctive class of freshwater environments, namely for the connection they offer between the freshwater and marine realms and for their important role to drain the world's freshwater reserves (Leclerc et al. 2008), there is still a large gap in knowledge of the hydrodynamics. This is especially true for fluvial lakes such as Lake Saint-Pierre (LSP) where hydrogeometry (velocity, flow, dispersion, depth, width, cross-sectional area and slope) play important roles in displacement of the water body (Chapra 1997). These parameters (characteristics) therefore determine how long passive particles and organisms of limited locomotion will remains in the system before being flushed out. Consequently, hydrodynamic modeling in those highly heterogeneous environments constitutes an interesting challenge.

Most of the work about the St. Lawrence hydrodynamics has been done on: (I) the upper part at the outlet of Lake Ontario (Tsanis and Murthy 1990, Brodeur et al. 2005); near the Montreal archipelago (Leclerc et al. 1987); and in Lake Saint-Louis (Carballada 1982), (II) the estuary segment (Leclerc et al. 1990a, Leclerc et al. 1990b, Saucier et al. 2003). However, at this stage, only few attempts have been made to model hydrodynamic of fluvial lakes. Existing models are based on bed morphology and an imposed water level at the downstream boundary (Morin et al.

2000a, Morin et al. 2000b, Frenette et al. 2006). However no validation using measured in situ velocity has yet been conducted on data issued from this modeling approach. Therefore more information about hydrodynamic regime of fluvial lakes would greatly improve our understanding of their functioning.

In other large rivers systems such Congo River (Laraque et al. 2001), hydrodynamic regime have only been studied using temporal series and statistical analysis. Mechanistic models have also been developed for such large rivers. For example, Paz et al. (2010) developed a hydrological model for ecologic purposes and also to investigate the impacts of climatic variability and land use changes in flow regime in Upper Paraguay River Basin. However, their model is only 1-D due to lack of data requirement from the field. Moreover, it has been discussed that large-scale hydrologic models were sensitive to the quality of data obtained at different scales (Vachaud and Chen 2002). To deal with the significant need in terms of appropriate data, Paiva et al. (2011) developed a large-scale hydrologic model (and case study on Purus River basin, one of the major tributaries of the Amazon) where hydrogeometry (river width, depth, etc.) is derived from public/free GIS data. The same approach has been used by Jung et al. (2010) on Congo river. Although easier to implement, such models provide limited spatial information being restricted to large scale hydrodynamic information and does not address processes that can occur at finer scale level.

Since little is known about the hydrodynamic regime of fluvial systems, it is of interest to investigate how the atypical bathymetry which characterize fluvial lakes such as LSP is driving the displacement of water masses and thus on the displacement of passive particles. To bring better insights on the flow dynamic prevailing in these complex heterogeneous systems, we developed a steady-state hydrodynamic model of high spatial resolution for the LSP which was calibrated with measured velocity using an *Acoustic Doppler Current Profiler* (n = 8 110). In that context, the main objectives of this study were: (1) to develop a fine scale hydrodynamic model in a fluvial lake integrating its complex geomorphology; (2) to highlight importance of the invisible riverscape structure on the transition time of water mass in a heterogeneous environment. Because LSP is representative of large fluvial lakes, we used this environment to conduct our experiments which can be generalized to other systems of this type in order to determine their fine scale pattern in hydrodynamic regime.

Methods

Study site: the Lake Saint-Pierre

LSP is the largest of the three fluvial lakes of the St. Lawrence River. On august of 2006, LSP had a surface area of 329.84 km^2, a volume of 1.05 km^3 and a mean depth of 3.18 m (these characteristics concern the total area presented in Fig. 1). The Canadian Coast Guard continually monitors the maritime channel bathymetry (see Fig. 1) and dredges it when necessary to maintain sufficient depth (11.3 m) for the commercial navigation. The mean range of water flow in the St. Lawrence River varies between 9500 and 14 500 m^3 s^{-1} (Centre Saint-Laurent 1996) where the mean discharges at entrance and exit of LSP are 9 725 and 10 500 m^3 s^{-1} respectively (Lessard 1991). The hydrological regime of LSP is mainly controlled by five dams located in Sorel's archipelago that represent an area of 151 km^2 of which 58% are occupied by the island (88 km^2) (Laviolette 2004). These structures are designed to maintain water levels upstream to the Port of Montreal, in times of low water, and concentrate flows to the navigation channel (Burton 1991).

In LSP, in addition to the main water mass originating form Great Lakes, six additional tributaries continually discharge water arising from a watershed of 21 127 km^2. The resulting river network: Great Lake, Saint-François, Yamaska, Richelieu, Nicolet, Maskinongé, and du Loup form a total of eight water masses, which impose a unique hydrodynamic regime to the fluvial lake in terms of residence time, physical and chemical properties (Frenette et al. 2006). In the LSP, the type and amount of material transported from the watershed by the tributaries is largely determined by the land-use (agriculture, forestry) characteristics, the degree of urbanization (Frenette et al. 2003, Frenette et al. 2006) and the structure of the drainage network. The confluences and watershed characteristics have already been recognized as key elements of physical heterogeneity in rivers (see references in Benda et al. (2004) and Rice et al. (2006)). During springtime flooding, lake surface area increase by more than 40%, representing an additional 100 km^2 of floodplain and thereby greatly increasing the aquatic/terrestrial contact zone (Vincent and Dodson 1999).

Sampling cruise

Sampling of the LSP was a part of a larger scale study covering the distance between Lake Saint-François and the estuarine transition zone. The sampling cruise took place aboard the RV Lampsilis from the Université du Québec à Trois-Rivières from August 8th to August 15th of 2006 where the LSP was sampled on August 11th (Fig. 1).

Water mass distribution

The water mass distribution map (Fig. 1) used to determine the relative position of the vessel to each water mass was based on the analysis of Landsat-5 Thematic Mapper (TM) satellite images of the LSP taken on August 17 of 2006, using the approach described in (Frenette et al. 2006). Briefly, inland waters were differentiated according to their spectral properties, which are mainly determined by chromophoric dissolved organic matter (CDOM) and suspended particulate inorganic matter (SPIM). Optical satellite sensors allow the characterization of CDOM and SPIM, since they have different spectral responses. The green band (520-600 nm) is particularly sensitive to absorption by CDOM, while the red band (630-690 nm) shows the reflection characteristics of SPIM. Based on a similarity matrix of the per-pixel red-to-green surface reflection ratio, a clustering analysis, processed by an unsupervised clustering algorithm (ISODATA/PCI-Geomatica 10), was used to identify the specific lateral limits of each water mass. Stations that were positioned close to the junction of two water masses were validated according to their bio-optical properties to ensure their exact localization. Inspection of the SLR and major tributaries showed little variation in flows and water levels between the date of satellite image acquisition and the date of the sampling campaign, supporting the assumption of the relative stability of water masses during this period.

Bathymetry

Bed morphology of LSP has been developed with bathymetric profile ($n = 3203$ sounding measurements) made by Fisheries and Oceans Canada (S-57 (ENC Electronic Navigational Charts) Hydrographic Data). Because their bathymetric profiles do not show sounding measurements in the dragged area (maritime channel), we exported the main channel delimitation as a polygon (ArcGiS *shapefile* format), which we then converted to points ($n = 825$). Those points were assigned depth values of 11.3 m accordingly to information provided by Fisheries and Oceans Canada. To account for the temporal variation in hydrographic regime, we then corrected depth values using water level measured during the corresponding sampling day. We determined the area under the influence of the correction factors using half the distance from the stations upstream and downstream of the current measurement station. Along the longitudinal west-east axis, we used four measurement stations to perform the temporal correction in water level. Additionally, sounding points taken with the ADCP during the cruise were added to the dataset (Fig. 1).

Measured velocity

During the cruise, a vessel-mounted Acoustic Doppler Currents Profiler (ADCP) for shallow water (four beams ADCP - RioGrande, 1200 KHz) was continuously measuring current velocities at a high degree of time resolution (2 seconds, $n = 17\,222$). In LSP (August 11th), acoustic doppler current profiler (ADCP) data were obtained in order to cover water masses velocity gradient from source to discharge. To do so, two transects were positioned perpendicularly to the main east-to-west axis of the fluvial lake in order to characterize the lateral velocity heterogeneity of the water masses (Fig. 1). Prior to the sampling, calibration of the

ADCP was made by a technician from *Teledyne RD Instruments* during an outing on the lake to ensure that the device was functioning properly. Water profiling mode 1 has been chosen accordingly to table 1 in *WinRiver II* user's manual (RD Instruments 2007). This recording mode is especially desirable for environment with fast water of all depths, rough and dynamic situations such as we find in LSP.

Bottom-track (BT) velocity, or the velocity measured by the ADCP over the river bed, was used over water-track (WT) velocity due to its longer acoustic pulses measurements which are more accurate than WT measurements, because of the much stronger acoustic reflections from the river bed (Oberg and Mueller 2007). Additionally, bottom-track measurements are less sensible to backscattered sound returned to the ADCP from small particles moving with the water (Gordon 1996, Simpson and Survey 2002).

A robust data screening process has been applied to ensure the quality of the data for the hydrodynamic model. The first step consisted to compare echoes returning to the ADCP and pings sent out from the four ADCP beams using their autocorrelation which is a measure of data quality (RD Instruments 2007). This process was applied for detecting small phase changes in ADCP measurements. Moreover, the output is scaled in units such that the expected correlation (given high signal/noise ratio) is 128 (Gordon 1996). As recommended by *Teledyne RD Instruments*, only data with correlation above 64 were kept for subsequent analysis. In addition, measurements with percentage of bad bins higher than 25% have been removed. Measured velocities also have been corrected for rocking or tilting of the ADCP using pitch and roll sensors. Error velocity thresholds (3 $m^3 s^{-1}$) have also been set in order to remove improbable water velocity which could occur by misinterpretation of the ADCP. After data screening, ADCP measurements counted 8 110 points.

Meshing

The finite element mesh used to discretize the LSP (Fig. 2) has been done on the basis of a constrained Delaunay triangulated irregular network on the bed topography in Matlab (Matlab 2008). The resulting meshing comprised a total of 43 513 elements and 23 694 nodes with a minimum and mean mesh quality index (QI) of 0.60 and 0.94 respectively. Denser meshes have been generated in areas with rapid variations in depth and areas of complex geometry to give a more gradual transition between triangles of different sizes and to give a better representation of the underlying bed topography (Fig. 3). The final meshing resulted into a high degree of resolution with an average of 0.1063 ± 0.5408 km between the nearest neighbours.

Hydrodynamic modeling

Hydrodynamic modeling of LSP has been done using River2D software (Vasquez et al. 2007). The hydrodynamic component of the River2D framework is based on the two-dimensional depth averaged St. Venant Equations expressed in conservative form which can be summarized as follow:

Conservation of mass:

$$\frac{\partial H}{\partial t}+\frac{\partial q_x}{\partial x}+\frac{\partial q_y}{\partial y}=0 \tag{8}$$

Conservation of x-direction momentum:

$$\frac{\partial q_x}{\partial t}+\frac{\partial}{\partial x}(Uq_x)+\frac{\partial}{\partial y}(Vq_x)+\frac{g}{2}\frac{\partial}{\partial x}H^2=gH\left(S_{0x}-S_{fx}\right)+\frac{1}{\rho}\left(\frac{\partial}{\partial x}(H\tau_{xx})\right)+\frac{1}{\rho}\left(\frac{\partial}{\partial y}(H\tau_{xy})\right) \tag{9}$$

Conservation of y-direction momentum:

$$\frac{\partial q_y}{\partial t}+\frac{\partial}{\partial x}\left(Uq_y\right)+\frac{\partial}{\partial y}\left(Vq_y\right)+\frac{g}{2}\frac{\partial}{\partial y}H^2=gH\left(S_{0y}-S_{fy}\right)+\frac{1}{\rho}\left(\frac{\partial}{\partial x}\left(H\tau_{yx}\right)\right)+\frac{1}{\rho}\left(\frac{\partial}{\partial y}\left(H\tau_{yy}\right)\right) \quad (10)$$

Where H is the depth of flow, U and V are the depth averaged velocities in the x and y coordinate directions respectively. g is the acceleration due to gravity and ρ is the density of water. q_x and q_y are the respective discharge intensities which are related to the velocity components through: $q_x = HU$ and $q_y = HV$. S_{0x} and S_{0y} are the bed slopes in the x and y directions; S_{fx} and S_{fy} are the corresponding friction slopes. τxx, τxy, τyx, and τyy are the components of the horizontal turbulent stress tensor. Velocity distributions in the vertical component are assumed to be uniform and pressure distributions are assumed to be hydrostatic. These equations were solved with the finite element method for all the unknown depths and velocities of our system. Outputs from the model are the two horizontal velocity components (east and north) and a depth at each point (or node) of the meshing. More information can be found in River2D user's manual (Steffler and Blackburn 2002).

Initial conditions consisted into inflow discharges measured in the main channel and in the major tributaries inflowing in the LSP and water level at one end of the river (outlet of LSP, see Fig. 1, data from Government of Québec and Hydro-Québec). External flow boundaries of the LSP have been determined using the Landsat-5 band 4 imagery. Inside flow boundaries for obstacles such as islands (*îles de Sorel*) were also determined using the same approach.

The resistance of the bed on the flow of water in the LSP has been handled by using the Manning's Roughness coefficient (n) which was then used to relate the velocity to channel characteristic. Manning's roughness coefficients have been set to every points of the meshing (thus locally) accordingly to spatial distribution of sediment textures classes (particles size) of LSP presented of Fig. 27 in Pelletier

(2008). Manning's coefficients associated to each class of substrate can be found in Table 1. Moreover, the roughness height (k_s) at each point of the meshing has been calculated as follow (Steffler and Blackburn 2002).

$$k_s = \frac{12H}{e^m} \tag{11}$$

and m can be evaluated as:

$$m = \frac{H^{1/6}}{2.5n\sqrt{g}} \tag{12}$$

Where H is approximately equals to the depth, n the Manning' coefficient and g the gravitational constant.

Fifty percent (50%) of the measured ADCP data ($n = 4\ 055$) have been randomly selected and used as forcing functions in the hydrodynamic model. This was done to force certain points in the meshing to take the observed velocity in east (u) and north (v) directions. Other 50% has been used for validation purposes by comparing predicted vs. observed velocities.

Hydrodynamic model was run until steady-state flow solution was obtained. Steady-state flow refers to the condition where the fluid properties at a point in the system do not change over time. The resulting output gave a velocity field describing the magnitude and the direction of the flow at each point of the meshing. Hence, steady state was used to estimate motion path and transport time between two points on the same stream line. The total distance within stream lines joining two disconnected points divided by velocity gave the residence time. The ArcGIS toolbox Marine Geospatial Ecology Tools (Roberts et al. 2010) has been used to display the vector field generated in River2D.

Numerical analysis

Numerical analyses were performed using the [R] graphical and statistical computing environment (R Development Core Team 2010).

Results

Lake Saint-Pierre morphology

As a result of the complex bed topography, bathymetry of the lake presented rapid depth transitions (as revealed by the denser mesh in Fig. 2 and the 3D view in Fig. 3) between the shores (northern ≈ 2 m and southern ≈ 1 m) and the dredged area (maritime channel ≈ 11.3 m, Fig. 1). Moreover, the north shore showed a more rapid lateral transition than the south shore as seen in both cross-sections presented in Fig. 3. Longitudinally, both shores presented a slight slope decreasing from upstream to downstream of the LSP. From the entrance of the LSP to its outlet near the Saint-Maurice river, the north shore presented a steeper slope of -0.0115° (-3.89 m variation over 19 366.85 m stretch) than the south shore with a slope of -0.0071 (-3.07 m variation over 24 774.24 m stretch). The dredged area depth decreased by -1.91 m over 30 643.52 m which represents a slope of -0.0036°.

Lake Saint-Pierre and tributaries hydrodynamic regimes

On august 11th of 2006, a monitoring station positioned at entrance of LSP measured a discharge of 8837.92 m^3 s^{-1} while the station at the outlet recorded a total discharge of 9425.52 m^3 s^{-1} (Fig. 1). These measures, taken in low water period, were below the annual mean discharge (*see material & methods*). This hydrologic regime resulted into a total water body area of 329.84 km^2. The discharge of tributaries ranged from 9 m^3 s^{-1} to 386 m^3 s^{-1} (see Fig. 1). Combined, the tributaries of LSP were responsible for an additional 582.41 m^3 s^{-1} (+7%) of newly imported water which represents 99.9% of the measured discharge at the outlet.

Modeling results and velocity vector field

Steady state model was obtained with a relative change in solution of 4.81×10^{-10} indicating that only little improvements were made in the final steps of the modeling. At the end of the simulation (at steady state), the total of outflow was 9419.15 $m^3\ s^{-1}$ which represent 99.99% of the measured total inflow (9420.33 $m^3\ s^{-1}$).

The model accuracy was validated by the linear relationship between predicted and observed velocities which presented a high degree of determination for the north and east components (Fig. 4, panel A: $R^2 = 0.90$, RSM = 0.06, panel B: $R^2 = 0.94$, $n = 4\ 055$, RSM = 0.04). The 1:1 dashed line indicates that the modeled values are in the same order of magnitude than the observed velocities.

Over LSP, velocities showed a high degree of heterogeneity varying from 0.07 $m\ s^{-1}$ to 1.25 $m\ s^{-1}$ (18 times of magnitude). Inside the channel islands of Sorel, the current speed varies greatly depending on the width and depth of the channels. We can observe higher velocity in the south branch of the archipelago where the maritime channel crosses. Alternatively, the shallower north areas showed lower velocity. At the exit of Sorel archipelago, water velocity varied between 0.6 and 1.25 $m\ s^{-1}$. Moreover, at the entrance of the lake, water current in the maritime channel presented a higher velocity ($\approx 1\ m\ s^{-1}$) than in the center of the LSP where the central water mass (Great Lakes) and the bed topography present a rapid enlargement. This can be observed by the fan effect of varying velocities at the outlet of Sorel archipelago (Fig. 5).

After Sorel, tributaries introduced water that was compressed between central water mass and lateral limits of the fluvial lake. On the resulting river network, the minimum modeled velocity can be observed in the near shore zones where the water level presents its lowest depth ($\approx$ 1 m). Velocity increased rapidly toward the central part particularly near the maritime channel (≈ 0.55 m s^{-1}). Moreover, average velocity was higher in north (0.225 m s^{-1}) than on the south shore (0.11 m s^{-1}). Accordingly, the area of slow velocities (< 0.15 m s^{-1}) is more restricted on the north than on the south shore of the LSP where this slack water area is rather dominant. Up north toward the maritime channel, we observe an increase in velocity which varies around 0.3 m s^{-1}. In the maritime channel, much faster velocity occurs between 0.3 and 0.6 m s-1. Water velocities respectively associated with these water masses remained persistent until the outlet of LSP were velocity increased dramatically as a result of the bottle neck shape morphology. From this point, average velocity increased by 2.5 times to reach roughly 1.25 m s^{-1}.

Residence time and streamlines

Accordingly to the velocity field presented at Fig. 5, we computed streamlines (tangent to each vector) for different pathways in the LSP. Although that the streamline presented approximately the same length, residence time varied between 19 and 41 hours from the north to the south shore. The slowest pathway (streamline 4) can be observed on the south shore where the slow current velocities are dominant. In the maritime channel, the residence time drop from 41 to 19 hours due to the much faster current velocities.

Discussion

The global changes in compounds and organisms turnover is dictated by two majors processes: kinetics, which is the rate at physicochemical mechanisms occur during the turnover processes, and transport dynamics, which is driven by hydrological processes and directly related to water masses movements (Chapra 1997). This is even truer in productive and integrating systems such as in fluvial lakes where the flow regime, in relation with the complex bed morphology, drive the spatial distribution of passive particles such as dissolved organic matter and phytoplankton and influence the ecology of organisms with limited locomotion. Essentially, the flow dynamic has many consequences on the biology of the aquatic ecosystems because it determines the pathway and the residence time of matter transiting in the system before being flushed out. This in turn determines how long the different mechanisms behind the kinetic of this matter will be processing the compounds under study (see examples in Berggren et al. (2009) and Kim et al. (2009)). For example, Lucas et al. (1999) found that in regions of short residence time (fast velocity), phytoplankton biomass may not be high despite local conditions favorable to bloom development such as in the shallow and productive San Francisco Bay. Interestingly, they also found that unproductive areas may be regions of high biomass accumulation if exportation (driven by residence time) is not sufficient to flush phytoplankton production. Although these models, developed in systems similar to the LSP, provide important insights on the effects of hydrodynamic on various biological processes, their low spatial resolution in such large scale environments may lead to bias in their interpretation. This situation is well described in Lucas et al. (2009) where it is shown that diverse relationships (negative, varying or no significant relationship) between hydrodynamic regimes phytoplankton biomass can be observed. De facto, the complex geometry of such systems creates patchiness and discontinuities in hydrological regime which make general models not suitable to truly understand the majority of biological processes. Even if recent studies proposed hydrodynamic models for large-scale environments, the lack of measured velocity data available doesn't allow implementing them in more physically realistic form (1-D vs. 2-D/3-D) which can bias their interpretation (*see cited references in introduction*). Another problem of these models is the fact that they are rarely calibrated and validated using data measured in situ.

In this context, our model overcomes these shortcomings by presenting a fine spatial resolution and an in situ calibration. First, the dense meshing (mean distance between nodes = 0.1363 km) is likely to capture the subtlety of the underlying bed topography and thus the fine scale and patchiness of the hydrodynamic regime. Secondly, our model was calibrated with in situ water velocities measurements over a complete gradient of water masses and water currents. Indeed, the high degree of correlations between the modeled and observed east and north components (Fig. 4) suggested that our model is truly representing the actual hydrological regime conditions found in LSP during our sampling. Thus, we believe that the model could be easily usable for another period (flood, etc.) and thus bring interesting insights on a completely different system dynamic.

Residence time as shaped by the complex bed morphology and the tributary network: implications on ecology of fluvial lakes

It is well known that the geometry of aquatic systems has important impacts on transportation of water bodies (Chapra 1997, Allan and Castillo 2007, Vasquez et al. 2007) which can lead to contrasting flow dynamic in systems of complex configuration. Fluvial lakes represent those kinds of systems where the complexity of bed morphology (velocity, flow, dispersion, depth, width, cross-sectional area and slope) combined to the tributary network control the water flow and ultimately contribute to create hydrodynamic discontinuities.

Tributaries constitute an important element driving the hydrodynamic regime of river systems. Indeed, their contributions to the natural regime vary as a function of their discharge. In LSP, the discharge of tributaries ranged from 9 $m^3 s^{-1}$ to 386 $m^3 s^{-1}$ (see Fig. 1). Combined, they were responsible for an additional 582.41 $m^3 s^{-1}$ (+7%) of newly imported water. However, because our model cover a particularly low water period, we hypothesis that the contribution from tributaries can be much more important during flooding period. This hypothesis can be supported by analyzing tributaries discharge from the past few years (data from Government of Québec and Hydro-Québec). For example, in our study the Saint-François River presented a discharge of 144.04 $m^3 s^{-1}$. Conversely, on October 17th of 2005, the discharge of this tributary showed a peak of 1525 $m^3 s^{-1}$ which is more than the cumulative discharge of all LSP tributaries in august of 2006. Thus, because tributaries greatly contribute to the hydrologic regime of large river systems, care need to be taken when integrating them in the modeling process.

The bathymetry of LSP presented rapid lateral variations which caused the water depth to vary rapidity from 13.27 m to 0.8 m in nearshore zones and the dredged area respectively. However, the southern and northern areas showed slightly different longitudinal slopes presumably because the matter of the dredged area (maritime channel) is continually displaced on the north shore which can be the major factor causing the rapid depth variation/transition over the north shore. Another explanation of this difference could arise from the fact that the north shore of the LSP is more affected by particles that are continually resuspended by currents or waves (see Fig. 29 in Pelletier (2008)). In fact, the longitudinal slope of the north shore (-0.0115) was slightly different than of south shore (-0.0071°) but it was enough to create differences in velocity between those two zones. Moreover, we hypothesis that this difference in slope is responsible for the portion of water body of slow velocity (< 0.15 $m s^{-1}$) being more important on the south shore than on the north shore (Fig. 5).

In those low-water areas of the nearshore zones, the friction tend to diminish the water velocity because the relative roughness (roughness height/ hydraulic radius, k_s/R) ratio is high (Chapra 1997). Additionally, on the nearshrore bank, the presence of important macrophyte biomass (Vis et al. 2007) may be another factor that contribute to significantly diminish the water velocity (Chambers et al. 1991, Janauer et al. 2010) and create slack water areas. These areas of slow water may have suitable effects on biology of fluvial lake. For example, slow-flowing nearshore and meandering areas favor retention of locally produced plankton and macrophyte (Chambers et al. 1991, Hudon et al. 1996). These areas of slow currents have also been reported to be important drivers for carbon cycling as they were contributing to increase biofilm thickness which favored uptake and microbial growth (Battin et al. 2003). In contrast to the slow moving regime of these zones, the main river channel is exposed to much more rapid current velocity since the water flow (≈ 0.55 m s^{-1}) has less resistance. We hypothesize that this fast moving regime has opposite effects on the ecology of the fluvial lake and is responsible for the reduction in plant biomass and the lower phytoplankton diversity and biomass generally observed in the central water mass (Frenette et al. 2006, Vis et al. 2007).

The resulting consequence of this physical heterogeneity (bed morphology) had predominant impacts on the creation of areas with distinct hydrodynamic regimes which ultimately create zones with contrasting and distinct residence time varying between 19 h^{-1} to 41 h^{-1} in central and lateral areas respectively. As demonstrated by the velocity field (Fig. 5), up to 11 zones with distinct residence times could be identified. These hydrological discontinuities have important consequences on the ecology of larger rivers systems and more specifically on fluvial lakes.

Depending on turnover time of the matter transiting in each of these zones, this can make difference between fully or partially processed material exported downstream toward the ocean. On non-living particles (CDOM, nutrients, pollutants, sediments, etc.), the contrasting residence times generated by the bed morphology determine how long this matter originating from the different sources (in situ and ex situ (watershed)) will be processed before being exported to the ocean. For example, DOM and nutrients are characterized by a turnover cycle varying from hours to days (Amon and Benner 1996, Allan and Castillo 2007, Guillemette and del Giorgio 2011) whereas the turnover time of pollutants could vary at a scale of weeks and months (Barth et al. 2007). Therefore only small changes in velocities could impact residences times and consequently the quality and quantity of matter exported. On living organisms of limited locomotion, it has been shown that water currents influenced the offshore movement of pelagic age-0 yellow perch in Lake Michigan which in turns could influence the recruitment success of this species (Dettmers et al. 2005). In the same manner, stream hydraulic has many consequences on the benthic invertebrates by affecting their distribution, morphology and behavior (Statzner and Holm 1982, Statzner and Higler 1986, Lacoursiere and Craig 1990). Additionally, Janauer et al. (2010) discretized water flow in Danube River into four classes of velocity (low to high) and demonstrated that the distribution of aquatic plants spices was closely related to the flow regime. Therefore, the effects of hydrodynamic regime on living and non-living matter reinforces the idea that the complex bed topography found in fluvial lake could play an important role in their global hydrodynamic by locally modulating the water currents which in turn impact the biology and distribution of living components.

The maritime channel as a physical barrier

The maritime channel (dredged area) has a huge impact on the hydrodynamic regime of the LSP by modulating the degree of connectivity between the northern and southern shores which in turn determines the degree of their physical separation. This has important implications for the ecology of LSP. Although the lateral and central water masses (with lower and higher speed, respectively) show a slight tendency to mix at the edges (see the vector field around the dredged area), the maritime channel constitutes a physical discontinuity which prevents lateral mixing between south and north water masses. This phenomenon contributes to the biochemical and biological heterogeneity commonly observed in LSP and on a general basis for the St. Lawrence River (Frenette et al. Submited). This zone of relatively high velocity may constitute a physical barrier for organisms with limited (phytoplankton)-to-moderate (zooplankton) locomotion capacities and could eventually influence their displacements (e.g. diel or reproductive migrations see Casper and Thorp (2007)).

Furthermore, it has previously been suggested that water flow varying between 45 and 60 cm s^{-1} could constitute a barrier for gene flow for the yellow perch (Fortin and Magnin 1972, Thorpe 1977, Centre Saint-Laurent 1996). We actually observed values greater than 0.5 m s^{-1} which are in the same magnitude than this suggested threshold which makes this zone an improbable area of reproduction for this species. Therefore, the high velocity area of the maritime channel could be a barrier for genetic exchange between populations which is in accordance with recent results describing the genetic structure of yellow perch populations in LSP (Leung and Angers, unpub. res.).

Our study is conservative since we modeled a period characterized by low-water and reduced differences in velocity between central and lateral areas. Therefore, it is reasonable to hypothesize that periods of flooding should exert deeper impacts on the disparity between those two contrasting zones, thus strongly contributing to the seasonal pattern in hydrological regime. This effect of physical barrier is likely to be modulated temporally in relation with discharge varying over the year from very low (6 000 $m^3 s^{-1}$) to high (20 000 $m^3 s^{-1}$) as observed at Sorel station during between 1931 and 2001 (Gouvernement du Québec 2002).

Lake Saint-Pierre as an integrator of upstream processes

Lakes and streams are generally considered as sentinels because they are usually the lowest point in the landscape (Williamson et al. 2008, Williamson et al. 2009) and is thus become processors of a large variety of carbon (Massicotte and Frenette 2011) and nutrient (Hillbricht-Ilkowska 1999, Pinardi et al. 2011) sources through the inflowing tributaries, which integrate the exchanges between lakes and their surrounding terrestrial environments (Frenette et al. Submited). Furthermore, as a result of the converging bed topography, the outlet of LSP act as bottle neck by mixing all water masses from upstream and increasing dramatically the water velocity from this point (Fig. 5). This situation is probably the main process contributing to the physicochemical mixing of the different water masses flowing further downstream in the fluvial estuary. This hypothesis is in accordance with a reduction in the number of water masses observed by satellite imagery in the fluvial estuary (Frenette et al. Submited). Vertical velocity has also been measured by *ADCP* (data not shown) and revealed high turbulence zones at the outlet. Hence, the particular hydrodynamic regime prevailing at exit of fluvial lakes could make these systems important integrators of upstream processes characteristics.

Accordingly, this mixing process contributes to the massive loading of the different types of matter such as DOC and nutrients which are ultimately transported downstream toward the ocean. This action further contributes to modulate underwater light characteristics (quality) which as many implications on the ecosystem particularly in terms of structuring agent of many biological species (Frenette et al. Submited).

The model: a tool of many applications

The physical complexity of fluvial lakes and the resulting heterogeneity in hydrodynamic regime are major factors contributing to their generally high biological productivity. Our hydrological model for LSP brings important insights on the flow dynamic in fluvial lakes by first determining how long particles stay in the system in the different zones. Secondly, our model deal with fine scale spatial resolution which is crucial to completely understand biological processes that can occurs in highly heterogeneous large scale environments.

For example, in water-quality monitoring, it can be used to give an overview of the propagation of contaminants and/or nutrients from agricultural industries which occupies the majority of the land use of LSP watershed and any fluvial lakes in general. Tributaries flowing in LSP generally contribute to a high loading of nutrients and remain responsible for significant concerns in the water quality of the lake (Centre Saint-Laurent 1996). From a biological point of view, such model can be also of interest for biologist studying spatial structure of limiting displacement organisms like zooplankton, bacteria, fish larvae, etc. Therefore, our model provides valuable insights for government management plans. Although LSP present some minor difference with other fluvial lakes of St. Lawrence River (Laviolette 2004), they share major characteristics which are typical for such system. Consequently, the general pattern modeled in FSL can be easily generalized to other systems of this type.

Upcoming work

Future developments of the LSP hydrodynamic regime will include few more variables in order the refine the current model (using River2D framework (Vasquez et al. 2007)). A third dimension (along the vertical axis) will be included to model turbulence phenomenon. This will be achieved by using the measured vertical velocity by the ADCP at every 10 cm layer. Additionally, care of physical obstacles with varying density such as macrophytes will be included in future version. Because macrophytes play important role in the modulation of water velocity (Chambers et al. 1991, Dodds and Biggs 2002, Janauer et al. 2010), this will allow a better representation of the hydrodynamic regime especially in summer where those aquatic plants are at their maximum abundance. Particular attention will be paid on the characterization of the stream bed in order to have a better representation of the flow friction. We also plan to model other parts of the St. Lawrence River (fluvial estuary, fluvial reach, etc.) which are a typical to all large river systems. This will allow to greatly improve our understanding of their global dynamic and how they behave at an ecosystem level.

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Figure Legends

Fig. 1. Distribution of water masses (August 2006) within Lake Saint-Pierre (LSP) which were discriminated by their spectral characteristics (see Material and Methods for details). Maritime channel and *Lampsilis* course are also indicated. White circles with black star inside represent the discharge monitoring station for the tributaries included in the modeling. The asterisk symbol near Sorel represents the discharge monitoring station for the St. Lawrence River at the entrance of LSP.

Fig. 2. Meshing obtained with a constrained Delaunay triangulation in Lake Saint-Pierre from Sorel to the outlet. Denser meshes have been generated in areas with rapid variations in depth to give a more gradual transition between triangles of different sizes and to provide a better representation of the underlying bed topography.

Fig. 3. 3D representation of Lake Saint-Pierre bed morphology with two cross-sectional sections near the entrance and the exit.

Fig. 4. Linear relationships between modeled and observed velocity for east (A) and north (B) components. The dashed and full lines represent the 1:1 line and linear model respectively.

Fig. 5. Resulting velocity field of the hydrodynamic model for the Lake Saint-Pierre. Arrow length and direction represent current magnitude and direction respectively. The black thick arrows denote streamlines with associated residence time.

Table 1. Manning's coefficients for different substrate size found in lake Saint-Pierre (LSP). Fig. 27 in Pelletier (2008) has been used for the spatial distribution of substrate size.

Substrate class	**Manning (n)**	**Description**
1	0.0160	Fine texture, sandy clay, silty clay
2	0.0170	Medium texture, silt loam
3	0.0175	Medium-to-coarse texture, silt loam
4	0.0180	Coarse texture and sand, sandy loam
5	0.0270	Very coarse texture, stones, pebbles and gravel – mainly from dredging processes

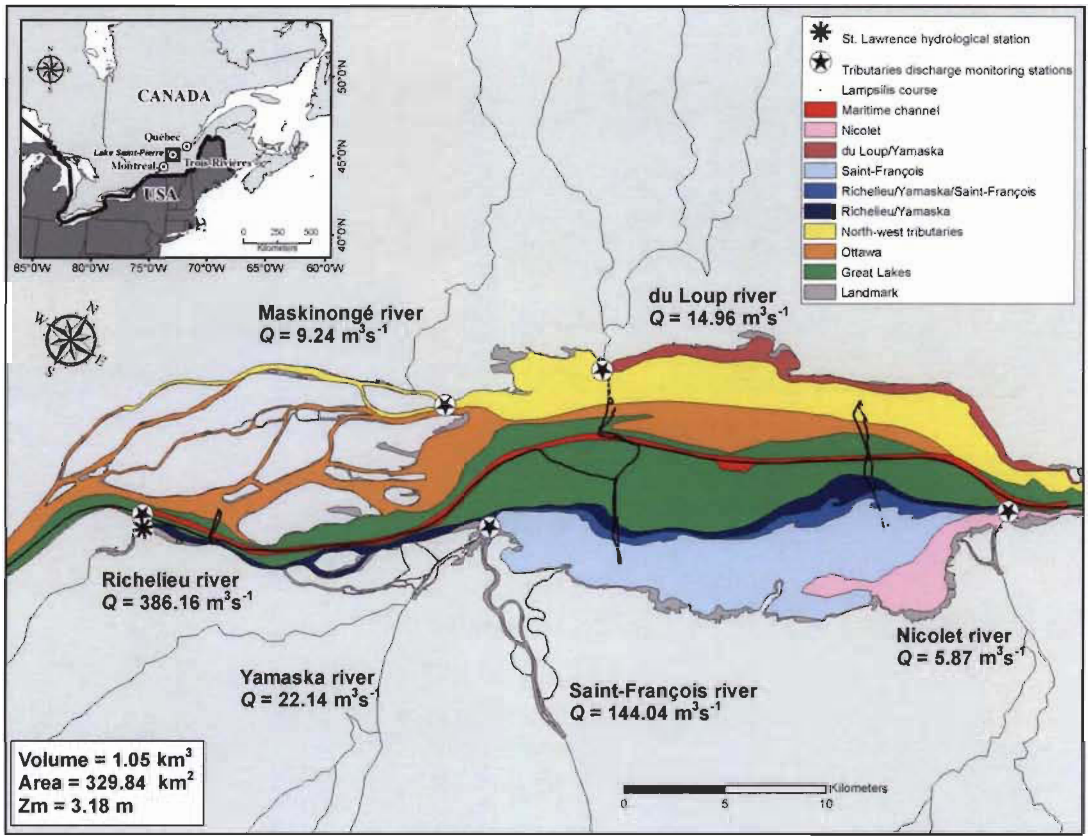
St. Lawrence hydrological station
Tributaries discharge monitoring stations
Lampsilis course
Maritime channel
Nicolet
du Loup/Yamaska
Saint-François
Richelieu/Yamaska/Saint-François
Richelieu/Yamaska
North-west tributaries
Ottawa
Great Lakes
Landmark
CANADA
Québec
Lake Saint-Pierre
Montréal
Trois-Rivières
USA
50°0'N
45°0'N
40°0'N
85°0'W
80°0'W
75°0'W
70°0'W
65°0'W
60°0'W
0 250 500
Kilometers
N
W
E
S
Maskinongé river
$Q = 9.24\ m^3s^{-1}$
du Loup river
$Q = 14.96\ m^3s^{-1}$
Richelieu river
$Q = 386.16\ m^3s^{-1}$
Yamaska river
$Q = 22.14\ m^3s^{-1}$
Saint-François river
$Q = 144.04\ m^3s^{-1}$
Nicolet river
$Q = 5.87\ m^3s^{-1}$
Volume = 1.05 km^3
Area = 329.84 km^2
Zm = 3.18 m
0 5 10
Kilometers

Fig. 1.

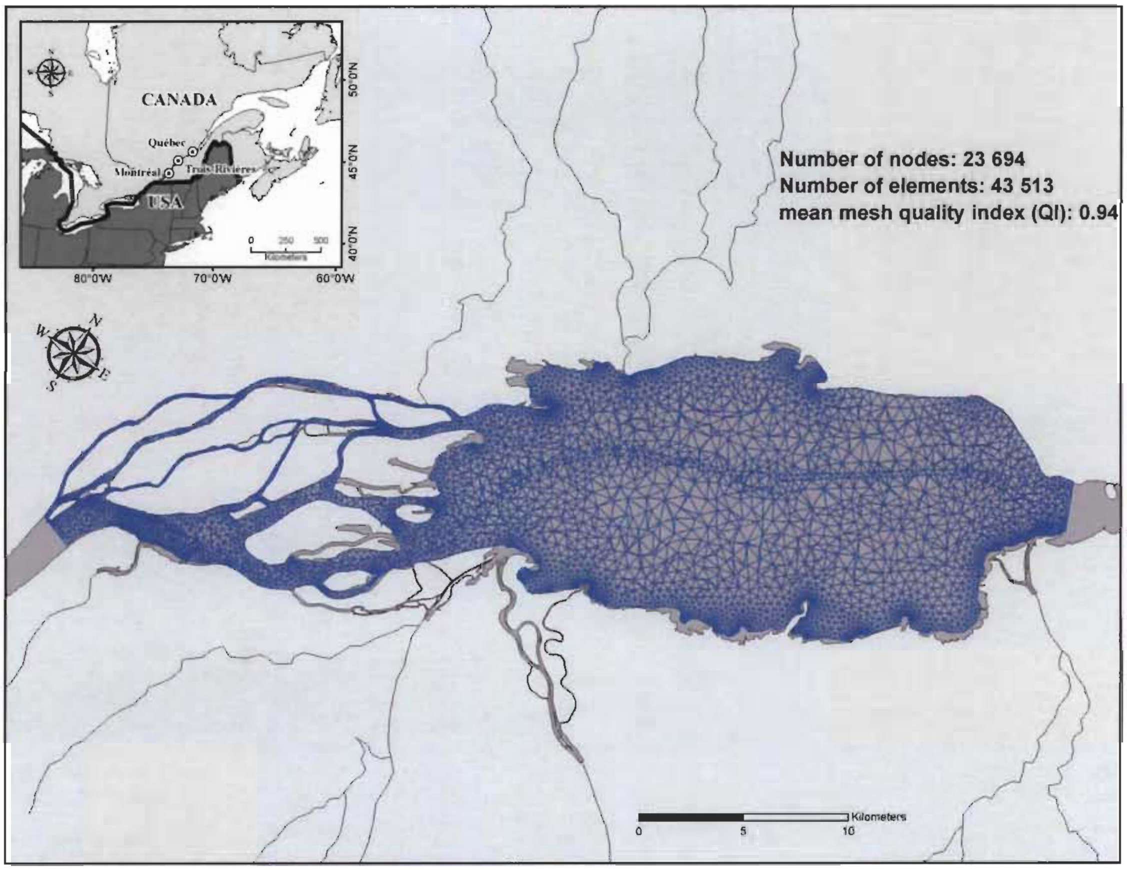
CANADA
Québec
Montréal
Trois-Rivières
USA
0 250 500
Kilometers
50°0'N
45°0'N
40°0'N
80°0'W
70°0'W
60°0'W
N
W
E
S
Number of nodes: 23 694
Number of elements: 43 513
mean mesh quality index (QI): 0.94
0 5 10
Kilometers

Fig. 2.

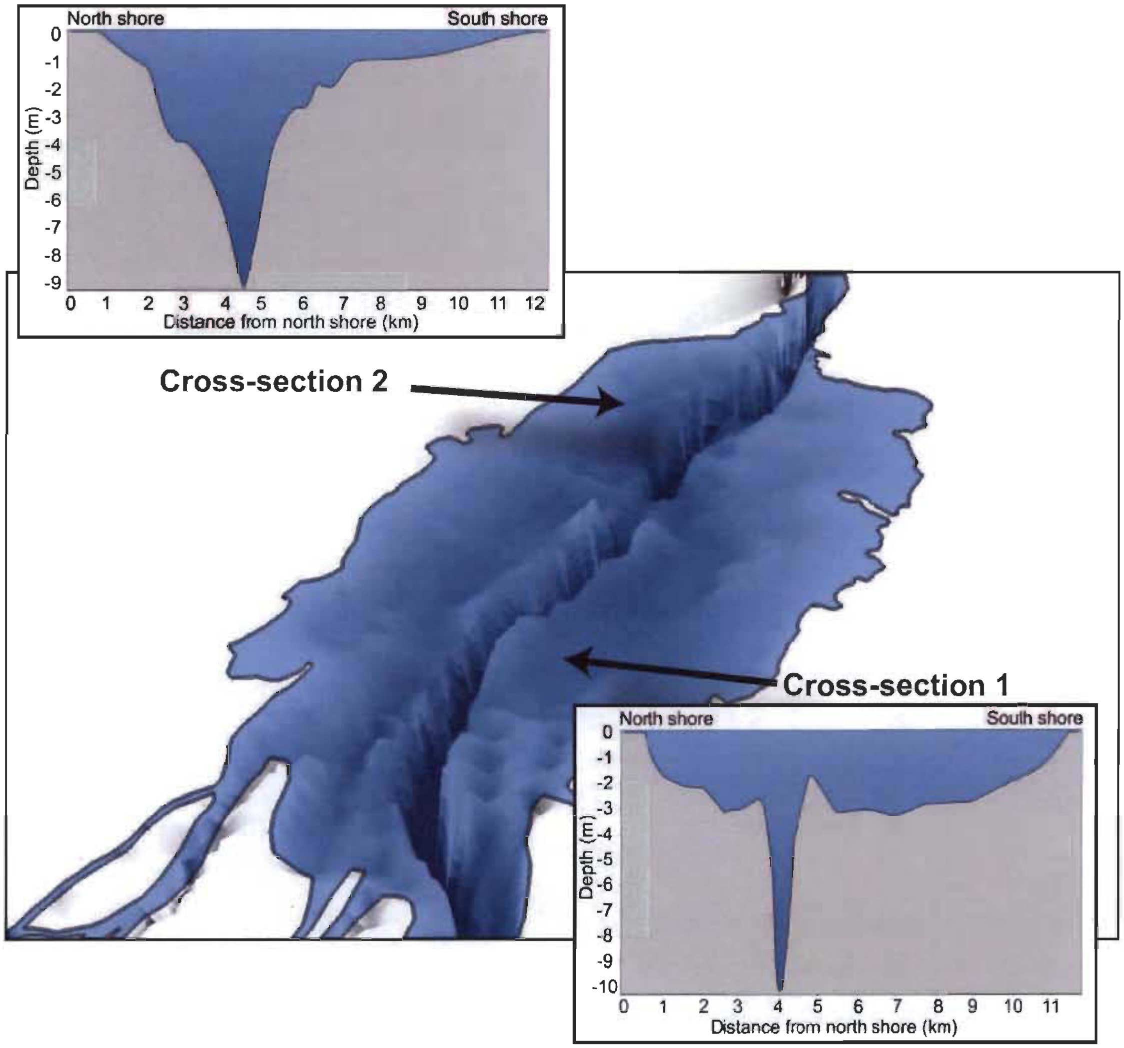
North shore
South shore
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
Depth (m)
0 1 2 3 4 5 6 7 8 9 10 11 12
Distance from north shore (km)
Cross-section 2
Cross-section 1
North shore
South shore
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
Depth (m)
0 1 2 3 4 5 6 7 8 9 10 11
Distance from north shore (km)

Fig. 3.

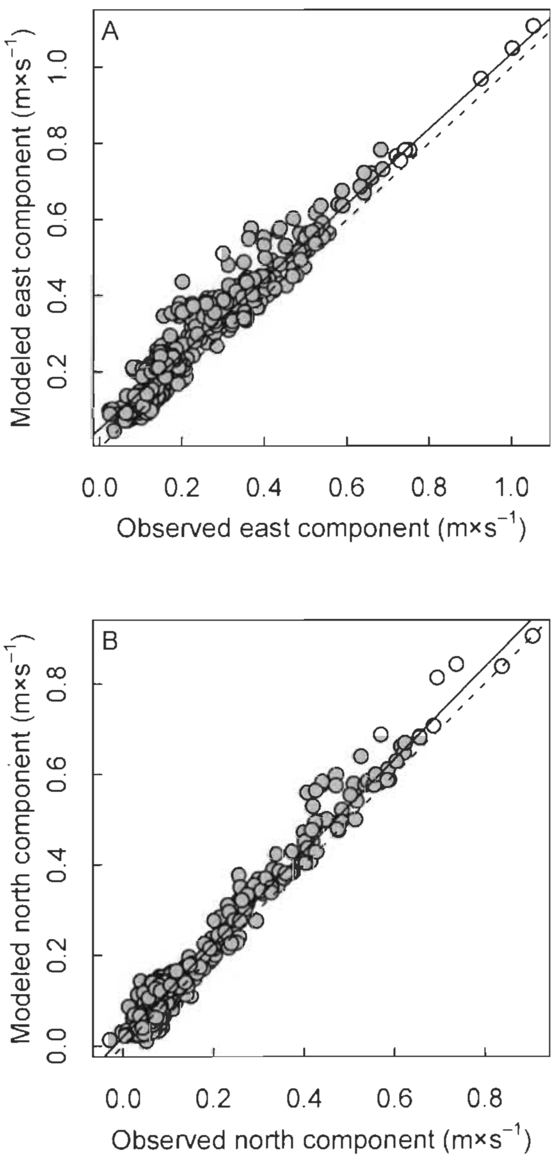
A
Modeled east component (m×s^{-1})
0.2
0.4
0.6
0.8
1.0
0.0
0.2
0.4
0.6
0.8
1.0
Observed east component (m×s^{-1})
B
Modeled north component (m×s^{-1})
0.0
0.2
0.4
0.6
0.8
0.0
0.2
0.4
0.6
0.8
Observed north component (m×s^{-1})

Fig. 4.

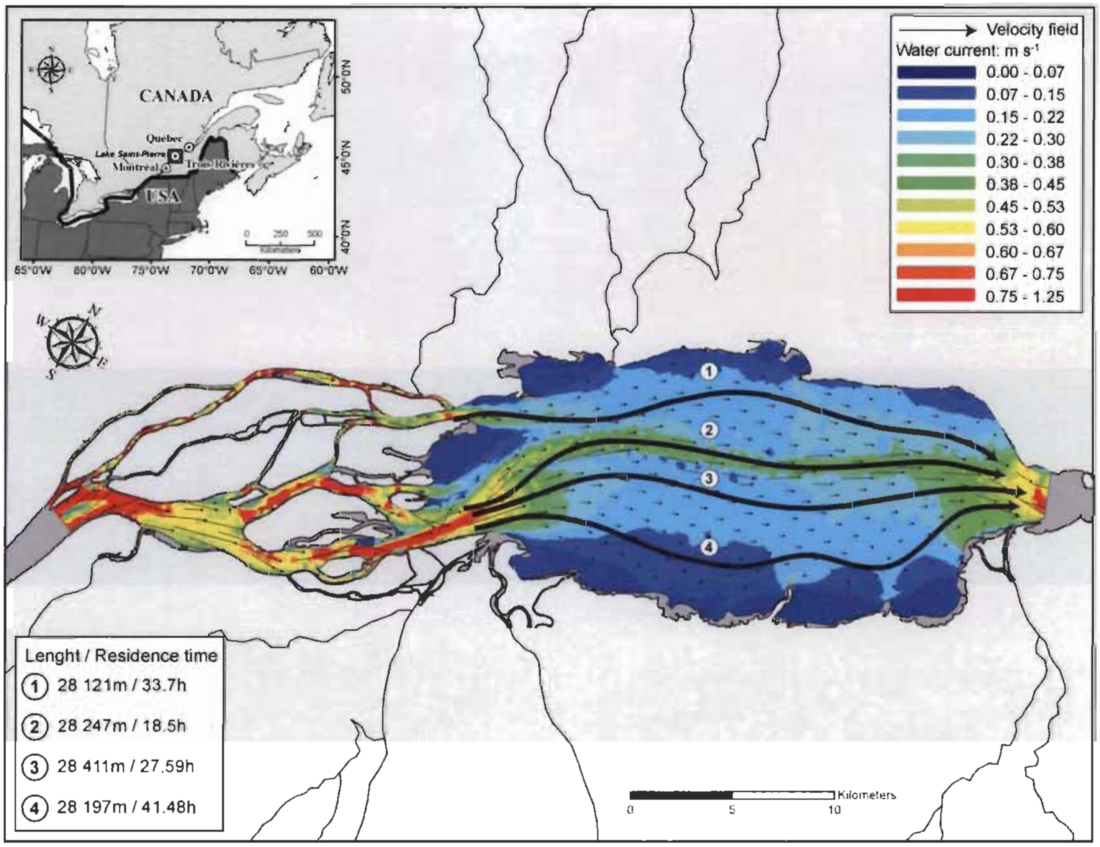
CANADA
Québec
Lake Saint-Pierre
Montréal
Trois-Rivières
USA
0 250 500
Kilometers
50°0'N
45°0'N
40°0'N
85°0'W
80°0'W
75°0'W
70°0'W
65°0'W
60°0'W
N
E
S
W
Velocity field
Water current: m s-1
0.00 - 0.07
0.07 - 0.15
0.15 - 0.22
0.22 - 0.30
0.30 - 0.38
0.38 - 0.45
0.45 - 0.53
0.53 - 0.60
0.60 - 0.67
0.67 - 0.75
0.75 - 1.25
①
②
③
④
Lenght / Residence time
① 28 121m / 33.7h
② 28 247m / 18.5h
③ 28 411m / 27.59h
④ 28 197m / 41.48h
0
5
10
Kilometers

Fig. 5

CHAPITRE III

MECHANISTIC MODELING OF DOC DYNAMICS: UNDERSTANDING INTERACTIONS BETWEEN KINETIC PROCESSES AND MASS TRANSPORT IN A LARGE FLUVIAL LAKE

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Résumé

Le carbone organique dissous (COD) joue un rôle fondamental sur l'écologie des systèmes aquatiques, mais son influence sur la dynamique des grands fleuves, tels que le fleuve Saint-Laurent (FSL), est encore mal comprise. Les grands fleuves sont caractérisés par des discontinuités hydrodynamiques importantes et une forte hétérogénéité environnementale qui entraînent des conséquences importantes sur la qualité et la quantité du COD exporté vers les océans. Divers processus cinétiques opèrent de concert avec le régime hydrologique et exercent une influence sur le cycle biogéochimique du COD transitant dans les grands fleuves. Pour ces raisons, des modèles mécanistiques faisant intervenir les principaux processus de production et de transformation sont nécessaires afin de comprendre le cycle biogéochimique du COD dans les grands fleuves. Nous avons développé et testé un modèle mécanistique qui intègre le rôle et l'amplitude des principaux processus impliqués dans la cinétique des fractions labiles et semi-labiles du COD au moyen d'une approche de modélisation de type « feedforward ». De plus, nous avons utilisé un modèle hydrodynamique à échelle fine afin de déterminer l'impact des temps de résidence sur le cycle du COD. Nous avons constaté que le patron de distribution spatiale des acides humiques (fraction semi-labile) est fortement contrôlé par les processus hydrologiques alors que le COD de type protéinique (fraction labile) est plus étroitement lié aux processus biologiques tels que la production primaire et l'activité des bactéries hétérotrophes.

Mots-clés: Croissance bactérienne, Production primaire, Modélisation, COD, Régime hydrodynamique, Photodégradation, Lumière UV, Cinétique

Abstract

Dissolved organic carbon (DOC) plays fundamental roles on the ecology of aquatic systems. However, its dynamics is generally poorly understood as a consequence of the different processes of production and transformation operating simultaneously and the specific hydrodynamic regime driving the spatial distribution of DOC. By modifying the bulk DOC pool, these mechanisms can profoundly alter the nature of the carbon exported to the coastal oceans. Such complexity has recently been pointed as strongly limiting the understanding of the dynamics and the biogeochemical cycle of DOC in natural systems. In a large fluvial lake, we developed and tested a mechanistic model (coupled with fine scale hydrodynamic model) which integrates the role and amplitude of the principal processes involved in the kinetic of labile (DOC_L) and semi-labile (DOC_{SL}) DOC pools using a simple feedforward framework. During their transition along the longitudinal axis (≈24h), both DOC pools were highly processed by bacteria. However, a large fraction of DOC_L was utilized for biomass production whereas DOC_{SL} (almost entirely transformed into CO_2) was found to only complete bacterial carbon demand. Photodegradation played a weak role in the global change of both pools presumably due to the short residence time which is insufficient for photochemical mechanisms to take place. We further argue that in productive environments, the processing of DOC_L drives the whole ecosystem metabolism through priming effect on DOC_{SL}.

Keywords: Bacterial-growth, Primary production, Modeling, DOC, Hydrodynamic regime, Photodegradation, UV-Light, Kinetic

Introduction

Dissolved organic matter (DOM) plays important roles in aquatic ecosystems. For example, the chromophoric fraction of DOM (CDOM) influences the penetration of the photosynthetically active radiation (PAR) and the blue portion of the light spectrum (refs in Frenette et al. (2012)). CDOM also constitutes a natural screen protecting aquatic organisms against UV radiations (Boily et al. 2011; Morris and Hargreaves 1997). The dissolved organic carbon content (DOC) is the major fraction of the DOM pool (Amador et al. 1990; Christian and Anderson 2002) and represents the main source of metabolic substrates for heterotrophic bacteria which affects the composition of aquatic microbial communities (Findlay and Sinsabaugh 2003; Kritzberg et al. 2006b). The efficiency with which bacteria transform this substrate into biomass depends on the source of the DOM, which in turn determines its chemical composition. Thus, the quality of DOM is likely to influence the metabolic activity of aquatic ecosystems (i.e. the balance between primary production and heterotrophic respiration), since it directly affects the rate at which the whole ecosystem processes carbon and, consequently, the carbon transfer to higher trophic levels (Daniel et al. 2005; Grey et al. 2001; Jansson et al. 2007).

The global dynamic of chemical compounds in aquatic ecosystems is dictated by two major processes: kinetics and transport (Chapra 1997). For the DOM (or DOC – here used interchangeably), the important kinetic processes involved in its cycling include: (I) UV-photodegradation (Amado et al. 2006; Benner and Ziegler 1999; Zhang et al. 2009), (II) microbial respiration and production (Berggren et al. 2010; Cole et al. 2006; del Giorgio et al. 1997; Kritzberg et al. 2006b), (III) sedimentation and flocculation (Sholkovitz 1976; von Wachenfeldt and Tranvik 2008) and (IV) production by photosynthetic organisms (Descy et al. 2002; Kritzberg et al. 2005; Lapierre and Frenette 2009). These processes operate simultaneously and drive the fate of DOM transiting in the various habitats of aquatic systems. The environmental conditions, which characterize a given habitat, further determine the magnitude of each mechanism implied in the biogeochemical cycling of DOM. Therefore the global dynamic of the DOM is likely to vary among aquatic ecosystems, meaning that patterns (models) that are well established in a system may not be exportable to another.

Large rivers, and more specifically fluvial lakes, represent hotspots for the transport and processing of organic material drained from the surrounding terrestrial landscape. For instance, in terms of magnitude, the amount of carbon (C) that is exported from terrestrial to aquatic ecosystems is comparable to the terrestrial carbon sink (Tranvik et al. 2009). Lakes, reservoirs, rivers and wetlands have been shown to return about half of that carbon to the atmosphere, under the form of CO_2, before it reaches the oceans (Cole et al. 2007), and rivers and streams have recently been pointed out as major contributors to this C loss (Butman and Raymond 2011; Humborg et al. 2010). This is especially true for large river systems which are known to convey substantial amounts (1.9 Pg C y^{-1}) of terrestrial organic matter of which, 0.9 Pg y^{-1} is delivered to the oceans (Cole et al. 2007). That exported matter represents also an important source of labile DOM (protein-like material) (Bianchi et al. 2004; Duan et al. 2007).

Riverine ecosystems have been long time described as continuum (Vannote et al. 1980). Accordingly to this old but changing paradigm, large rivers were viewed to act passively as simple transport conduits rather than active component of the global carbon cycling as stated in (Cole et al. 2007; del Giorgio and Pace 2008; Kaplan et al. 2008). However this common view of the river as a continuum has recently been challenged. For instance, an empirical investigation of hydraulic connectivity mechanisms in the St. Lawrence River (along a 450 km upstream-downstream gradient) has revealed strong longitudinal and lateral heterogeneity patterns for the physical and biological components which rather emphasized a discontinuous perspective of large river ecosystems directly linked to hydrodynamic discontinuities (Frenette et al. 2012). Amongst these, fluvial lake Saint-Pierre (LSP) constitutes a significant discontinuity largely influenced by a complex tributary network and a heterogeneous hydrodynamic regime (Massicotte and Frenette Submited) which contribute to DOM (Massicotte and Frenette 2011) and bio-optical heterogeneity (Frenette et al. 2012). For instance, this view is also supported by the theoretical framework proposed by Thorp et al. (2006) where rivers constitute a downstream array of large hydrogeomorphic patches. Although this patchiness in habitats has been shown to have important consequences in terms of quantity and quality of DOM exported toward oceans (Massicotte and Frenette 2011), such discontinuities and environmental heterogeneity have not been expressly addressed in existing numerical models dealing with DOM cycling in large rivers and fluvial lakes.

Different numerical models have been proposed to understand how the DOM is processed in aquatics ecosystems including lakes (Kritzberg et al. 2005; Miller et al. 2009), small headwater streams (Boyer et al. 1996; Karlsson et al. 2005), floodplains (Mladenov et al. 2007), and oceans and coastal marine regions (Anderson and Williams 1998; Bendtsen et al. 2002; Polimene et al. 2007),. The first major concern is related to the disparity amongst the hydrodynamic mechanisms which ultimately affects the transport time of matter between habitats and determine how long the matter is processed during its transition in the system (Anderson and Williams 1999; Loiselle et al. 2010). For example, Miller et al. (2009) developed a three-pools first-order decay model to investigate the transport and production of DOM in an alpine lake. They found that the major losses of terrestrially derived DOM resulted from photodegradation while in situ derived DOM was more influenced by heterotrophic bacterial degradation. This agrees with Boyer et al. (1996) and Mladenov et al. (2007) who found that the main processes responsible for the removal of DOM were water currents, which acted to move the DOM downstream and further promoted degradation by bacteria and UV light. However in large rivers and fluvial lakes ecosystem, hydrodynamic connectivity imposes a strong asymmetric gradient (upstream-downstream current) and terrestrial aquatic exchanges from the watershed which exerts a significant influence on the spatial distribution and composition of DOM (see Massicotte and Frenette (2011)).

For ocean and marine coastal system, the DOC pool is partitioned into different components which prevent direct comparisons with freshwater ecosystems. For example, an old refractory DOC-pool aged between 4000 and 6000 years has been argued to represent the main DOM fraction in the deep seas (see Anderson and Williams (1999) and references therein). In river systems, it is very unlikely that a biologically and physically inert pool could develop considering the rapid transition time between habitats imposed by the upstream-downstream currents which do not allow a comparable aging process to operate. Rather, it is generally recognized that in freshwater systems, the DOC pool can be separated into a "labile" and a "semi-labile" pool with a typical turnover timescale of hours to weeks (Christian and Anderson 2002; Guillemette and del Giorgio 2011; Kaplan et al. 2008). Furthermore, Hernes et al. (2007) recently emphasized the importance of age on DOM cycling where the terrestrial riverine DOM pool might be quite "fresh" (or young) and less recalcitrant than previously thought. These disparities between existing biogeochemical models of DOM doesn't allow a direct transfer to large river systems and support the general need for further development of mechanistic models integrating the loss and gains processes of DOM which are representative of lotic systems (Christian and Anderson 2002; Fellman et al. 2010).

In that context, the objectives of this research were to: (1) develop a mechanistic model to understand the role and amplitude of the different mechanisms involved in the dynamic of labile and semi-labile DOC dynamic using a simple feedforward framework (which involves a series of interconnected reservoirs); (2) determine the impact of water current's residence time on DOC cycling in a large fluvial lake system characterized by important hydrodynamic discontinuities. For sake of simplification, the model was developed during a low water level period corresponding to stable tributary discharges from the surrounding watershed. It constitutes a theoretical basis for further development and could be easily adapted to take into account the temporal aspect of cycling of organic matter.

Methods

Study site: the Lake Saint-Pierre

LSP is the largest of the three fluvial lakes of the St. Lawrence River (SLR). On August 11th of 2006, LSP had a surface area of 329.84 km^2, a volume of 1.05 km^3 and a mean depth of 3.18 m (Fig. 1). The mean range of water flow in the SLR varies between 9500 and 14 500 m^3 s^{-1} (Centre Saint-Laurent 1996) where the mean discharges at entrance and exit of LSP are 9 725 and 10 500 m^3 s^{-1} respectively (Lessard 1991). In LSP, six tributaries continually discharge water arising from the surrounding watershed (21 127 km^2), in addition to the main water mass originating form Great Lakes, The resulting river network: Great Lake, Saint-François, Yamaska, Richelieu, Nicolet, Maskinongé, and du Loup form a total of eight water masses, which impose a unique hydrodynamic regime to the fluvial lake in terms of residence time (Massicotte and Frenette Submited), bio-optical and chemical properties (Frenette et al. 2006). In the LSP, the type and amount of material transported from the watershed by the tributaries is largely determined by the land-use (agriculture, forestry) characteristics, the degree of urbanization (Frenette et al. 2003; Frenette et al. 2006) and the structure of the drainage network (Frenette et al. 2012). The confluences and watershed characteristics have already been recognized as key elements of physical heterogeneity in rivers (see references in Benda et al. (2004). and Rice et al. (2006)). The sampling cruise took place aboard the RV *Lampsilis* from the Université du Québec à Trois-Rivières on August 11th of 2006.

DOC measurements

As a quantitative measure of the total DOM, dissolved organic carbon (DOC) was measured as follows. At each sampling site, 200 mL of water was filtered through a 45 mm diameter, 0.2 µm nominal poresize polycarbonate membrane (Isopore, Millipore). Membranes were prerinsed with 100 mL of MilliQ water to remove potential impurities. The filtrate was stored in acid-washed borosilicate bottles and kept in the dark at 4°C until analysis. DOC concentrations were determined with a total organic carbon analyzer (OI Analytical, TOC-1010) by sodium persulfate digestion.

The concentrations of the semi-labile pool (DOC_{SL}) and the labile pool (DOC_L) have been done on the basis of three dimensional excitation-emission fluorescence matrices combined with parallel factor analysis (PARAFAC). Moreover, we found seven fluorescence components of which two were identified to be of terrestrial origin and three from algal exudates (Massicotte and Frenette 2011). At each station, the relative proportion between the sums of these two groups has been used to determine the composition of the total DOC pool.

Bacterial abundance

The abundance of bacterial cells were enumerated by flow cytometry according to the protocol described in Belzile et al. (2008). Briefly, the technique consists of staining the bacterial nucleic acid and then measuring the fluorescence intensity. Bacterial carbon was computed from bacterial abundance using a conversion factor of 20 fg C cell^{-1} (Sherr et al. 2006).

Primary production

As coarse estimates, phytoplankton primary production was derived from Chl a and temperature (Table 1) as described in Morin et al. (1999). Thus, the rough estimates have been used as boundaries during the parameterization process (Table 2). To ensure that the phytoplankton primary production was within the range of recent measurements in LSP, we compared our modeled estimates with those found in field studies conducted in LSP by Martin (2005) and Vis et al. (2007) in 2003 and 2005 respectively. We found that predicted primary production on the basis of Chl a and temperature were falling within the range of their in situ measurements. Literature estimates of percentage extracellular release (PER) of DOC have a mean of about 13% of primary production, although considerably higher estimates exist (Baines and Pace 1991; Nagata 2000). Based on that literature (see Christian and Anderson (2002)), parameterization of PER has been constrained between 0 and 80% (Table 2).

General modeling approach

The modeling approach used to model the dynamic of DOC in LSP is based on the principle of feedforward systems of continuous stirred-tank reactors (CSTR). This involves a chain of CSTR connected to each other where the matter is allowed to transit in only one direction (upstream to downstream) which is useful to characterize natural water stream systems (Fig. 2A). Each reactor can be viewed as a particular section of the stream with its own parameters values. Because LSP is a highly heterogeneous system, this ultimately contributes to have a better representation of the true spatial distribution/arrangement of these variables. Hence, the input of the next reactor consists of the output of the previous reactor (Fig. 2B). In our case, the succession of the different reactors were placed in the central water mass between stations 20, 24, 32 and 37 (Fig. 1 and Fig. 2A) accordingly to a streamline generated by a hydrodynamic model of the LSP (Massicotte and Frenette Submited). Therefore, the residence time in each reactor (Fig. 2) is determined by the modeled hydrodynamic regime of the LSP during the sampling cruise.

Model description

DOC was divided into labile (DOC_L) and semi-labile fraction (DOC_{SL}) (Fig. 3). DOC_L is representative of simple compounds that are readily used by bacteria while DOC_{SL} includes more complex compounds that are also readily used by bacteria but that are less optimal for growth. The main input of DOC enters in the model via primary production where a certain fraction goes to the labile pool (φ_1), to the semi-labile pool (φ_2) and the remaining fraction (1- φ_1-φ_2) to CO_2 through zooplankton respiration. Both DOC pools (labile and semi-labile) are degraded by bacteria with fractions going for cell production (Φ_1 and Φ_2) and the residual fractions (1-Φ_1 and 1-Φ_2) lost as CO_2 during respiration. Upon death, bacterial carbon content is either released back into the substrate pools (ε) or loss as CO_2 (1-ε) as illustrated in McKnight et al. (2001). The fraction directed to DOC is further separated into the labile (β) and semi-labile (1-β) pools. Finally, the semi-labile DOC is photochemically degraded by ultraviolet radiation, due to its larger molecules and its higher aromaticity (Mostofa et al. 2007; Xie and Lou 2006; Zhang et al. 2009), producing simple substrates suitable for rapid bacterial metabolism (Bano et al. 1998; Benner and Ziegler 1999; Daniel et al. 2006).

Kinetic

Model equations are given as follows along with the list of contributing parameters and state variables described in Table 2.

$$\frac{dB}{dt} = \left(\left[\phi_1 k_{g,\max(L)} \frac{DOC_L}{k_{s(L)} + DOC_L} \right] + \left[\phi_2 k_{g,\max(SL)} \frac{DOC_{SL}}{k_{s(SL)} + DOC_{SL}} \right] - dr - \frac{Q}{V} \right) B \qquad (13)$$

$$\frac{dDOC_L}{dt} = -\frac{1}{\phi_1} k_{g,\max(L)} \frac{DOC_L}{k_{s(L)} + DOC_L} B + \varepsilon \cdot \beta \cdot dr \cdot B + P_{BL} + \frac{Ptot}{1000 Z_{\max}} \cdot PER \cdot \varphi_1 + \frac{Q}{V} \left(DOC_{L,in} - DOC_L \right) \qquad (14)$$

$$\frac{dDOC_{SL}}{dt} = -\frac{1}{\phi_2} k_{g,\max(SL)} \frac{DOC_{SL}}{k_{s(SL)} + DOC_{SL}} B + \varepsilon (1-\beta) \cdot dr \cdot B - P_{BL} - P_{DIC} + \frac{Ptot}{1000 Z_{\max}} \cdot PER \cdot (1-\varphi_1) + \frac{Q}{V} \left(DOC_{SL,in} - DOC_{SL} \right) \qquad (15)$$

In each reactor, the residence time (τ_w, s) is linked with the reactor volume (V, m^3) and volumetric flow (Q, $m^3\ s^{-1}$) as follows (Chapra 1997):

$$Q = \frac{V}{\tau_w} \tag{16}$$

The bacterial kinetic (production and loss) has been modeled according to the simplest Michaelis-Menten's equations (or Monod's equations) taken from Chapra (1997) and Connolly et al. (1992) in order to minimize parameters estimations. In equation 4, bacterial abundance is increasing with production and is decreasing with mortality (*dr*). Precisely, $k_{g.max(SL)}$ and $k_{g.max(L)}$ are the maximum growth rate for DOC_L and DOC_{SL}, which represent the labile and semi-labile substrate concentrations, $k_{s(SL)}$ and $k_{s(L)}$ constitute the half-saturation constants (concentration at which growth is half the maximum, $k_s = k_{g.max}/2$) for DOC_{SL} and DOC_L respectively. Φ_1 and Φ_2 represent the bacterial growth efficiency for DOC_L and DOC_{SL}. The right sided part of Eq. 5 and 6 represent the inflow and the outflow terms of both pool of DOC flowing in each reactor (Chapra 1997).

The losses due to photodegradation where divided into two separate processes which consist in production of dissolved inorganic carbon P_{DIC} and biologically labile DOC P_{BL}. More specifically, P_{DIC} and P_{BL} (both expressed in mol C m^{-2} d^{-1}) were calculated as described in Bélanger et al. (2006).

$$P_{DIC} = \int_{\lambda=300}^{500} E_d\left(0^-,\lambda\right) \frac{a_{CDOM}(\lambda)}{a_t(\lambda)} \phi_{DIC}(\lambda) d\lambda \tag{17}$$

$$P_{BL} = \int_{\lambda=300}^{500} E_d\left(0^-,\lambda\right) \frac{a_{CDOM}(\lambda)}{a_t(\lambda)} \phi_{BL}(\lambda) d\lambda \tag{18}$$

Where $Ed(0^-,\lambda)$ (mol photons m^{-2} d^{-1}) is the spectral daily downward irradiance just beneath water surface, $a_{CDOM}(\lambda)$ and $a_t(\lambda)$ are CDOM and total absorption coefficients (m^{-1}) respectively at wavelength λ (nm).

Daily spectral surface irradiance (Ed(0^-,λ), 1-nm resolution) values was estimated as in Bélanger 2012 (préciser) using a radiative transfer model with inputs from geostationary satellite cloud observations. In brief, we used the Santa Barbara DISORT Atmospheric Radiative Transfer (SBDART) of (Ricchiazzi et al. 1998), which was run at a time interval of 3 hours by varying the solar zenith angle, the total ozone concentration, the cloud fraction and cloud optical thickness. The last three parameters, estimated from satellite data following the method developed by (Zhang et al. 2004) to produce global radiative flux data (FD), were obtained from the International Satellite Cloud Climatology Project (ISCCP) web site. The irradiance just beneath the water surface was evaluated considering specular reflexion at interface of both direct and diffuse components of the incident downwelling irradiance above the surface.

The apparent quantum yield (i.e. moles of product (DIC or DOC_L) / moles of photons absorbed by sample) associated with equations 6 and 7 for production of DIC ($\emptyset_{DIC}$) and DOC_L ($\emptyset_{BL}$) were estimated from the literature (see Table 2) (Bélanger et al. 2006; Miller et al. 2002; Vahatalo et al. 2011; White et al. 2010). Because both quantum yields were derived from exponential-like models parameterized with two or three fitting parameters, we remodeled all apparent quantum yield ($R^2 > 0.99$, $n = 22$) curve using the following equation (Bélanger et al. 2006):

$$\phi_x(\lambda) = k_1 e^{k_2/(\lambda + k_3)} \tag{19}$$

Where k_1, k_2 and k_3 are fitting parameters used for calibration (Table 1). For modeling simplification, the a_{CDOM}/a_t ratio has been assumed to be approximately equal to 1 as stated in Bélanger et al. (2006). Finally, P_{DIC} and P_{BL} production (P_x in equation 9) were transformed from mol C m^{-2} d^{-1} to mg C L^{-1} h^{-1} as follow:

$$P_x = \frac{P_x}{2Z_{\max}} \tag{20}$$

where $Z_{\max}$ is the maximum depth measured in meters.

Numerical analysis

Numerical analyses were performed using the [R] graphical and statistical computing environment (R Development Core Team 2010) and in Matlab (Matlab 2008). Differential equations 2, 3 and 4 have been resolved explicitly with fourth-order Runge-Kutta formula using measured values of the three state variables (DOC_{SL}, DOC_L and B) at station 20 (Fig. 1) as initial values. To fit the observed values, parameterization was done in Matlab using trust-region-reflective algorithm using a tolerance function value of $10e^{-10}$. As a starting point, parameter values were taken from the literature (Table 2). For each parameter, search for the optimal value has been constrained to domain boundaries (min-max) taken from literature (Table 2) in order to maintain their biological interpretation. Sensitivity analysis was conducted by varying each parameter by ±50% while maintaining all other fixed from the standard model. Because the sampling design was not planned for a fine scale representation, we used the cubic splines in Matlab (Matlab 2008) to interpolate the various variables and parameters between the whole lake study sites. For modeling purpose, those interpolated variables have been considered as measured variables.

Results

Parameterization

The parameterization allowed finding optimal values for parameters to best fit the observed data. The solver achieved convergence as the size of the current step was less than the selected value of the step size tolerance ($10e^{-6}$). The solver reached a global minimum for which each parameter values stayed within boundaries of what we can observe in the literature (Table 2).

Bacterial biomass and DOC dynamic

Bacterial biomass (carbon content) ranged over 0.05 and 0.07 mg C L^{-1} for the observed series whereas the modeled biomass ranged between 0.03 and 0.08 mg C L^{-1} (Fig. 4). As both pool of DOC decreased between t = 0 and t = 8, bacterial biomass increased considerably. After t = 3, bacteria started to decrease which induced accumulation in both of DOC pool. Along the longitudinal axis in the central water masses, DOC_L showed a sinus behavior decreasing and increasing between 0.91 and 1.28 mg C L^{-1} (Fig. 4). DOC_{SL} followed the same trend but varied with a much greater extend between 1.69 and 3.38 mg C L^{-1}. Overall, the model showed a high correlation (Pearson's r) between both observed and modeled DOC pools (DOC_{SL}, r = 0.89, DOC_L, r = 0.84) and bacterial biomass (r = 0.84).

Carbon pathway

The relative contribution of principal mechanisms has been assessed by comparing their effect on the net balance of both DOC pool between t = 0 and t = 24. Along the longitudinal axis, primary production contributed to increase DOC_L and DOC_{SL} by 12.74 and 8.5 mg C respectively. Photodegradation removed 0.0029 mg C to DOC_{SL} which were transferred to DOC_L. Carbon release upon bacterial death increased DOC_L and DOC_{SL} by 0.013 and 0.247 mg C respectively. Bacterial carbon demand (uptake) removed 12.17 and 13.07 mg C from DOC_L and DOC_{SL}.

Relative contribution of kinetic processes shown by the sensibility analysis

Because the model has a total of 21 parameters, the sensibility analysis produced many different scenarios (Fig. 5). Therefore, to avoid excessing wording, only principal results will be presented in this section. Among the three state variables (B, DOCL, DOCSL), DOCSL showed the highest variability following sensibility analysis (Fig. 5B). Primary production (Ptot) was an important driver of the biomass of heterotrophic bacteria (Fig. 5A). Maximum growing rate of bacteria on both DOC pool (kg,max(L), kg,max(SL)) showed different patterns. Indeed, following an increase in bacterial maximum uptake rate, each pool diminished with a predominant effect on DOCSL. Inversely, decrease of bacterial maximum uptake rate induced important accumulation in both pool of DOC. However, decreasing in kg,max(L) caused bacterial biomass to diminish considerably whereas a decrease in kg,max(SL) had no influence on bacterial biomass. In the same manner but with inversed trend, half-saturation constants (ks(L), ks(SL)) affected both pool of DOC but with a greater effect on DOCSL. Bacterial decay rate (mortality, dr) had huge impacts on dynamic of the three state variables. Bacterial mortality increased both pools of DOC in the same order of magnitude. However, upon death of bacteria variation in the release of carbon cell content did not cause any significant changes to either the DOC (ε) or the labile pool (ß). Varying the fractions of Ptot (φ1, φ2) going into DOCL and DOCSL had primary effect on DOCSL pool. Accordingly, increasing φ1 did not increased DOCL while bacteria biomass increased by 73%. The coefficient yield (or the BGE, Φ1) associated with DOCL pool showed to be an important mediator of this substrate. Finally, increasing photodegradation rate (a0) caused a weak decrease in DOCSL and a slight augmentation of the bacterial biomass (not visible on Fig. 5).

Discussion

Mechanistic modeling of DOC: an integrative approach to the DOC cycling in natural aquatic systems

To the best of our knowledge, this mechanistic model is the first attempt to integrate the key processes which operate in the global biogeocycling of DOC in a large fluvial lake system characterized by a complex hydrodynamic regime. It integrates simultaneously the spatial discontinuities (via the residence time) occurring along the longitudinal axis and the principal gains and losses processes involved in DOC dynamic. In our modeling approach, the measured variables in relation with DOC (Table 2) fall in range within a large set of lakes and rivers and are thus representative of freshwater ecosystems (Table 1; Smith and Prairie (2004) and in Wu et al. (2005), Table 2; Mulholland (1997)). This is suggesting that comparable sources and processing are involved in the dynamic of DOC from a variety of freshwater environments and ultimately validate the applicability of our model to a broad range of inland waters. This study reveals that the tested mechanistic model was highly efficient at predicting, both in quality and in quantity, the spatial distribution of DOC flowing in a large fluvial lake (DOC_{SL}, r = 0.89, DOC_L, r = 0.84, B, r = 0.84). This underscore that the selected model structure (i.e. how the carbon fluxes were directed between compartments, Fig. 3) was able to capture the global dynamic of the DOC cycling. Moreover, phytoplankton primary production has been shown to represent the main input of the DOC_L (60%) and DOC_{SL} (40%). For both pools, bacterial consumption was the principal pathway of degradation. Indeed, between t=0 and t=24 approximately the same amount of both DOC pools has been utilized by bacteria. However, we noted a clear preference of heterotrophic bacteria to use DOC_L for biomass production compared to DOC_{SL} which was mostly burned into CO_2. Such results have also been reported in mesocosm experiments (Amado et al. 2006; Kritzberg et al. 2005; Kritzberg et al. 2006a), open oceans, lakes (Ask et al.

2009; Berggren et al. 2010; Stenuite et al. 2009) and stream systems (del Giorgio and Pace 2008; Williams et al. 2010).

Solving the relative importance of kinetic processes by the sensitivity analysis

Search for the optimal parameter values has been constrained to domain boundaries observed in natural systems (min-max) taken from literature (Table 2). This process constitutes a crucial step toward achieving mechanistic models with biologically interpretable parameters. Furthermore, we tested how each parameter affected the biogeocycling of DOC using sensibility analysis. For instance, a sensitivity analysis allows the measurement of the net fluxes between compartments which gives insight on how the carbon flows in the model. This involves observing how the state variables change as the parameters and forcing functions are varied (Chapra 1997). By investigating the "relative sensitivity" of model parameters, a user can become knowledgeable of the relative importance of parameters in the model. In our model, the sensitivity analysis (Fig. 5) showed that increase and decrease in parameters had drastic impacts on the three state variables. Accordingly, the following paragraphs discuss about the important parameters influencing the behavior of each of these state variables (B, DOC_L, DOC_{SL}).

Dynamic of dissolved organic carbon

Along the longitudinal axis of the lake, we observed sinusoidal behavior in the spatial distribution of both DOC pools (Fig.4). Yet, the minimum peak of DOC_L was observed 4h before the once occurring on DOC_{SL} suggesting that the labile fraction of the total DOC pool is the favorite form consumed by bacteria. Because the modeling presented here was done before the outlet of the LSP, we did not observed any change between the relative contributions of both DOC pools along the longitudinal axis. However, recent study using fluorescence and PARAFAC analysis on DOM (Massicotte and Frenette 2011), showed discrepancies in the relative abundance of both DOC pools further downstream of LSP. This is reinforcing the idea that most DOC_{SL} comes from lateral water mass inputs and that additional efforts (such as those provided by Mladenov et al. (2007)) should be devoted to understand mechanisms involved in lateral transport of DOC. This would greatly improve the fitting of DOC_{SL} (Fig. 4) especially at the outlet of LSP (Fig. 1) where strong lateral mixing can be observed (Frenette et al. 2012).

Dynamic of bacteria

As both pools of DOC decreased between $t = 0$ and $t = 8$, bacterial biomass increased slightly. From t = 3, bacteria started to decrease which promoted the accumulation of DOC until bacterial biomass started to increase again. This 'prey-predator' behavior is typical of systems relying on the principle of carrying capacity (Lotka 1925; Volterra 1926). Although following this prey-predator dynamic, bacteria showed the highest discrepancy between the modeled and observed values of the three state variables (Fig. 4). Indeed, the minimum peak of observed bacterial biomass occurs at t=18 whereas the same peak occurs at t = 14 for the modeled series. We hypothesize that this 4 hours lag in both peaks (Fig. 4) is caused by variations in bacterial uptake rates with the quality of DOC. Recent studies have pointed out the influence of DOC composition (i.e. quality) on the bacterial community structure (Cottrell and Kirchman 2000; Kritzberg et al. 2006b). Therefore, such potential differences in community structure could lead to contrasting rates of uptake and/or utilization of both labile and semi-labile pools of DOC. Pelagic bacterial obtain their carbon content most exclusively from DOC of either terrestrial or in situ origin (Cole et al. 2006) but it is known that they can also rely (to a lesser extend) on particulate organic carbon to fulfill their carbon demand (Barnard et al. 2006; del Giorgio and Pace 2008). Therefore, this missing compartment in our model could explain why we observed this difference between biomass of observed and modeled bacteria (Fig. 4).

In that context, further research is needed to assess the coupling between the structure and the function of bacterial communities.

As shown by the sensibility analyses, many variables related to the dynamic of in situ DOC (DOC_L) caused important shift in the bacterial biomass (Fig. 5). For example, decreasing $kgmax_L$ caused an important diminution of bacterial biomass whereas decreasing $kgmax_{SL}$ had no effect on bacterial biomass. This is suggesting that the DOC_L pool is composed of molecules readily usable by heterotroph bacteria and converted into biomass as opposed to the DOC_{SL} which is mostly burned into CO_2. Our results support this hypothesis that the bacterial community firstly rely on labile DOC and eventually switch to the semi-labile DOC pool when the labile DOC is no longer available in sufficient quantity. This is demonstrated by the sensitivity analysis which examined the contrasting effect of both coefficient yields on the bacterial density. Increasing both BGE (Φ_1 and Φ_2) caused the same effects on DOC_L pool (i.e. a diminution, Fig. 5B). However, increasing Φ_2 caused a non-intuitive accumulation of DOC_{SL} in the system (Fig. 5C) supporting the hypothesis that DOC_{SL} is mostly used once the bacterial carbon demand in DOC_L demand has been fulfilled. Then, DOC_{SL} simply accumulates and transferred afterwards along the longitudinal axis. This could explain why DOC_{SL} was shown to increase in the St. Lawrence River along the longitudinal axis (Massicotte and Frenette 2011). Therefore, we hypothizese that during period of maximum growth in LSP, the global carbon dynamic (and, consequently, the carbon transfer at higher trophic level) is driven by the processing of DOC_L (i.e. priming effect by which the availability of labile substrate promote utilization of more recalcitrant source of C, see Heimann and Reichstein (2008)). This finding is also in agreement with a growing literature that tend to prove that bacteria can rely on more recalcitrant DOC when labile DOC is present in insufficient quantity to support bacterial growth (Bade et al. 2007; Cole et al. 2006) even though this pool is of less nutritional quality as demonstrated by lower bacterial growth efficiency (BGE) (del Giorgio and Cole 1998; Kritzberg et al. 2005;

Kritzberg et al. 2006a). Furthermore, recent studies from lake productive environments, revealed that DOC from in situ production could potentially support all bacterial production (Berggren et al. 2010) reinforcing the idea that only a very small fraction of the semi-labile pool tend to reach higher trophic level when DOC_L is abundant (Kritzberg et al. 2005). Our results are also pointing into this direction since both pools of DOC have been used for cell production with great discrepancy (DOC_L 0.2738 mgC, DOC_{SL} 0.0203, which is approximately a factor of 13).

Phytoplankton primary production

Even though primary production was not directly measured, a releasing rate of 1.6 mg C m^{-2} h^{-1} (Table 2) was obtained by multiplying primary production (*Ptot*) with percent of extracellular release (*PER*), which is also consistent with measures made in the nutrient-rich waters of the Muse river (Belgian) by Descy et al. (2002). Primary producers (phytoplankton,macrophyte and epiphyte) are known to be important sources of labile DOC of high quality fulfilling bacterial demand and increasing BGE. Koch et al. (2007) have shown a strong correlation between heterotrophic bacterial production and algal production in large freshwater rivers. Therefore, we can hypothesize that a large fraction of the exuded material by primary producer is continuously replenishing the DOC_L pool. This can be confirmed by analyzing the parameterization process (Table 2) and the sensibility analyses (Fig. 5) where a large fraction (φ_1 = 60%) of algal exudate was directly incorporated into the DOC_L pool.

Sensitivity analysis also showed that an increase of 50% of φ_1 induced an augmentation of the DOC_{SL}. This is suggesting that the increase in DOC_L was enough to support bacterial growth and ultimately caused augmentation in less optimal food (DOC_{SL}) in the system. Although contributing for less, primary production by phytoplankton showed to be an important source of DOC_{SL} pool (φ_2 = 40%). Because we did not take lateral mixing into account (i.e. DOC_{SL} inputs form the surrounding water masses), we believe that the contribution of primary producer to DOC_{SL} has been slightly overestimated during the calibration process although high contributions (ranging between 20% and 35%) have nevertheless been reported in the literature (Lapierre and Frenette 2009; Maki et al. 2010; Romera-Castillo et al. 2010). However, those results are in contradiction with Anderson and Williams (1999) who found an inverse pattern where a minor fraction (14%) of DOC from primary production excretion were directed into the labile DOC pool and a larger fraction (41%) directing to the semi-labile pool.

Photodegradation

Photomineralization of DOC to dissolved inorganic carbon (CO_2) was shown to be a major pathway for the terrestrially derived DOC (Miller and Zepp 1995; Wang et al. 2009) although most ecosystem based-models do not address such processes (Christian and Anderson 2002). A relatively recent literature demonstrated that UV radiation on riverine DOC was substantially altering the bulk of DOC which in turn has an important impact on bacterial carbon demand and ecosystems carbon budget (Amado et al. 2006; Smith and Benner 2005; Spencer et al. 2009). Although still debated (Benner and Ziegler 1999), the most probable effect of UV photodegration is proposed to enhance bacterial uptake by producing more labile substrate. Conversely, a decrease in BGE following UV-radiation of DOC has also been reported (Bianchi et al. 2004). In this model, photodegradation contribution to DOC cycling represented roughly 23% of bacterial respiration.

The absence of important effect of photodegradation in our model and the subsequent lack of good fit of DOC_{SL} at the exit of LSP can be explained by two hypotheses. First of all, the transport of DOC in the central water mass of LSP is very rapid (24h) which certainly does not allow sufficient time for photodegratation to occur. In other large river systems, much longer residence time have been observed. For example, in Congo river, a 57-days photodegradation experiment has shown that the major loss of DOC took place during the first 12 days of irradiation in the solar simulator (Spencer et al. 2009). This is also supported by recent studies in the Mackenzie River where the half-lives of CDOM and DOC were estimated to 3.7 days and 4.8 days, respectively under full sunlight conditions (Osburn et al. 2009). Secondly, the DOC entering LSP through the central water mass constitutes an old, uncolored and refractory pool of DOC coming from Greats Lakes ($2 < \tau_w < 200$) characterized by an already long history of photodegradation from its source diminishing the probability of photodegradation to take place.

Consequences of the hydrodynamic regime

Hydrogeometry characteristics (velocity, flow, dispersion, depth, width, cross-sectional area and slope) are among the principal factors influencing the dynamic of water current flow and the displacement of water body (Chapra 1997). These parameters (characteristics) hence play important roles in the DOC cycling by determining how long the matter will remain in the system. The feedforward approach used in this study allowed to precisely characterize the residence times resulting from the complex bed topography of LSP and adequately describes the enormous hydrodynamic heterogeneity of LSP. For example, along a particular streamline (central water mass, Fig. 1) 24-h was needed to transport the DOC pool from entrance to exit of LSP. Divided into 25 sections, this streamline showed residence time varying between 0.7 and 2 hr which constitutes a large domain of variation and shows to be adequately described by our fine-scale hydrodynamic approach. Therefore, an appropriate spatial and temporal representation of the hydrologic regime in large river is crucial to fully understand how the DOC is processed in such heterogeneous systems (Massicotte and Frenette Submited).

Here, for sake of simplicity, we modeled DOC dynamic in a low-water period which showed to be stable over the time of the modeling. However, hydrodynamic regime in large rivers can be very dynamic especially during flood or high discharge events. Furthermore, our hydrodynamic model (Massicotte and Frenette Submited) did not account for the lateral mixing between water masses. During springtime, flooding greatly increase the aquatic/terrestrial contact (Vincent and Dodson 1999) and the potential input of DOC of terrestrial origin. This could ultimately modify the balance between in situ (DOC_L) and terrestrial DOC (DOC_{SL}) in the aquatic system. Indeed, lateral exchanges by dispersion and diffusion certainly occurs in most large river systems and which have to be taken into account for the interpretation of the modeled DOC dynamic. Additional analyses of the consequences of hydrodynamic regime in period of high variability are thus needed and constitute future challenges for modelers.

Conclusion

Our mechanistic model for DOC dynamic in freshwater ecosystems represents a basic framework to understand the biogeochemical cycling of DOC in such heterogeneous systems. Obviously, more compartments (zooplankton, nutrients cycling) should be added to our ecosystem based-model to fully understand the potential role of all actors implied in DOC dynamic. Therefore, complementary attempt to redefine some black-boxes in our model could be deployed. For example, instead of using simple constant death rate of bacteria (*dr*), one would try model the grazing by zooplankton. However, as in all models, efforts should be dedicated to keep the model as simple as possible to maintain the level of abstraction sufficiently high to avoid unnecessary details that could mask the basic assumptions regarding the global biogeocycling of DOC in freshwater environments. The model structure, the selected kinetic processes and the hydrodynamic model used here showed to be relevant for predicting the spatial distribution of both DOC pools in a low level water period. We believe that this mechanistic model provides a framework that can be easily extended to take into account the seasonal variations and related environmental changes occurring in aquatic ecosystems such as water level fluctuations or growing phases (i.e. senescence) of macrophytes (Lapierre and Frenette 2009) which are known to influence the DOM dynamic. Additionally, the feedforward approach used (Fig. 2) can be easily adapted to a more complex connectivity scheme such as presented in Massicotte and Frenette (2011).

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Figure Legends

Fig. 1. Distribution of water masses (August of 2006) within Lake Saint-Pierre according to their spectral characteristics (see Material and Methods for details).

Fig. 2. Approach used to model DOM dynamic. Panel A: Feedforward system illustrating the displacement of the DOC pool in a succession of five CSTR along a streamline (black thick arrow) in Lake Saint-Pierre. Panel B: schematic representation of the feedforward system. The duration of each mechanism in each CSTR is determined by calculation of residence time. Time of transition of DOC pool in each CSTR was determined by a 2D hydrodynamic model (velocity field) (Massicotte and Frenette submitted).

Fig. 3. Flow diagram of the model including state variables (gray rectangles) and parameters describing the distribution of the flow between DOC pools and bacteria. Parameters and variables descriptions can be found in Table 1.

Fig. 4. Carbon content of bacteria, DOC_L and DOC_{SL} over their course along the central streamline in Lake Saint-Pierre (24 hours duration). Filled symbols represent observed values at transect 1, 2, 3 and 4 (see Fig. 1). Open symbols are the modeled data using cubic splines. Lines are the modeled results using mechanistic model (see Eq. 1, Eq. 2 and Eq. 3).

Fig. 5. Sensibility analysis to varying parameters +50% (gray) or -50% (black) for the 3 state variables (DOC_{SL}, DOC_L and B).

Table 1. Sampled variables.

Station	Bacteria (Cells mL^{-1})			Chla	aCDOM (m^{-1})		DOC	$K_{d(UVA)}$
	HNA	LNA	Total	(μg L^{-1})	340nm	440nm	(mg L^{-1})	(m^{-1})
20	1.52E+04	7.45E+05	2.63E+06	4.09	3.15	0.55	4.63	3.99
21	1.25E+04	9.87E+05	2.40E+06	1.45	7.55	1.44	3.96	6.47
22	6.35E+03	1.99E+06	3.55E+06	4.23	31.43	5.61	10.48	11.01
23	1.87E+04	7.11E+05	2.31E+06	7.01	5.58	0.98	3.69	12.05
24	1.55E+04	6.18E+05	2.42E+06	2.98	2.63	0.44	2.59	5.84
25	1.45E+04	6.81E+05	2.06E+06	1.51	3.38	0.62	2.83	4.57
26	1.33E+04	6.45E+05	1.69E+06	2.27	8.76	1.53	4.46	6.42
27	1.86E+04	6.72E+05	1.77E+06	4.94	11.92	2.17	5.58	11.41
28	5.72E+03	7.88E+05	2.30E+06	3.79	15.30	2.75	6.00	12.10
29	2.50E+04	1.01E+06	2.61E+06	NA	20.95	3.77	7.91	11.81
30	2.07E+04	6.05E+05	1.95E+06	6.69	6.86	1.24	4.49	5.32
31	2.72E+04	6.64E+05	2.41E+06	4.84	3.24	0.60	2.82	5.62
32	1.47E+04	5.68E+05	1.81E+06	1.65	3.00	0.54	3.97	4.10
33	1.39E+04	5.31E+05	1.47E+06	2.67	5.81	0.95	3.98	7.70
34	1.35E+04	6.49E+05	1.79E+06	2.80	9.78	1.78	4.79	7.50
35	9.15E+03	9.87E+05	3.39E+06	4.54	14.85	2.64	6.00	9.58
36	1.71E+04	5.04E+05	2.15E+06	2.16	4.05	0.52	3.31	7.05
37	2.05E+04	6.06E+05	2.20E+06	2.06	4.89	0.74	3.40	0.29
38	1.61E+04	3.63E+05	1.13E+06	1.84	24.08	4.52	7.41	12.07

Table 2. Model parameters and state variables. Initial guesses for parameter values are from literature. References are as follow: (I) Anderson and Williams (1999), (II) Anderson and Williams (1998), (III) Connolly et al. (1992), (IV) Chapra (1997), (V) Kritzberg et al. (2005), (VI) Wu et al. (2005), (VII) Vis et al. (2007), (VIII) (Okpokwasili and Nweke 2006), (VIV) Christian and Anderson (2002), (X) Carlson (2002), (XI) Okpokwasili and Nweke (2006). PP stands for primary production. The min and max parameter values have been used to constrain the domain of search during the optimization process.

Symbol	Description	Units	Values Initial guess (min-max)	Optimized
Parameter				
β	Fraction of bacterial mortality to DOC_L	%	0.1 (0.01-0.5)	0.02
Φ_1[V, VIII, VIV, XII, XIII]	Bacteria gross growth efficiency on DOC_L	Unitless	0.5 (0.12-0.804)	0.46
Φ_2[V, VIII, VIV, XII, XIII]	Bacteria gross growth efficiency on DOC_{SL}	Unitless	0.1 (0.07-0.3)	0.18
$Ptot$[VII]	Primary production	mg C m^{-2} h^{-1}	10.46 (6.7-11.51) variable	9.43
PER[I, VIV, X]	Percentage of extra-cellular released by $Ptot$	%	0.2181 (0-80)	0.40
φ_1[I, II, XIII]	Fraction of $Ptot$ to DOC_L	%	0.82 (0.2-0.90)	0.6
φ_2[I, II, XIII]	Fraction of PP to DOC_{SL}	%	0.18 (0.10-0.6)	0.4
ε[I]	Fraction of bacterial mortality to DOC	%	0.51 (0-1)	0.62
$k_{s(L)}$[I, II, III, XI]	Half-saturation constant of DOC_L	mg C L^{-1}	0.3 (0.1-115.02)	0.91
$k_{s(SL)}$[I, II, III, XI]	Half-saturation constant of DOC_{SL}	mg C L^{-1}	5 (0.1-115.02)	2.6
$k_{g,max(L)}$[I, II, III, IV, XI]	Maximum growth rate on DOC_L	hr^{-1}	0.55 (0.024-1.013)	0.76
$k_{g,max(SL)}$[I, II, III, IV, XI]	Maximum growth rate on DOC_{SL}	hr^{-1}	0.17 (0.024-1.013)	0.09
dr[I,II]	Bacteria death rate (mortality)	hr^{-1}	0.01 (0.005-0.05)	0.04
$K_{d(UV)}$	UV-light attenuation coefficient	m^{-1}	measured - variable	
Z_{max}	Maximum depth	m	measured - variable	--
k_1^{DIC}	Fitting parameter for calculation of $\emptyset_{DIC}$	Unitless		
k_2^{DIC}	Fitting parameter for calculation of $\emptyset_{DIC}$	Unitless		
k_3^{DIC}	Fitting parameter for calculation of $\emptyset_{DIC}$	Unitless		
k_1^{BL}	Fitting parameter for calculation of $\emptyset_{BL}$	Unitless		

k_2^{BL}	Fitting parameter for calculation of $\emptyset_{BL}$	Unitless
k_3^{BL}	Fitting parameter for calculation of $\emptyset_{BL}$	Unitless
State variable		
DOC_L	Labile DOC	mgC L^{-1}
DOC_{SL}	Semi-labile DOC	mgC L^{-1}
B	Bacteria	mgC L^{-1}

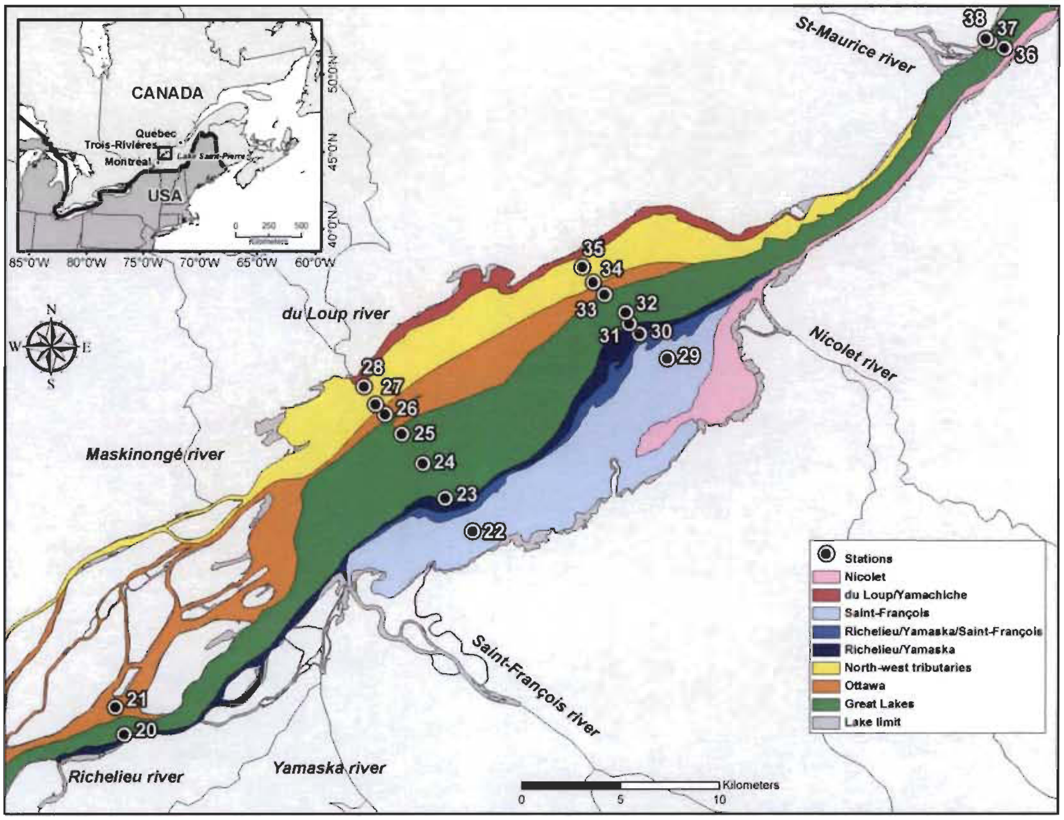

CANADA
Québec
Trois-Rivières
Montréal
Lake Saint-Pierre
USA
0 250 500
Kilometers
50°0'N
45°0'N
40°0'N
85°0'W
80°0'W
75°0'W
70°0'W
65°0'W
60°0'W
N
S
W
E
St-Maurice river
du Loup river
Maskinongé river
Nicolet river
Saint-François river
Yamaska river
Richelieu river
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
Stations
Nicolet
du Loup/Yamachiche
Saint-François
Richelieu/Yamaska/Saint-François
Richelieu/Yamaska
North-west tributaries
Ottawa
Great Lakes
Lake limit
0
5
10
Kilometers

Fig. 1

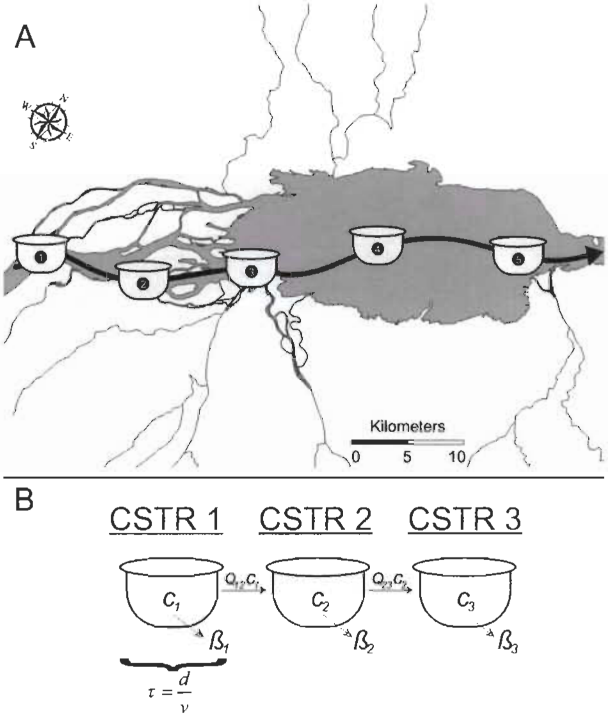

A
N
W
E
S
1
2
3
4
5
Kilometers
0
5
10
B
CSTR 1
CSTR 2
CSTR 3
C_1
Q_{12}, C_1
C_2
Q_{23}, C_2
C_3
β_1
β_2
β_3
$\tau = \frac{d}{v}$

Fig. 2

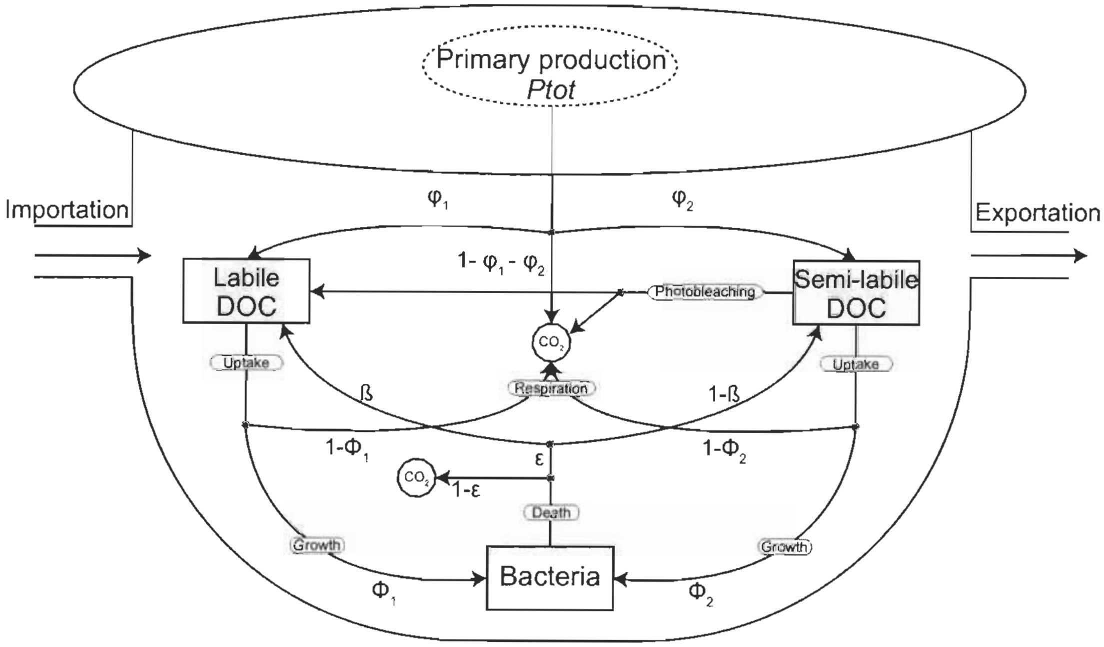

Primary production
Ptot
Importation
φ_1
φ_2
Exportation
$1- \varphi_1 - \varphi_2$
Labile DOC
Photobleaching
Semi-labile DOC
CO_2
Uptake
Uptake
ß
Respiration
1-ß
$1-\Phi_1$
ε
$1-\Phi_2$
CO_2
$1-\varepsilon$
Death
Growth
Growth
Bacteria
Φ_1
Φ_2

Fig. 3

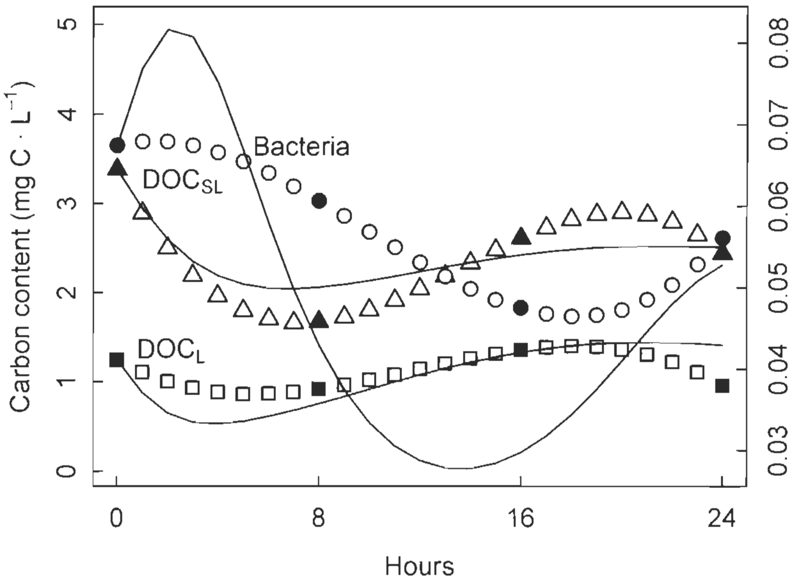
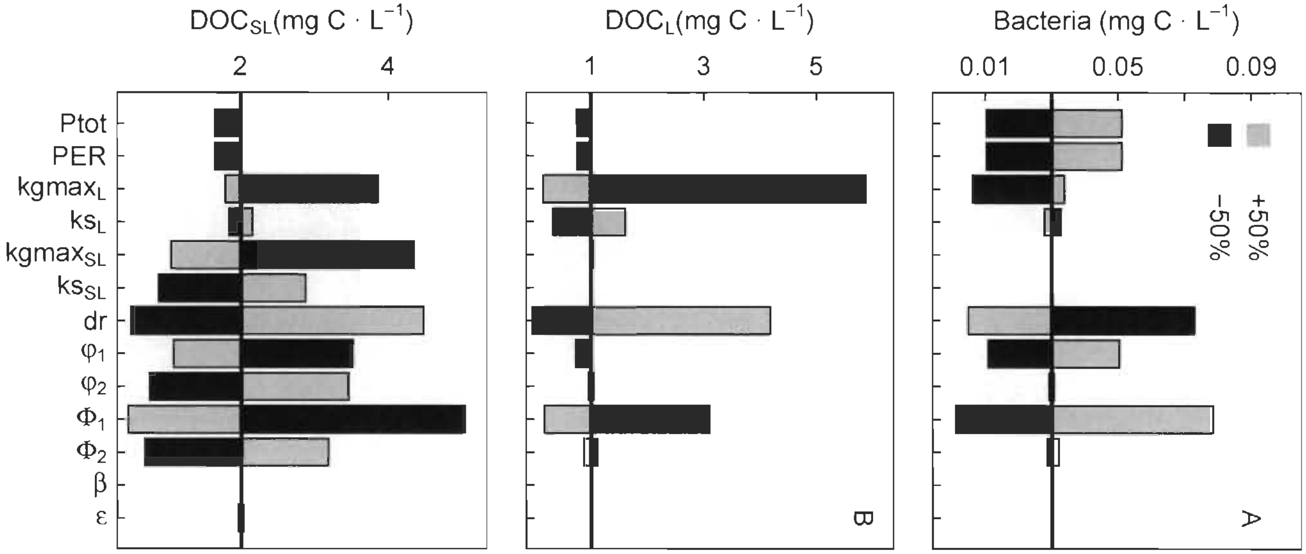

Carbon content (mg C · L^{-1})
5
4
3
2
1
0
0.08
0.07
0.06
0.05
0.04
0.03
Bacteria
DOC$_{SL}$
DOC$_L$
0
8
16
24
Hours

Fig. 4

Fig. 5


DOC$_{SL}$(mg C · L^{-1})
2
4
DOC$_L$(mg C · L^{-1})
1
3
5
Bacteria (mg C · L^{-1})
0.01
0.05
0.09
Ptot
PER
kgmax$_L$
ks$_L$
kgmax$_{SL}$
ks$_{SL}$
dr
φ_1
φ_2
Φ_1
Φ_2
β
ε
B
A
+50%
−50%

DISCUSSION GÉNÉRALE

Synthèse et contributions scientifiques de la thèse

La compréhension du fonctionnement des écosystèmes terrestres et aquatiques est un des objectifs ultimes de l'écologie. Si nous pouvons tirer des conclusions intéressantes et même cruciales des observations empiriques (observations faites sans aucune idée préconçue et dans le seul but de constater les faits sans chercher à les comprendre), il demeure néanmoins que celles-ci fournissent peu d'éléments de réponse quant à la mécanique œuvrant derrière les phénomènes observés. Afin de pallier à cette lacune, les écosystèmes ont commencé à être considérés selon une perspective mathématique et orientés sur les mécanismes qui les régissent (Lotka 1925, Volterra 1926). Les observations empiriques combinées aux approches d'analyses numériques ont été utilisées dans cette thèse afin d'étudier la dynamique de la matière organique dissoute (MOD) et de son principal constituant, le carbone organique dissous (COD) en milieu fluvial (Fig. 1). Plus précisément, cette thèse doctorale examine les conséquences de la connectivité spatiale, de l'hétérogénéité environnementale et du régime hydrodynamique sur la dynamique de la matière organique dissoute dans le fleuve Saint-Laurent (FSL).

L'étude de la MOD a pris son essor en milieu océanique dès le début du 20^{e} siècle (Pütter 1909) bien que les premières découvertes fondamentales virent le jour plus tard (Waksman 1933, Waksman and Carey 1935a, b, Kalle 1949). De fait, les écosystèmes d'eau douce, en particulier les rivières, ont longtemps été considérés comme de simples vecteurs de matière organique vers les océans tel qu'en témoigne la disparité entre les références citées dans cette thèse provenant des écosystèmes d'eau douce et marins. Or, les grands fleuves transportent d'importantes quantités de MOD (Hedges et al. 1997) composée de molécules appartenant à différentes classes chimiques (humiques et protéiniques) et ayant des dynamiques de production et de transformation contrastées (Massicotte and Frenette 2011). Toute transformation affectant les différentes classes de MOD peut avoir des conséquences importantes au niveau du fonctionnement des écosystèmes aquatiques (Prairie 2008, Battin et al. 2009).

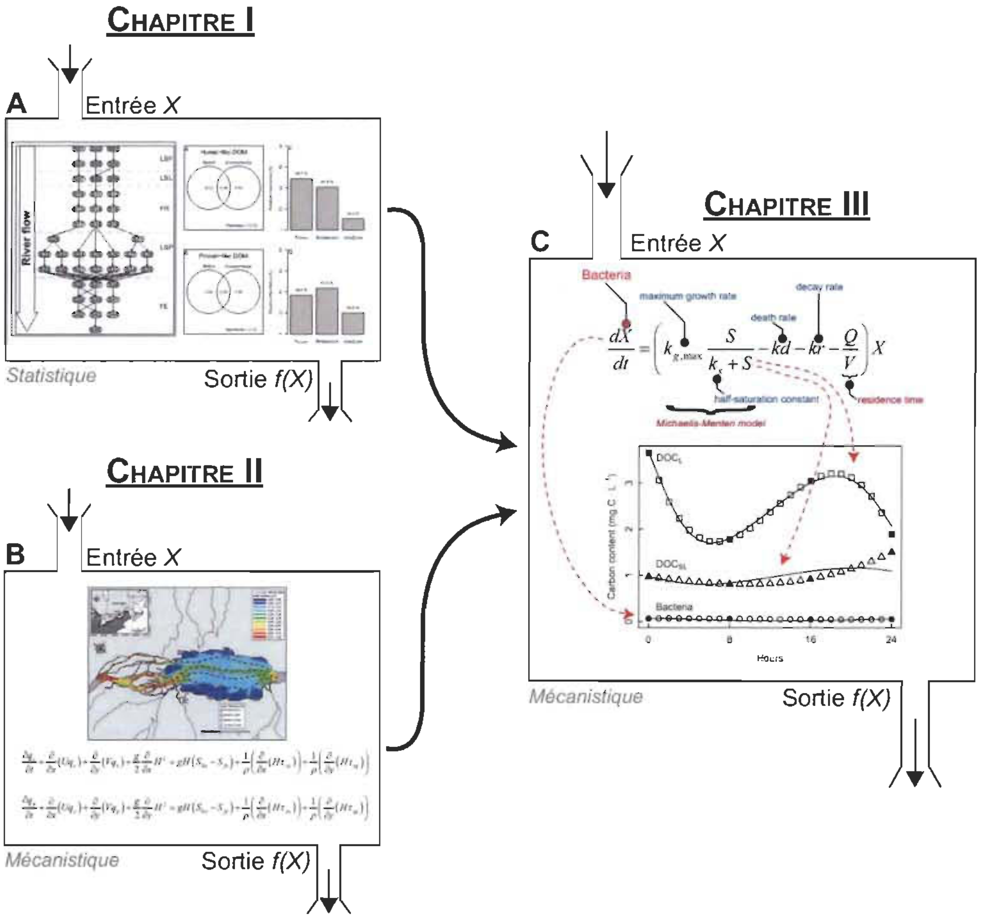


Figure 1 : Les nombreuses masses d'eau du FSL liées au réseau de tributaires sont à l'origine de la connectivité observée entres les habitats (A). Le régime hydrodynamique du LSP est parsemé de discontinuités qui influencent le déplacement de la MOD et de la durée d'action des différents processus impliqués dans son cycle biogéochimique (B). La dynamique complexe de la MOD implique divers processus de production et de transformation opérants simultanément, mais de manière contrastée en fonction des conditions environnementales et de la composition chimique de la MOD (C).

Par exemple, en tant que médiateur de la quantité et de la qualité de la lumière dans la colonne d'eau, la fraction chromophorique de la MOD (CDOM) joue un double rôle. D'une part, elle atténue les rayons UV généralement nuisibles aux organismes aquatiques (Morris and Hargreaves 1997, Zhang et al. 2007, Boily et al. 2011). D'autre part, lorsqu'en grande quantité, elle limite la pénétration de la lumière dans la colonne d'eau et donc la croissance des organismes photosynthétiques tels les macrophytes et le phytoplancton. De plus, de par son influence sur le métabolisme microbien, la composition chimique de la MODjoue un rôle déterminant au sein des cycles biogéochimiques des éléments et conditionne le transfert de matière et d'énergie le long des chaines trophiques ainsi que la balancemétabolique (c.-à-d. l'importance relative des processus autotrophes et hétérotrophes) des écosystèmes aquatiques (Grey et al. 2001, Daniel et al. 2005, Jansson et al. 2007, Prairie 2008, Fellman et al. 2010). Cependant, le fonctionnement des écosystèmes fluviaux a rarement été considéré au regard de l'importance conjointe de la quantité et de la qualité de la MOD (Jaffe et al. 2008, Fellman et al. 2010).

Chapitre I

Les travaux fondamentaux de Bro (1997) et de Stedmon et al. (2003) concernant la caractérisation physicochimique de la MOD à l'aide de techniques de décomposition spectrale ont ouvert de nouvelles perspectives de recherche relatives à l'étude de la composition et de la dynamique de la matière organique dissoute. De plus, de nouvelles méthodes d'analyses statistiques (Blanchet et al. 2008b) permettent aujourd'hui de mieux discriminer l'importance de la connectivité spatiale au sein d'environnements où l'hydrologie exerce un forçage majeur sur la distribution de la matière organique.

Afin de caractériser le réservoir complexe de MOD dans le FSL provenant d'une grande diversité de sources, nous avons utilisé une technique de décomposition spectrale (*parallel factor analysis*, PARAFAC) (Stedmon et al. 2003). Cette technique requiert un maximum de matrices de fluorescence 3D (EEM), idéalement avec des signatures spectrales hétérogènes, afin de décomposer convenablement le signal de fluorescence de la MOD (Stedmon and Markager 2005a, Stedmon and Bro 2008, Fellman et al. 2009c). Les études récentes en milieu fluvial ou côtier n'utilisent qu'un nombre réduit de matrices 3D de fluorescence (Holbrook et al. 2006, Wang et al. 2007, Williams et al. 2010, Bertolosh and Pepinosh 2011) limitant ainsi la capacité à bien capter toute la variabilité présente dans le signal de fluorescence et ainsi à bien discriminer l'ensemble des molécules composant le réservoir de MOD. Au meilleur de nos connaissances, la diversité des sources de matrices 3D et le nombre important d'échantillons qui composent notre base de données demeurent les plus complets en milieu d'eau douce ($n = 1100$, Tableau 1; Massicotte and Frenette (2011)). Cette diversité de sources a permis d'obtenir une décomposition spectrale très fine identifiant certaines classes de MOD qui n'étaient pas discriminées par les études précédentes. Sept composantes ont ainsi été identifiées à l'aide de la modélisation PARAFAC. Pour simplifier l'interprétation, ces sept composantes ont été classées selon deux grandes classes de MOD : la MOD de type humique d'origine terrestre (essentiellement importée par les tributaires), donc externe au système fluvial, et la MOD de type protéinique « fraichement » produite in situ par les organismes photosynthétiques (phytoplancton et macrophytes). Afin de déterminer les rôles de l'hétérogénéité environnementale et de la connectivité spatiale sur la distribution de ces deux classes de MOD dans le FSL (objectif principal du chapitre I), nous avons élaboré deux modèles. Le premier traite de l'effet environnemental en considérant les variables clés impliquées dans la dynamique de la MOD. Le second modèle détermine l'effet de la connectivité sur le patron de distribution spatial de la MOD.

Les analyses statistiques utilisées dans cette étude ont démontré que les bactéries hétérotrophes ayant une forte croissance, le coefficient d'atténuation des UV ($K_{d(UV)}$) ainsi que la température étaient les meilleurs prédicteurs de la MOD d'origine terrestre et aquatique parmi un ensemble de variables environnementales à notre disposition. Afin d'éliminer les biais potentiels d'autocorrélation spatiale, nous avons supprimé l'influence de la connectivité sur la distribution de la MOD. L'un des principaux résultats est que les bactéries hétérotrophes ayant une croissance rapide sont plus corrélées à la MOD aquatique de type protéinique par un facteur de deux par rapport à la MOD de type humique d'origine terrestre. En cohérence avec de nombreuses études précédentes, notre étude met en évidence la préférence des bactéries hétérotrophes pour la MOD labile, probablement fraichement produite par le phytoplancton et les macrophytes (Baines and Pace 1991, Benner 2003, Kritzberg et al. 2005, Koch et al. 2007, Stenuite et al. 2009). Nos résultats sont également en accord avec ceux de Kritzberg et al. (2005), qui ont utilisé la simulation numérique et qui ont mis en évidence que la MOD protéinique était deux fois plus disponible (assimilable) pour les bactéries que les sources terrestres de MOD.

Nous démontrons également, au moyen d'approches géostatistiques récentes (Blanchet et al. 2008b), que la connectivité asymétrique engendrée par le régime hydrodynamique joue un rôle prépondérant dans la distribution spatiale de la MOD des grands fleuves. En effet, le déplacement des masses d'eau, en lien avec le réseau de tributaires du FSL, détermine le patron de distribution de la MOD. Contrairement à d'autres grandes rivières ayant moins d'apports de matière organique par les tributaires (del Giorgio and Pace 2008), nous avons noté une augmentation longitudinale relativement continue, mais d'amplitudes différentes, des deux grandes classes de MOD. Ceci suggère que la structure du bassin versant joue un rôle important en termes d'apport de nouvelle MOD en dépassant les pertes liées à différents mécanismes tels que la consommation bactérienne, la photodégradation, la sédimentation et la floculation. La production primaire, particulièrement importante dans le LSP (Vis et al. 2007), laisse également croire à une production de MOD d'origine aquatique de type protéinique supérieure aux pertes. Celle-ci augmente en fait sur le plan longitudinal, mais de manière beaucoup plus modérée que la MOD humique. Dans les deux cas, ces résultats suggèrent que la production de MOD (gains) surpasse les pertes.

En accord avec nos hypothèses, la connectivité hydrologique observée dans le FSL influence davantage la distribution spatiale de la MOD humique d'origine terrestre que celle de la MOD produite *in situ*. Cela peut être expliqué par le fait que la MOD terrestre est essentiellement introduite dans le FSL par le biais des tributaires qui sont par définition structurés géographiquement. La nature réfractaire de la MOD humique favorise donc son accumulation entre les différentes sections du FSL. D'autre part, la MOD protéinique produite *in situ*, de nature plus labile, est plus efficacement utilisée par les microorganismes hétérotrophes. Cette MOD est plus rapidement utilisée qu'elle n'est produite et sa distribution le long du FSL ne présente donc pas de patron d'accumulation importante. La dégradation bactérienne, la photodégradation et la connectivité spatiale influencent conjointement la dynamique de la MOD lors de son transport vers l'océan. La combinaison des modèles environnementaux et spatiaux a permis d'expliquer les patrons de distribution des deux classes de MOD avec une haute précision (85 %).

Chapitre II

Le régime hydrodynamique est au cœur du fonctionnement des grands fleuves. La plupart des travaux au sujet de l'hydrodynamique du FSL ont porté sur : (i) la partie supérieure à la sortie du lac Ontario (Tsanis and Murthy 1990, Brodeur et al. 2005); (ii) les archipels de Montréal (Leclerc et al. 1987), (iii) le lac Saint-Louis (Carballada 1982) et (iv) le corridor fluvial (Leclerc et al. 1990a, Leclerc et al. 1990b, Saucier et al. 2003).

Les lacs fluviaux sont des composantes importantes des grands fleuves où la bathymétrie présente de fortes variations. Par exemple, dans le lac Saint-Pierre (LSP, le plus grand lac fluvial du FSL), la bathymétrie passe rapidement de plus de 13 m dans une étroite zone centrale (chenal maritime) à moins de 3 m sur les 80 % restant de sa superficie. Bien que d'un point de vue physique il semble évident que les zones de faibles profondeurs, caractéristiquesdes lacs fluviaux, ne favorisent pas l'écoulement rapide de l'eau (et inversement pour les zones de forte profondeur), leur régime hydrodynamique demeure mal connu notamment en raison de cette géométrie (bathymétrie) plus complexe et plus variable que la plupart des rivières traditionnelles. Pour ces raisons, le rôle du régime hydrodynamique particulier des lacs fluviaux sur le cycle biogéochimique de la MOD n'est pas bien compris.

À ce jour, seules quelques tentatives de modèles hydrodynamiques pour les lacs fluviaux ont été proposées (Boudreau et al. 1994, Morin et al. 2000a, Morin et al. 2000b). De plus, les modèles existants n'ont pas été validés à l'aide de mesures de courants *in situ*. Le régime hydrodynamique des lacs fluviaux se doit d'être précisément étudié au regard de l'importance de ces lacs dans la dynamique et le fonctionnement d'un écosystème fluvial (Vincent and Dodson 1999, Frenette et al. 2006; 2012, Allan and Castillo 2007, Vis et al. 2007, Lapierre and Frenette 2008, 2009, Massicotte and Frenette 2011, Pinardi et al. 2011).

Considérant l'influence majeure de la connectivité hydrologique sur la distribution spatiale et la dynamique de la MODau sein du FSL (chapitre I) et afin de pallier au manque de connaissances concernantle régime hydrodynamique des lacs fluviaux, un modèle hydrodynamique 2D de fine résolution spatiale pour le LSP a été développé. Ce modèle prend en compte les caractéristiques bathymétriques du LSP ainsi que l'influence du réseau de tributaires De plus, le maillage adaptatif utilisé pour la discrétisation du LSP permet d'avoir un niveau de résolution spatiale suffisamment élevé pour étudier les conséquences du régime hydrodynamique sur à peu près n'importe quel processus biologique. Au meilleur de nos connaissances, ce modèle est le seul à avoir été directement calibré avec des mesures de courants prises en continu à l'aide d'un courantomètre à effet Doppler (*Acoustic Doppler Current Profiler* ou ADCP). La principale contribution de ce chapitre réside dans la démonstration de l'existence de discontinuités hydrodynamiques dans le LSP favorisant l'apparition de zones ayant des temps de résidences variant entre 19 heures pour le chenal et 41 heures pour les zones latérales où l'écoulement de l'eau est plus lent en période d'étiage (août 2006).

Ce modèle hydrodynamique a le potentiel d'être appliqué à divers axes de recherche puisque le régime hydrodynamique des systèmes aquatiques influence également : (1) la structure des communautés de macroinvertébrés benthiques (Statzner and Holm 1982, Statzner and Higler 1986), (2) l'abondance des producteus primaires (Janauer et al. 2010) telles que les macrophytes (Chambers et al. 1991) et (3) le périphyton (Biggs et al. 1999, Dodds and Biggs 2002, Trudeau and Rasmussen 2003), (4) la composition et les concentrations des communautés planctoniques (Hudon et al. 1996, Twiss et al. 2010), (5) la distribution des larves de poissons (Dettmers et al. 2005), (6) la déposition et le transport des sédiments (Haschenburger and Church 1998, Topping et al. 2005), (7) l'ostéogenèse des vertébrés (Cloutier et al. 2010), (8) le transfert d'énergie dans les chaînes alimentaires lotiques (Finlay et al. 1999, Allan and Castillo 2007) ainsi que sur la dispersion des polluants (Kim et al. 2009). En conséquence, la compréhension des modèles d'écoulement en rivière est cruciale, car elle a de nombreuses implications sur une variété de processus biologiques et leurs mécanismes proximaux.

Chapitre III

Dans ce dernier chapitre de thèse, nous avons tiré profit des résultats des deux premiers chapitres pour explicitement modéliser le cycle biogéochimique du carbone organique dissous (COD, principal constituant de la MOD) à l'aide des connaissances sur les processus fondamentaux impliqués dans sa production et dans sa transformation (Fig. 1). Les résultats du chapitre I ayant démontré les variables importantes impliquées dans le cycle de la MOD ($K_{d(UVA)}$, abondance des bactéries, température), nous avons précisé les principaux processus auxquels étaient liées ces variables. Les processus principaux liés à la dynamique du COD (production primaire, dégradation bactérienne, photodégradation) ont été explicitement modélisés à l'aide d'équations différentielles décrivant la nature non linéaire des interactions entre les diverses composantes du système. Afin de déterminer le déplacement et le temps de résidence du COD dans le LSP, nous avons utilisé le modèle hydrodynamique développé au chapitre II (Fig. 1). Le modèle développé dans ce chapitre III constitue un premier effort de modélisation de la dynamique du COD en milieu fluvial en combinant à la fois la cinétique (processus de production et transformation) et le transport à l'aide d'un modèle hydrodynamique (chapitre II).

L'ajustement des paramètres (paramétrisation) est une étape cruciale de la modélisation des modèles mécanistiques (Holzbecher 2007, Bolker 2008, Sokolowski et al. 2009, Barnes and Chu 2010). Il ne suffit pas qu'un modèle prédise efficacement pour être considéré valide (Connolly et al. 1992, Chapra 1997). Les valeurs des paramètres des équations qui composent le modèle doivent aussi demeurer entre certaines limites afin de conserver leurs caractères interprétables. Une revue de la littérature a permis de contraindre l'étendue des valeurs possibles des paramètres de notre modèle. L'interprétation de ces paramètres a mis en évidence plusieurs éléments importants liés au cycle biogéochimique du COD dans le LSP. Les principaux résultats de ce chapitre démontrent que le patron spatial des acides humiques est fortement contrôlé par les processus hydrologiques alors que le COD de type protéinique est plus étroitement lié à des processus biologiques tels que la production primaire et la consommation bactérienne. Contrairement à l'une des hypothèses originales, le temps de séjour très court du COD dans le LSP ne favorise pas une photodégradation importante de la fraction humique et réfractaire (provenant essentiellement des Grands Lacs) présente dans la masse d'eau centrale.

Perspectives de recherche

Améliorations futures du modèle

Le COD d'origine terrestre est reconnu pour être introduit en grande quantité dans le LSP via le système de tributaires. Ce substrat de nature réfractaire s'accumule de manière importante le long du FSL ce qui favorise les échanges latéraux entre les masses d'eau lors de sa transition vers l'océan. Puisque le processus de diffusion (tendance naturelle d'un système à rendre homogènes les concentrations chimiques en son sein[2]) n'est pas pris en compte dans notre modélisation, il se peut que la cinétique de photodégradation du COD d'origine humique ne soit pas totalement représentée telle qu'en témoigne la moins bonne capacité prédictive de notre modèle. La problématique précédemment évoquée concernant la sous-évaluation de la photodégradation du COD et l'absence de modélisation du mélange latéral entre les masses d'eau riveraines et centrales constituent des défis intéressants pour de futures recherches qui amélioreront notre compréhension du cycle biogéochimique du COD dans les systèmes hétérogènes tel que le FSL.

Caractérisation de la MOD

L'un des débats actuels en limnologie concerne la notion de labilité de la MOD (Hernes et al. 2007). En effet, la matière organique terrestre est généralement caractérisée comme étant de mauvaise qualité nutritive pour les bactéries hétérotrophes, car composée essentiellement de macromolécules difficilement assimilables (Jiao et al. 2010). Or, il semblerait qu'il serait plus approprié de classer le réservoir de MOD à l'aide des ratios stœchiométriques (Benner 2002, Lonborg et al. 2010) plutôt qu'à l'aide du poids moléculaire qui est présentement l'un des indicateurs standards. Par exemple, certaines études en milieux marins ont démontré l'existence des relations stœchiométriques suivantes; C:N = 16.7, C:P = 298,

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[2] *http://fr.wikipedia.org/wiki/Diffusion_de_la_mati%C3%A8re*

C:N:P = 298:18:1 (Benner 2002). Ces ratios laissent supposer que l'azote et le phosphore dissous, sélectionnés préférentiellement par les bactéries hétérotrophes, sont les éléments limitants du réservoir de MOD. Bien que l'utilisation des propriétés optiques de la MOD ait déjà été reconnue comme de bons traceurs de son origine (Coble et al. 1990, Coble 1996, Bro 1997, Stedmon et al. 2003, Murphy et al. 2010), des études en laboratoire sont nécessaires afin de lier la stœchiométrie aux analyses de fluorescence. D'autres approches basées sur les isotopes stables ont précédemment été envisagées (Finlay et al. 1999, Cole et al. 2006, Kritzberg et al. 2006a, Bade et al. 2007, Kaplan et al. 2008), ce qui permettrait de dater et de déterminer l'origine de la MOD et ultimement son degré de labilité.

L'analyse d'images

L'une des perspectives de recherche intéressante concernant la distribution spatiale de la MOD concerne l'utilisation des systèmes d'information géographique (SIG). Premièrement, il serait intéressant de caractériser le bassin versant du FSL (agriculture, pâturage, industrie, ville), car la majorité de la MOD entre dans le FSL par le biais des tributaires drainant ce bassin versant. Puisque les caractéristiques physiques et chimiques des tributaires sont intimement liées aux caractéristiques des bassins versant (Burton 1991, Centre Saint-Laurent 1996, Laviolette 2004, Frenette et al. 2006, Frenette et al. Submited), il serait intéressant de les relier à la composition de la MOD. Par exemple, des plans d'aménagement sur divers territoires pourraient être élaborés afin de contrôler la quantité et la qualité de la MOD exportée vers le FSL. Deuxièmement, l'une des applications très prometteuses des SIG consiste à faire le lien entre l'imagerie satellitaire et la fluorescence mesurée in situ de la MOD (télédétection). Au chapitre I nous avons démontré que le réservoir de MOD du FSL se caractérise par sept composantes ayant des signatures de fluorescence bien distinctes. Il est donc envisageable de lier l'information acquise par les satellites via diverses bandes spectrales aux signatures de fluorescence. Dès lors, la caractérisation du réservoir de MOD à grande échelle sur l'ensemble du FSL permettrait de bien saisir l'influence du bassin versant sur les patrons de distribution spatiaux de la MOD.

Conclusion générale

En conclusion, la limnologie est un domaine de recherche de nature multidisciplinaire intégrant les sciences biologiques, physiques, hydrologiques, statistiques et les analyses numériques sont les disciplines qui ont été nécessaires à la réalisation de cette thèse doctorale. La mise en commun de ces différents axes de recherche a démontré que les grands fleuves ainsi que leurs lacs fluviaux jouent un rôle important dans le cycle biogéochimique de la MOD. L'hétérogénéité physique et chimique des masses d'eau, provenant de tributaires drainant des bassins versants d'utilisation diversifiée, influence la quantité et la qualité de la MOD transitant dans les écosystèmes fluviaux. Puisque la MOD influence considérablement l'écologie des écosystèmes aquatiques à plusieurs niveaux, les conséquences de cette diversité de sources et de types de MOD gagneraient à être étudiées à des niveaux trophiques supérieurs. Maintenant que nous disposons d'outils de modélisation de la cinétique biogéochimique de la MOD, des hypothèses plus précises peuvent être testées à l'ensemble des écosystèmes fluviaux.

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