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La dégradation de la matière organique dissoute comme indicateur de la réactivité écosystémique du fleuve Saint-Laurent

Par

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Ce mémoire intitulé

La dégradation de la matière organique dissoute comme indicateur de la réactivité écosystémique du fleuve Saint-Laurent

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Résumé

La matière organique dissoute (MOD) joue un rôle clé dans le fonctionnement des rivières à titre de vecteur de carbone organique et d'énergie, tout en contribuant au transport de nutriments, de métaux et de divers contaminants. Elle est principalement dégradée à travers la minéralisation photochimique et la respiration bactérienne. La vitesse à laquelle se produit cette dégradation est influencée à la fois par la composition chimique et moléculaire de la MOD et par les conditions environnementales dans lesquelles elle est transformée. Toutefois, les études évaluant simultanément ces effets intrinsèques et extrinsèques sont rares en milieu fluvial et la plupart se concentrent sur un seul des processus de dégradation. De plus, les résultats de ces expériences sont rarement transposés à une colonne d'eau entière, ce qui limite l'évaluation de la réactivité écosystémique en rivière. Durant l'été 2019, nous avons échantillonné 40 sites le long d'un transect de 207 kilomètres sur le fleuve Saint-Laurent, une grande rivière tempérée dans laquelle s'écoulent côte-à-côte deux masses d'eau contrastées en termes de propriétés chimiques et physiques. En laboratoire, nous avons évalué la bio- et la photo-réactivité de la MOD au moyen d'incubations et d'expositions sous un simulateur solaire pour ensuite transposer ces données à l'écosystème en estimant pour tous les sites échantillonnés des taux surfaciques de dégradation *in situ* à partir de profils lumineux et bathymétriques. Nos résultats indiquent que la dégradation *in situ* de la MOD est essentiellement déterminée par la dégradation biologique. Cette dernière est généralement un à deux ordres de grandeur plus importante que la dégradation photochimique. Les taux surfaciques totaux de dégradation (calculés comme la somme des taux de dégradation photochimique et biologique) vont de 36,7 à 892,1 mg C m^{-2} j^{-1}. Les taux surfaciques de dégradation photochimique sont principalement influencés par la photoréactivité de la MOD. En revanche, nous avons identifié un pool relativement constant de MOD bioréactive qui semble indépendant de la concentration initiale, de la composition ou des conditions environnementales. Des taux disproportionnellement élevés de biodégradation (2,5 à 4 fois la moyenne) ont été observés pour quelques sites peu profonds et situés près d'effluents urbains ou d'îles. Ces taux sont probablement stimulés par une combinaison de concentrations élevées en nutriments et une proportion plus importante de composantes protéiniques dans la MOD. Nos travaux fournissent l'une des rares démonstration expérimentale de la dominance de la dégradation biologique dans les grandes rivières, mais révèlent que la dégradation photochimique peut être d'importance comparable dans certaines zones de faible profondeur plus fortement connectées au milieu terrestre. En somme, ces observations suggèrent l'existence de points de contrôle écosystémiques pour la réactivité de la MOD dans les grandes rivières et laissent entrevoir de nouveaux questionnements quant à leur rôle dans l'export et le transport de matière terrestre.

Mots-clés : matière organique dissoute, carbone, dégradation, fleuve Saint-Laurent, photodégradation, biodégradation, composition, PARAFAC, réactivité écosystémique

Abstract

Dissolved organic matter (DOM) is central to rivers functioning as it is a complex mixture composed of vast amounts of organic carbon and energy, also acting as a vector for nutrients, metals and various contaminants. Both the chemical and molecular composition of the DOM and the environmental conditions in which it is processed can influence its rate of removal from the water column, mainly through photochemical mineralization and bacterial respiration. Studies evaluating these intrinsic and extrinsic aspects simultaneously, particularly on both the biological and photochemical degradation are rare, particularly in large fluvial systems. During the summer of 2019, we sampled a 207 km transect of the St. Lawrence (SLR), a large temperate river in which flows two strikingly distinct water masses in terms of origin as well as chemical and physical properties. We then assessed DOM bio- and photo-reactivity at 40 sites along the river through a series of standardized incubations and exposure to simulated sunlight, and then used water irradiance and morphometric profiles to estimate in situ areal rates of processing across the river. We found that the in situ reactivity was mostly driven by biological degradation, which was typically one to two order of magnitude higher than photochemical degradation. Total daily processing (calculated as the sum of photochemical and biological degradation) across the whole water column ranged from 36.7 to 892.1 mg C m^{-2} d^{-1}. In situ photochemical degradation was largely driven by DOM photoreactivity. In contrast, we found a relatively constant baseline pool of biolabile DOM that appeared to be independent from changes in concentration and environmental conditions. Disproportionately high biodegradation rates (2.5-4x the average) were found in a few shallower sites, near effluents or islands, potentially driven by a combination of local increases in nutrient concentration and compositional changes in the proportion of protein-like DOM. We provide rare experimental evidence for the often-assumed dominance of biodegradation over photodegradation in large rivers, but also emphasize that photodegradation can locally be just as important in terrestrially connected areas of low depth. In turn, these observations hint at the presence of ecosystem control points in large and heterogenous rivers with contrasting sources and composition of DOM, opening new research perspectives into the role of large rivers in the export and retention of terrestrial matter.

Keywords: dissolved organic matter, carbon, degradation, St. Lawrence River, photodegradation, biodegradation, composition, PARAFAC, ecosystem reactivity

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C : carbone

CO_2 : dioxyde de carbone

MOD/DOM : matière organique dissoute/*dissolved organic matter*

COD/DOC : carbone organique dissout/*dissolved organic carbon*

CDOM : matière organique dissoute colorée

FDOM : matière organique dissoute fluorescente

PARAFAC : analyse de facteurs parallèles (*PARAllel FACtor analysis*)

Ode à l’eau

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Chapitre 1 : Introduction générale

1.1 Préambule

Les rivières du monde constituent un vaste réseau de transport de la matière terrestre vers le milieu océanique. Elles ratissent la surface des continents et drainent chaque année sur leur passage plusieurs millions de tonnes de carbone, d'azote et de phosphore (Drake et al. 2018; Maranger et al. 2018). À ce rôle de convoyeur s'ajoute un éventail bien documenté de processus biogéochimiques qui contribuent à la transformation, à la dégradation et la rétention de la matière durant toute la durée de son voyage (Aufdenkampe et al. 2011; von Schiller et al. 2017). Ces processus ont des répercussions directes sur le fonctionnement des rivières puisqu'ils régulent notamment la quantité et la qualité des nutriments et du carbone disponibles pour l'alimentation des organismes aquatiques (Riedel et al. 2016). Les humains bénéficient aussi quotidiennement des capacités de dégradation des rivières puisqu'elles permettent par exemple d'y réduire considérablement la charge de nombreux contaminants et substances indésirables (Phelps & Streeter 1958), diminuant ainsi notamment les risques et les coûts associés à la consommation d'eau potable (Wen et al. 2017). À plus large échelle, la minéralisation en CO_2 de la matière organique présente dans les rivières et son dégazage vers l'atmosphère constitue une part appréciable des bilans globaux de carbone (Raymond et al. 2013). Le potentiel des rivières à agir non pas comme de simples tuyaux, mais bien comme des réacteurs complexes, est donc largement accepté (Cole et al. 2007; Casas-Ruiz et al. 2017; Tranvik et al. 2018). Toutefois, de nombreuses interrogations demeurent en regard des facteurs et des dynamiques contrôlant la dégradation de la matière organique dissoute (MOD) dans les grandes rivières (Kothawala et al. 2020).

Le présent mémoire contribue donc à présenter, dans un premier temps, une synthèse des connaissances actuelles et des plus récentes frontières et objectifs en recherche (Chapitre 1) pour ensuite dresser un portrait des principaux facteurs influençant la réactivité écosystémique de la MOD au sein du fleuve Saint-Laurent (Chapitre 2, article scientifique en anglais). Une mise en contexte des nouvelles connaissances acquises ainsi que de futures avenues de recherche y sont finalement proposées (Chapitre 3).

1.2 La matière organique dissoute (MOD)

À l'échelle globale, on estime qu'approximativement la moitié du carbone présent dans les rivières l'est sous forme de matière organique (MO) (Cole et al. 2007). La MO est constituée d'un complexe assemblage de composés organiques issus de la dégradation d'organismes vivants (Derrien et al. 2019). On distingue opérationnellement la fraction dissoute (MOD) de la fraction particulaire (MOP) selon qu'elle passe ou non à travers les pores de filtres dont la taille varie entre 0,2 µm et 0,7 µm (le plus souvent 0,45 µm) (Leenheer & Croué 2003; He et al. 2016; Derrien et al. 2019). C'est la fraction dissoute qui possède le plus grand potentiel d'être minéralisée en CO_2 puis dégazée vers l'atmosphère (Hansen et al. 2016). Son abondance relative par rapport à la MOP tend à augmenter progressivement avec l'ordre hydrologique de Strahler pour finalement largement dominer les exports de MO vers les océans (Wipfli et al. 2007; Battin et al. 2008). La MOD joue un rôle primordial dans le fonctionnement des écosystèmes aquatiques puisqu'elle représente un substrat énergétique pour la respiration des bactéries hétérotrophes au bas de la chaîne trophique (del Giorgio & Cole 1998; Wetzel 2003), régule l'environnement lumineux dans la colonne d'eau (Frenette et al. 2006) et facilite le transport de nutriments et de contaminants (Yamashita & Jaffé 2008; Hernandez-Ruiz et al. 2012). La MOD produite dans un écosystème terrestre par la décomposition de feuilles d'arbres, de matière ligneuse, de cadavres d'animaux ainsi que par percolation de l'eau de pluie sur la canopée et les tiges des arbres et dans les sols (Van Stan et al. 2017) est dite allochtone (parfois désignée comme terrigène), alors que celle produite à même l'écosystème aquatique est dite autochtone. Cette dernière peut être constituée de résidus végétaux et algaux générés par la lyse virale, par le broutage inefficace du zooplancton (*sloppy feeding*) ainsi que par le relâchement passif de déchets cellulaires par le phytoplancton et les bactéries (Fujiwara et al. 2001; Kawasaki & Benner, 2006; Jiao et al. 2010). Certaines perturbations humaines telles que les rejets d'eaux usées, de microplastiques ou d'autres déchets organiques peuvent aussi représenter d'importantes sources de MOD dans les écosystèmes aquatiques fortement urbanisés (Guo et al. 2010; Derrien et al. 2019).

1.3 Techniques de caractérisation

Ces multiples sources impliquent un éventail hautement diversifié de compositions moléculaires : les plus récentes avancées dans les techniques de caractérisation en laboratoire ont en effet permis de révéler qu'un seul échantillon peut être composé de plus de 12 000 formules moléculaires distinctes (Kellerman et al. 2015) et il n'existe aucun consensus quant au nombre total de composés présents dans les écosystèmes aquatiques (Sandron et al. 2015). Des approches répandues de caractérisation optique permettent néanmoins d'extraire à faible coût et de manière non-destructive des informations concernant le processus de production (ex : microbien ou algal) et la source (c.-à-d. terrestre ou aquatique) d'un échantillon de MOD (Derrien et al. 2019). Ces techniques d'analyse reposent sur l'interaction entre la lumière et les chromophores, un sous-groupe de molécules contenues dans la MOD et capable d'absorber la lumière. Une partie de cette MOD colorée (*CDOM*) est également fluorescente (*FDOM*) (Figure 1.1), c'est-à-dire qu'elle émet de la lumière après une exposition aux longueurs d'onde dans le spectre des UV et des UV-proches.

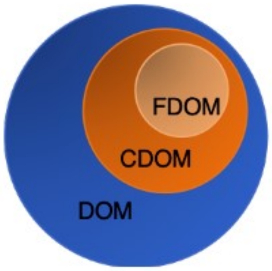

Figure 1.1 Représentation schématique des fractions fluorescentes (*FDOM*), colorées (*CDOM*) et totale (*DOM*) de la matière organique dissoute. Tirée de Stubbins et al. 2014

Des approches telles que l'analyse en facteurs parallèles (PARAFAC) ou le calcul de divers rapports ou pentes spectrales permettent d'identifier les patrons d'absorbance et de fluorescence récurrents et de les associer à des processus de production et/ou origine spécifiques à l'aide de base de données en libre accès (www.openfluor.org; Murphy 2013). Ces techniques d'analyses sont donc souvent utilisées par les écologistes de plusieurs disciplines (écologies des sols, limnologie, océanographie, géochimie) afin de retracer le parcours de la MOD. Notons que l'une des principales limites de ces analyses spectrales est qu'elles ne nous renseignent que sur les fractions colorées ou fluorescentes de la MOD. Les groupes de molécules identifiées semblent toutefois être un bon proxy pour un grand nombre d'autres molécules non-colorées co-variant avec la *FDOM* dans l'environnement (Stubbins et al. 2014) Le plus souvent, ces analyses compositionnelles sont aussi accompagnées de mesures de concentration en carbone organique dissout (COD) afin d'établir diverses relations et rapports entre les deux types de mesures et de mieux comprendre la place de la matière colorée au sein d'un *pool* total de MOD (Lee et al. 2018; Derrien et al. 2019).

1.4 La dégradation de la MOD

La MOD est progressivement dégradée le long de son parcours à travers les écosystèmes aquatiques (Figure 1.2). Les deux principaux processus menant à sa transformation (et ultimement à sa minéralisation en CO_2) sont la dégradation photochimique et la respiration bactérienne hétérotrophe (Hansen et al. 2016; Jones et al. 2016). La dégradation photochimique résulte de l'excitation des chromophores par le rayonnement solaire dans le spectre du visible et des UV. Lorsque la dose énergétique reçue est suffisante, les liens moléculaires sont brisés, ce qui entraînent une minéralisation partielle ou complète de la MOD (Osburn et al. 2001). Les bactéries aquatiques hétérotrophes utilisent quant à elles la MOD comme unique substrat organique pour la respiration et la production d'ATP (del Giorgio & Cole 1998) puisque les formes dissoutes de carbone sont les seules à pouvoir traverser la membrane cellulaire (Marschner & Kalbitz 2003). Des processus mentionnés moins fréquemment dans la littérature limnologique et agissant comme puits de MOD sont la sorption, la précipitation et la formation de colloïdes pouvant transformer la fraction dissoute en matière particulaire (MOP) (Hansen et al. 2016). La MOD peut aussi être emmagasinée dans les sédiments (via des processus de sédimentation, de précipitation ou de floculation) (Von Wachenfeldt & Tranvik 2008; Guillemette et al. 2013; He et al. 2016), temporairement dans la biomasse bactérienne à des fins de croissance (del Giorgio & Cole 1998) ou tout simplement exportée hors de l'écosystème par transport passif lorsque le temps de résidence de l'eau est trop court pour permettre l'action de ces processus de transformation (Casas-Ruiz et al. 2017). Néanmoins, les voies de transformation biologiques et photochimiques demeurent les destins prédominants de la MOD dans les écosystèmes d'eau douce.

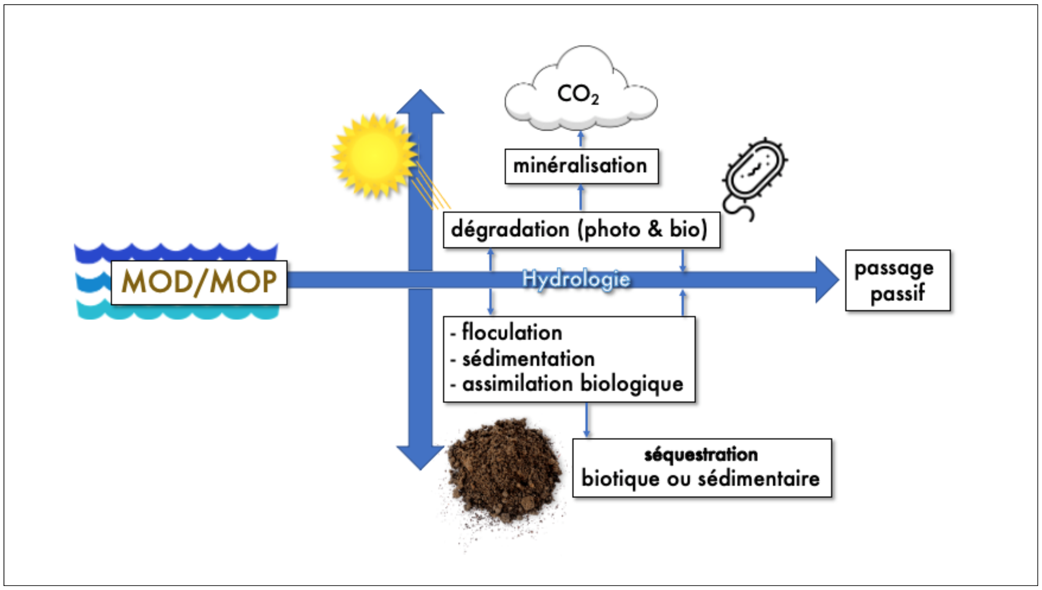

Figure 1.2 Schématisation des voies de transformation de la matière organique le long de son parcours dans une rivière

1.5 Les facteurs de contrôle régulant la dégradation de la MOD

La propension de la MOD à être dégradée est fortement influencée par sa composition moléculaire (Kellerman et al. 2015; Catalán et al. 2020; Kothawala et al. 2020). Dans des conditions de dégradation identiques, les molécules de MOD humique et colorée seront typiquement plus sensibles à la photodégradation (Bertilsson & Tranvik 2000; Moran et al. 2000), alors que les molécules de type protéinique non-colorées seront préférentiellement biodégradées (Berggren et al. 2017). Cette plus grande susceptibilité à la dégradation résulte en partie d'un contrôle thermodynamique, c'est-à-dire que la différence d'énergie libre entre l'état chimique initial de la MOD et son état final permet à la réaction de s'amorcer plus facilement (LaRowe & Van Cappellen 2011). C'est pourquoi, à l'échelle d'un réseau hydrographique d'eau douce, on observe typiquement un épuisement préférentiel de la MOD en commençant par celui des composés plus labiles, laissant en aval des composés plus réfractaires (Lapierre & del Giorgio 2014; Catalán et al. 2016). L'idée voulant que la composition de la MOD joue un rôle très important, voir même dominant dans la régulation de ses taux de dégradation semble donc s'être bien imposée dans la communauté limnologique. En revanche, dans le domaine de la recherche s'intéressant aux sols et dans une certaine branche de la recherche en milieu marin, l'idée reçue semble plutôt être que c'est l'environnement réactif qui domine la régulation de la MO(D). Dans les sols, les molécules de MO (pas nécessairement dissoute) peuvent être physiquement adsorbées ou isolées, voire même complètement encapsulées à l'intérieur de micropores, ce qui contribue à en ralentir considérablement la dégradation (Semenov et al. 2013). Des molécules potentiellement très labiles en raison de leur composition peuvent ainsi persister des milliers d'années lorsqu'elles sont isolées d'un environnement réactif favorable (Kleber et al. 2011; Kothawala et al. 2012). Dans les océans, l'hypothèse de la dilution est l'un des nombreux mécanismes proposés pour expliquer l'extrême persistance de certains composés labiles (Dittmar 2015). Des expériences en laboratoire ont en effet montré que les coûts énergétiques encourus afin de concentrer ces composés dilués à l'intérieur d'une cellule sont plus grand que l'énergie fournie par ceux-ci (LaRowe et al. 2012). Ce sont donc des facteurs environnementaux bien spécifiques à ces deux systèmes d'étude qui semblent y dicter la dégradation de la MOD. Dans les écosystèmes d'eau douce, la MOD est par définition bien solubilisée dans la colonne d'eau et présente en concentration relativement abondante. Sa réactivité intrinsèque (c.-à-d. celle imposée par sa structure moléculaire) est donc plus libre de s'y exprimer. Le rôle joué par les conditions environnementales dans l'expression des taux de dégradation étant toutefois mal évalué et encore peu étudié (Marín-Spiotta et al. 2014; Kothawala et al. 2020), il est probablement prématuré de supposer une « dominance » de la composition. On sait par exemple que des températures et des concentrations de nutriments élevées sont associés à des taux plus importants de dégradation biologique (Sand-Jensen et al. 2007; Guillemette et al. 2013; Mao et al. 2017). Certains taxons bactériens peuvent aussi dégrader la MOD particulièrement rapidement ou en extraire des fractions à plus haut poids moléculaire et typiquement peu bioassimilées (Berggren et al. 2010; Logue et al. 2016). Les taux de photodégradation sont quant à eux stimulés à la fois par des pH élevés et faibles ainsi que par la présence de fer en conditions acides (Wu et al. 2005; Porcal et al. 2014; Timko et al. 2015; Selvam et al. 2017). De plus, de par ses propriétés chromophoriques, la MOD contribue à réguler la pénétration de la lumière, limitant ainsi la très grande majorité de sa photodégradation aux premiers décimètres de la colonne d'eau (Koehler et al. 2014; Vachon et al. 2016). La propension à la dégradation de la MOD est donc vraisemblablement dictée à la fois par sa propre composition moléculaire et par les caractéristiques physiques et chimiques de l'environnement réactif. Toutefois, l'influence de l'hétérogénéité environnementale sur les taux *in situ* de dégradation demeure peu étudiée dans les écosystèmes d'eau douce en général, et l'est encore moins dans les grandes rivières.

1.6 Le fleuve Saint-Laurent comme système d'étude

La zone d'étude dans le cadre de ce projet est un tronçon de 207 km de la portion d'eau douce du fleuve Saint-Laurent (Figure 1.3, voir la section *Study area* du chapitre 2 pour une description détaillée).

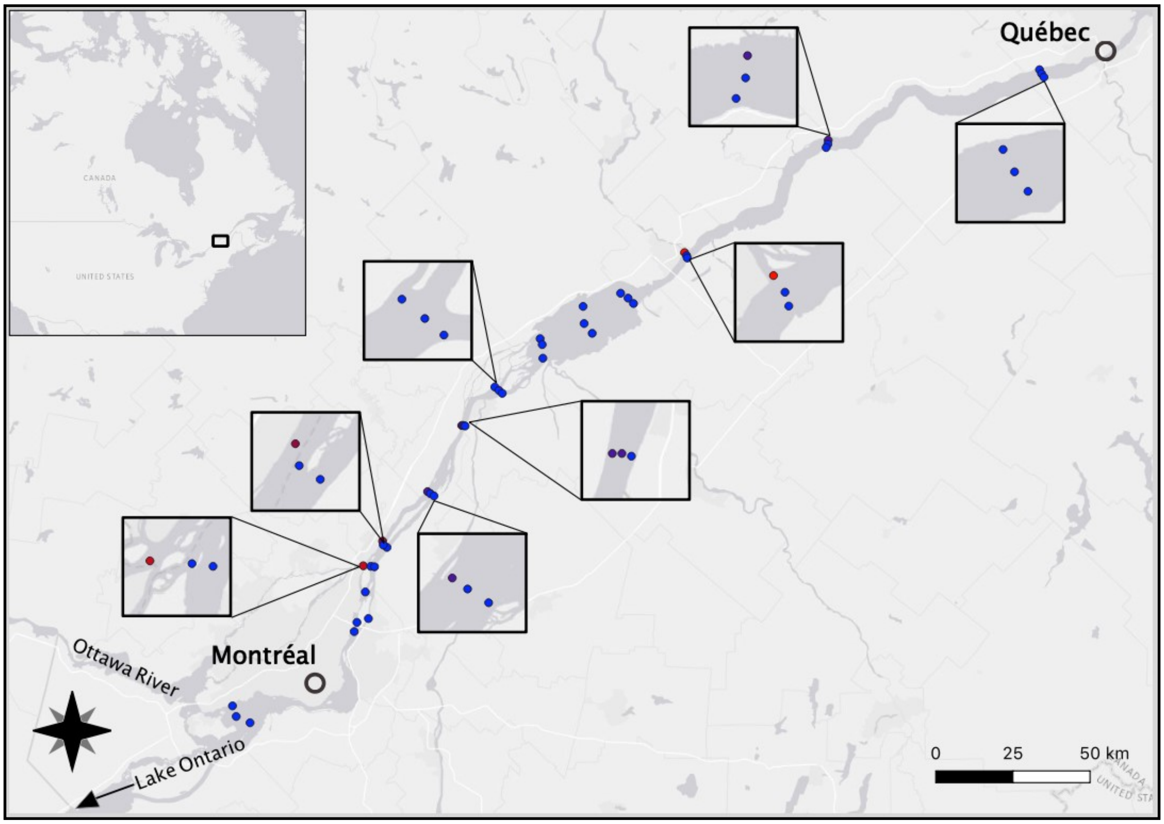

Figure 1.3 Distribution des 40 sites échantillonnés à l'été 2019 à bord du navire de recherche Lampsilis. Le gradient de couleur indique l'origine hydrologique basée sur les valeurs de conductivité de bleu (conductivité élevée, eau provenant des Grands Lacs) à rouge (conductivité faible, eau provenant de tributaires plus fortement influencés par le milieu terrestre).

En termes de débit, il s'agit de la deuxième plus grande rivière d'Amérique du Nord avec un débit annuel moyen de 12 600 $m^3 s^{-1}$ à la fin du transect étudié (Hudon & Carignan 2008). On y retrouve la plus faible concentration de matière particulaire en suspension de toutes les grandes rivières du monde (Gleick 1993). Les concentrations moyennes annuelles de MOD y sont environ 38 fois plus élevées que les concentrations de MOP dans la masse d'eau principale et environ 15 fois plus élevées dans la rivière des Outaouais, son principal tributaire (Hélie & Hillaire-Marcel

2006). Cette caractéristique en fait une rivière propice à l'étude de la MOD puisqu'elle limite les transferts possibles entre les fractions dissoutes et particulaires de la MO via la floculation ou l'adsorption à des particules (Moody & Worrall 2021). L'approche expérimentale peut ainsi faire l'économie de temps et de ressources en se focalisant sur une meilleure compréhension de la dégradation de la fraction dissoute et en considérant les échanges avec la phase particulaire comme négligeables. Le long du transect étudié, on retrouve une grande variété d'éléments morphologiques tels qu'un chenal maritime d'environ 11 mètres de profondeur entouré de zones nettement moins profondes, quelques dizaines d'îles de taille variable ainsi que deux lacs fluviaux. Cette importante hétérogénéité spatiale permet d'évaluer l'impact de différents environnements réactifs contrastés (c.à-d. profondeur, disponibilité de la lumière, nutriments, pH, oxygène, *etc.*) sur les taux de dégradation de la MOD. De plus, deux sources hydrologiques aux signatures bien distinctes et se mélangeant peu (les Grands Lacs et la rivière des Outaouais) y acheminent des apports de MOD bien différents en termes de couleur, de composition et donc, possiblement, de dégradabilité. Ces deux particularités, combinées à un plan d'échantillonnage adéquat, favorisent l'identification de potentielles zones disproportionnellement importantes pour la dégradation de la MOD. Pour ce faire, ce projet vise à estimer des taux surfaciques (dits *in situ*) prenant en compte la taille de la colonne d'eau et la pénétration de la lumière (Maranger et al. 2005; Cory et al. 2014; Vachon et al. 2016). Ces taux *in situ* se concentrent sur l'importance (absolue et relative) d'environnements distincts, en considérant à la fois a) les aspects intrinsèques liés à la MOD qui s'y trouve, b) les conditions environnementales et c) la structure physique de l'environnement à l'intérieur duquel a) et b) s'expriment. La compréhension des patrons spatiaux et des facteurs de contrôle de cette « réactivité écosystémique » constitue une frontière en recherche presqu'inexplorée dans les grandes rivières du monde, qui représentent la dernière interface entre les milieux continentaux et océaniques.

1.7 Objectifs du projet

L'objectif principal de ce projet est de quantifier la réactivité écosystémique de la portion d'eau douce du fleuve Saint-Laurent en évaluant la dégradation biologique et photochimique de la MOD.

Le premier sous-objectif est de comparer l'importance et la répartition spatiale des deux principaux processus de dégradation de la MOD, soit la photo- et la biodégradation. Les eaux exceptionnellement claires qui occupent la plus grande part du système d'étude créent des environnements propices à une pénétration relativement profonde de la lumière photo-oxydative, mais la MOD qu'on y retrouve est peu colorée (et donc théoriquement moins photosensible). Elle contient aussi davantage de composés protéiniques fraichement produits (et est donc théoriquement plus biolabile). Les tributaires apportent quant à eux des eaux fortement colorées (et donc théoriquement plus photosensible), mais dans lesquelles la pénétration de la lumière photo-oxydative est limitée aux premiers décimètres de la colonne d'eau. Ces grandes généralisations théoriques ainsi que la place quasi-terminale du fleuve Saint-Laurent dans le continuum sol-océan laisse supposer une dominance de la biodégradation dans la transformation de la MOD, mais ce projet de recherche vise à supporter ces hypothèses à l'aide de données empiriques en quantifiant la proportion de MOD transformée *in situ* par chacun de ces deux processus.

Le deuxième sous-objectif est d'évaluer l'influence des facteurs compositionnels et environnementaux sur les taux de dégradation de la MOD. Si l'identité de ces facteurs potentiels est déjà bien documentée dans la littérature, on comprend par contre moins bien à quel point ils peuvent contribuer à structurer la distribution des taux de dégradation exprimés dans un écosystème fluvial puisqu'ils sont rarement étudiés de pair en milieu fluvial. Ces questions méritent donc d'être investiguées à l'aide d'outils statistiques multivariés tels que la régression des moindres carrés partiels (*PLS regression*).

Le troisième sous-objectif est d'estimer le potentiel total de dégradation *in situ* de la MOD pour l'ensemble des stations échantillonnées. En admettant que la sommation des taux de photo- et de bio-dégradation constitue une bonne approximation de la dégradation totale de la MOD dans le fleuve St-Laurent, il est possible d'estimer, à partir de nos résultats, des taux surfaciques journaliers de dégradation totale (en mg C m^2 j^{-1}). Une des forces de cette étude est le nombre relativement élevé de stations échantillonnées (n = 40) par rapport à la superficie totale du transect. Cette résolution a le potentiel de mettre en valeur des zones ayant une importance disproportionnée dans la dégradation de la MOD. De telles zones pourraient être engendrées par des conditions de dégradation particulièrement favorables, par des apports hautement susceptibles à la dégradation ou tout simplement par un effet volumétrique (toutes choses étant égales, une colonne d'eau plus grande transformera plus de matière). L'atteinte de cet objectif réside donc dans une évaluation de la réactivité intrinsèque de la MOD combinée à une caractérisation de son environnement réactif.

Cette approche a rarement été appliquée aux grands écosystèmes fluviaux et constitue la principale nouveauté du projet.

Chapitre 2 : Ecosystem-level reactivity of DOM in the freshwater portion of the St. Lawrence River

2.1 Contribution des auteurs

Maisonneuve, P., Guillemette, F., Lapierre, J.-F. Ecosystem-level reactivity of DOM in the freshwater portion of the St. Lawrence River. *Limnology and Oceanography*, soumis pour publication.

Le Chapitre II de ce mémoire est sous forme d'article scientifique en anglais et a été réalisée grâce aux contributions de trois auteurs :

- Philippe Maisonneuve : conception du projet, échantillonnage, analyse des échantillons, traitement des données, rédaction
- Jean-François Lapierre : conception du projet d'étude, supervision du projet, rédaction, révision et édition de la version finale
- François Guillemette : Conception du projet, co-supervision du projet, révision et édition de la version finale

2.2 Ecosystem-level reactivity of DOM in the freshwater portion of the St. Lawrence River

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Keywords: dissolved organic matter, carbon, degradation, St. Lawrence River, photodegradation, biodegradation, composition, PARAFAC, ecosystem reactivity

Running title: DOM reactivity in the St. Lawrence River

Author contribution

PM, JFL and FG came up with the research question and designed the study approach. PM performed the sampling as well as all laboratory and data analyses with guidance from JFL and FG. PM wrote the first draft of the manuscript with help from JFL. All authors revised and approved the final version of the manuscript.

2.3 Scientific Significance Statement

Large rivers of the world are well known for their export of continental material to the oceans, but little is known on their role as reactors of dissolved organic matter (DOM), a critical element of ecosystem functioning, because of a lack of integrative studies on the DOM intrinsic properties and extrinsic environmental properties that dictate DOM degradation rates in ambient waters. Here we show that, across the freshwater portion of the St. Lawrence River, a combination of DOM composition, environmental properties and river morphometry can lead to ecosystem control points in terms of DOM processing. In heterogenous large rivers, such areas may be of disproportional importance for the flow of energy and the retention of elements before they leave the continent.

2.4 Abstract

Large rivers are critical conduits from continents to oceans as they receive, produce and process huge amounts dissolved organic matter (DOM), but the intrinsic DOM properties and extrinsic environmental properties that dictate these processes at the ecosystem-level remain poorly understood. We assessed DOM optical properties as well as bio- and photo-reactivity at 40 sites along a >200 km transect of the freshwater portion of the St. Lawrence River through a series of standardized microbial incubations and exposure to simulated sunlight, and then estimated in situ areal rates of processing across the river. We found that biological and photochemical processes preferentially targeted contrasting pools of DOM, but that DOM composition had an undiscernible effect on in situ degradation rates compared to other environmental factors (e.g. CDOM, pH, nutrients). Total daily processing across the whole water column ranged from 36.7 to 892.1 mg C m^{-2} d^{-1}. In situ photochemical degradation was largely driven by DOM photoreactivity. In contrast, we found a relatively constant baseline pool of biolabile DOM that appeared to be independent from changes in concentration and environmental conditions. In situ DOM processing was mostly driven by biological degradation (on average 95%), and disproportionately high biodegradation rates (2.5-4x the average) were found in a few shallower sites near effluents or islands, potentially driven by local increases in nutrient concentration and in the proportion of bioreactive protein-like DOM. These results integrate how DOM composition and degradability interact with ambient environmental and morphological properties to dictate an ecosystem-level reactivity of DOM.

2.5 Introduction

Large rivers are dynamic and heterogeneous ecosystems that receive and export large amounts of material from land. This material is exposed to an array of biogeochemical processes such that a majority of it is removed from the water before it reaches the ocean (Drake et al. 2018; Maranger et al. 2018). Dissolved organic matter (DOM) represents an important fraction of this material and is central to rivers functioning as it is a complex mixture composed of vast amounts of organic carbon (C) and energy (Drake et al. 2018), also acting as a vector for nutrients, metals (Aiken et al. 2011) and various contaminants (Hernandez-Ruiz et al. 2012). Not all rivers, however, are equal in their capacity to process DOM (Casas-Ruiz et al. 2017). For example, depth physically limits the potential for photochemical degradation (Cory et al. 2015) while surrounding land use can influence the bioavailability and quantity of terrestrial inputs (Riedel et al. 2016). Changes in river flow, both natural and human-induced, also regulate an unstable balance between DOM supply, transport and transformation (Creed and McKnight 2015; Raymond et al. 2016). As different drivers of biogeochemical processing in rivers including flow regime, climate, and loading of terrestrial matter are changing globally (Arnell and Gosling 2013; Solomon et al. 2015; Weigelhofer et al. 2021), DOM processing can be expected to change rapidly. A better understanding of the various drivers shaping material processing in rivers is therefore needed.

Both the chemical composition of the DOM (Kellerman et al. 2015) and the environmental conditions in which it is processed (Marín-Spiotta et al. 2014; Catalán et al. 2020) can influence its rate of removal from the water column, mainly through photochemical mineralization and bacterial respiration into CO_2 (Hansen et al. 2016). Environmental conditions associated to increased DOM processing by bacteria include high nutrient concentrations (Mao et al. 2017) and temperature (Sand-Jensen et al. 2007) while high photodegradability has been linked to both high and low pH (Wu et al. 2005; Selvam et al. 2017) and to a combination of high iron concentrations and low pH (Porcal et al. 2014). In addition, in any given environmental conditions, DOM composition also plays a crucial role as colored humic-like molecules with high molecular weight seem to consistently be more susceptible to photodegradation (Bertilsson and Tranvik 2000; Moran et al. 2000). Non-colored proteinic-like substances with low molecular weight and high nutrient content are generally considered as more biolabile (Berggren et al. 2017), and recently produced or imported DOM in soils or in the water column is typically associated to higher degradation rates (Lapierre and del Giorgio 2014). Therefore, both environmental and compositional aspects drive the biological and photochemical processing of DOM, but the absolute and relative contributions of these pathways to in situ C carbon losses in rivers with contrasting ecological and physical properties remain poorly understood.

Different studies have typically explored either the intrinsic reactivity of DOM, depending on its molecular composition, or the extrinsic reactivity of DOM based on environmental conditions in which DOM is found. Much rarer are evaluations of both the intrinsic and extrinsic aspects simultaneously, particularly on both the biological and photochemical degradation (but see Parham 2012). Combining the environmental and composition drivers on the two main facets of DOM reactivity (bio & photo) would lead to an estimation of an integrated "ecosystem reactivity", which, in conjunction with ecosystem morphometry (size, depth), can then be quantified in terms of mass of C processed per meter squared of ecosystem (see Vachon et al. 2016 for a similar estimate in lentic systems). This integrated estimate would represent the realized potential of a riverine environment to process organic matter, potentially highlighting control points of disproportionate importance in the riverine continuum (Bernhardt et al. 2017). Yet, these transpositions of laboratory incubations to in situ environments remain rare, especially for large river systems.

In this context, our objectives were (1) to compare the relative importance of in situ photo- vs bio-degradation, (2) to apportion the influence of compositional vs environment factors and ultimately (3) to evaluate how those four aspects of DOM processing (photo- and bio-degradation, composition, environment) result in an integrated ecosystem reactivity for different sites along a heterogenous river system. To do so, we sampled a 207 km transect of the St. Lawrence River (SLR), a large temperate river in which flows with little to no lateral mixing distinct water masses in terms of origin as well as chemical and physical properties (Hudon and Carignan 2008; Frenette et al. 2012). The SLR is influenced by strong anthropogenic pressures, its watershed being home to more than 45 million people (ECCC 2017) and draining rivers with contrasting catchments and water chemistry (Thorp et al. 2005). We thus assessed DOM bio- and photo-reactivity at 40 sites through a series of standardized microbial incubations and exposures to simulated sunlight, and then used water irradiance and morphometric profiles to estimate in situ areal rates of processing across the river.

2.6 Methods

2.6.1 Study area

The St. Lawrence River (SLR) is North America's second largest river in terms of discharge (yearly average of 12 600 m^3/s at the end of the studied transect; Hudon & Carignan 2008). Downstream of the Montreal island, two main water masses flow alongside each other with little to no lateral mixing (Frenette et al. 2006; Hudon and Carignan 2008). The main water source originates from Lake Ontario, the last of the North American Great Lakes, a series of six lakes with a combined residence time of over 260 years (Quinn 1992). Water at the source of the SLR therefore exhibits low DOC concentration (< 3 mg L^{-1}), absorption coefficient ($a_{440} < 1$ m^{-1}) and transports the smallest amount of suspended sediment of the world's major rivers (Gleick 1993). Water chemistry remains fairly constant until the island of Montreal city, where it is joined by the Ottawa river, its most important tributary (yearly average of 1 838 m^3 s^{-1}, Hudon & Carignan 2008), carrying darker and more concentrated DOC (> 5 mg L^{-1}; $a_{440} \sim 2$ m^{-1}). The conductivity of this water mass is also markedly lower (< 100 µS cm^{-1} compared to > 250 µS cm^{-1} for the main water mass). These distinct features allow for reliable modelling of the mixing dynamics between the two main water bodies (Martin et al. 2016). Several morphological features further contribute to the SLR spatial heterogeneity. Namely, several fluvial lakes, a complex network of islands and a deep maritime channel present a wide range of reactive environments in terms of light, depth, and residence time. Average water residence time (WRT) in the river ranges from a few hours in the main channel to several days in shallower sections. The surrounding landscape on the northern shore is mainly composed of forested areas, with some agricultural land concentrated near the shore while intense agricultural land use is dominant on the south shore (Goyette et al. 2016). Urban development is omnipresent on both shores and many surrounding municipalities dispose of their wastewater directly in the SLR (Fondation Rivières 2020). Most notably, near the eastern-most tip of the Montreal island is located the city's wastewater treatment plant. This plant discharges between 2.5-7.6 million m^3 d^{-1} of undisinfected water into the SLR. It only carries out primary treatment of the sewage, which mainly targets the removal of particulate matter and phosphorus (City of Montreal 2020).

2.6.2 Sampling

A total of 40 sites located in the SLR were sampled onboard the R/V *Lampsilis* of the University of Quebec at Trois-Rivieres, Quebec, Canada over the course of three days during the summer of 2019. Sites were distributed along a 207 km transect between Montreal and Quebec City (Fig. S2). In order to account for the lateral gradient induced by SLR distinct water masses (Fig. 2.1), sampling was conducted following orthogonal cross-sections consisting in three stations each. Depth of sampled sites ranged from 12 m in the main maritime channel of the river to around 2 m in shallower areas.

Surface water was collected using an 8L GO-FLO water sampler (model 1080; General Oceanics) at a depth of 1 m below the surface. Water from the sampler was poured into conditioned glass bottles and immediately brought to the wet lab on board. A portion of the sampled water was used to characterize initial DOM quality and DOC content and to perform photodegradation experiments. This portion was immediately filtered through 0.2 μm polycarbonate membrane (Isopore; Millipore) in acid-washed and muffled (550°C for four hours) borosilicate glass tubes. Each filter was conditioned by filtrating 200 ml of site water through it before sample collection. Total phosphorus, nitrogen and nitrates samples were collected in acid-washed HDPE bottles. Total iron samples were collected in certified metal-free polypropylene tubes. All samples were stored in the dark at 4°C until further analysis (except for phosphorus, nitrogen and nitrates which were immediately frozen). A suite of standard physical and chemical variables was measured at each site using a multi-probe (Yellow Springs Instrument).

Light attenuation profiles were obtained at five wavelengths (313, 320, 340, 443, and 550 nm) with a profiling radiometer (PUV-800, Biospherical Instruments Inc.). The instrument was lowered vertically through the water column on the unshaded side of the vessel at a steady rate of 0.1 m/s to ensure reliable measurements. Attenuation coefficients ($K_{d,\lambda}$, m^{-1}) were calculated at each wavelength λ based on the relation between downwelling irradiance ($E_{\lambda,z}$, W m^{-2}) and depth (z, m^{-1}) using the following equation:

(Equation 1) $$E_{\lambda,z} = E_{\lambda,0} * e^{K_{d,\lambda} * z}$$

2.6.3 Chemical analyses

Total phosphorus concentrations were determined with a flow injection analyzer using the molybdenum-blue method after persulfate digestion (EPA 365.3, Astoria2, Astoria-Pacific). Total nitrogen and nitrate concentrations were measured through colorimetry as nitrates following persulfate digestion and cadmium reduction (EPA 353.2; Lachat QuikChem 8000, Lachat Instruments).

Total iron concentrations were measured by Triple Quadrupole Inductive Coupled Plasma Mass Spectrometry (8900 ICP-MS/MS, Agilent Technologies).

DOC concentrations were measured using the heated persulfate wet oxidation method with a total organic carbon analyzer (Aurora Model 1030, O.I. Analytical). Two injections were made for each sample and average concentrations were calculated. Instrument accuracy was monitored throughout each run using Milli-Q blanks and potassium hydrogen phthalate standards (DOC = 5 mg L^{-1}). Average variation from the expected KHP concentration was ± 0.11 mg L^{-1} (2.2%).

2.6.4 Optical analyses

Samples were warmed to room temperature just prior to analysis. Absorbance spectra were obtained at 1 nm increments from 250 to 900 nm with a UV-Vis spectrophotometer (Shimadzu) using a 1 cm quartz cell. Ultrapure water (MilliQ, Millipore) was used to measure baseline absorbance. CDOM absorption coefficients (a_λ) were calculated in Naperian units as follows:

(Equation 2)

$$a_\lambda = \frac{A_\lambda}{l} 2.303$$

where A is the absorbance at wavelength λ and l is the pathlength of the cuvette in meters (Green and Blough 1994). DOM fluorescence was measured with a Cary Eclipse spectrofluorometer (Agilent Technologies). Emission-excitation matrices (EMMs) were obtained for emission from 230 to 600 nm by 2 nm increments at excitation 220 to 450 nm with 5 nm increments using a 1 cm quartz cell. Fluorescence data were corrected for instrument bias, inner filter effect and Raman scattering using the script from Labrie et al. (https://github.com/RichardLaBrie/paRafac_correction), based on Murphy et al. 2010. A parallel factor (PARAFAC) model (Stedmon et al. 2003) was developed to identify and quantify groups of DOM that shared similar optical properties across sampled sites using the drEEM toolbox (Murphy et al. 2013) for MatLab (Mathworks). The model was based on a total of 198 samples from surrounding tributaries, island channels and the SLR itself, and from photochemical and biological experiments. The validation of the model using a split-half validation procedure and the identified fluorescent components are presented as supplementary material (Fig. S1). Briefly, three components were characterized as humic-like components (C1, C2, and C3; ex/em: 345/474, 310/412, and 275,435/514, respectively) and two were characterized as protein-like components (C4 and C5; ex/em: 285/352, 280/324). All components have been previously reported in the online library www.openfluor.org.

2.6.5 Biological degradation experiments

Immediately after collection, a volume of 400 ml was filtered through pre-combusted (500°C) 2.7 µm glass filters (Whatman GF/D) in order to remove most planktonic biota and preserve the bulk of ambient bacterial biomass, therefore avoiding reinoculation (Guillemette and del Giorgio 2011). Each filter was conditioned by filtrating 200 ml of site water through it before sample collection in acid-washed and muffled borosilicate glass amber tubes. Water samples were incubated in the dark at a constant temperature (~20°C). After 7, 14, 28 and 112 days, a portion of the water was filtered through 0.2 µm conditioned syringe filters (Isopore; Millipore) and stored in the dark at 4 °C in order to halt any further degradation before analysis. DOC measurements and spectral scans were performed within a week after filtration. We assessed biological DOC processing by fitting a one-reactant multi-G model to the decay curves (Westrich and Berner 1984; Guillemette and del Giorgio 2011). This model captured well the exponential patterns in DOC loss (R^2 between 0.57-0.99, mean: 0.96).

2.6.6 Photochemical degradation experiments

Filtered water (0.2 µm) was poured in 24 mm diameter acid-washed and muffled borosilicate glass clear tubes and laid horizontally inside a solar simulator (Suntest CPS+, Atlas Material Testing Solutions) under a standard light dose (467 W m^{-2} between 300-800 nm, spectrum shape representative of natural sunlight). The spectrum of the solar simulator was measured beforehand using a radiometer (Jaz, Ocean Optics). Temperature was maintained at 20°C through the use of a shallow recirculating bath (the samples were not fully submerged). After 24, 48 & 72 hours of exposure, samples were removed from the incubator and stored in the dark at 4 °C until analysis. DOC measurements and spectral scans were performed within a week after irradiation.

DOC concentration generally decreased linearly overtime following simulated sunlight exposure. We quantified photodegradable DOC loss rates (Pd, mg C L^{-1} h^{-1}) as the slope of the linear regression between DOC concentrations and exposure time in the laboratory.

2.6.7 Estimated photochemical in situ losses

In situ photochemical areal loss rates (In situ PDOC, mg C m^{-2} d^{-1}) were estimated by calculating the amount of carbon lost per light energy absorbed in laboratory experiments (Pd-E_w, mg C J^{-1} m^2) and multiplying it by the total amount of light energy absorbed by CDOM in the water column at the corresponding site (Equation 3). To do so, we first calculated the amount of light energy absorbed by CDOM during laboratory experiments ($E_{w,lab}$, J m^{-2}) based on the solar lamp irradiance ($I_{0,\lambda}$, W m^{-2}), on the exposition time (T_{UV}, s) and on the average absorption of irradiation in the glass vials at a specific wavelength ($(1-10^{-a})_\lambda$) (Bertilsson and Tranvik 2000).

(Equation 3)

$$E_{w,lab} = T_{UV} \sum_{\lambda=313}^{\lambda=450} \left(I_{0,\lambda}(1-10^{-a})_\lambda\right)$$

To account for the impact of potential self-shading within the vials, we horizontally divided the vial into ten different sections and calculated the mean irradiation path length of different section of the vial (L, cm) at each wavelength (Equation 4).

(Equation 4)

$$(1-10^{-a})_\lambda = \sum_{1}^{10} \frac{(1-10^{-a*L})}{10}$$

Pd-E_w (mg C J^{-1} m^2) was then obtained by dividing Pd (mg L^{-1}) by the volume of the vials (0.039 L) and by $E_{w,lab}$ (J m^{-2}). We calculated the average surface irradiance (E_0, W m^{-2}) between 313 and 450 nm (wavelengths responsible for most photodegradation (Vähätalo et al. 2000)) from data collected by the radiometer's surface irradiance sensor during the 3-days sampling campaign ($E_{0,313\text{-}450}$ = 36.44 W m^{-2}). The days of sampling were generally sunny and this value was assumed to represent the irradiance of a typical summer day at the surface of the SLR. We used the attenuation coefficient ($K_{d,\lambda}$, m^{-1}), depth (z, m) and the ratio of light absorption by CDOM to total light absorption ($aCDOM_\lambda/aT_\lambda$) to calculate the fraction of the total light dose absorbed by CDOM and multiplied it by Pd-E_w (Equation 5). Total light absorption (aT_λ, m^{-1}) was linearly interpolated at 1 nm interval from the five wavelengths of $K_{d,\lambda}$ values measured in the field

(Equation 5) $$In\ situ\ PDOC\ =\ Pd{-}E_w * \int_{313}^{450} [E_{0,\lambda}(1 - e^{K_{d,\lambda}*z})]\,\frac{aCDOM_\lambda}{aT_\lambda}$$

Similar estimates have been conducted in previous studies (Bertilsson and Tranvik 2000; Cory et al. 2013; Vachon et al. 2016, 2017) and R scripts detailing the complete process are available (see Supplemental Information).

2.6.8 Estimated biological in situ losses

In situ areal loss rates explained by biological degradation (In situ BDOC, mg C m^{-2} d^{-1}) were estimated by multiplying the volumetric loss rates (BDOC, mg L^{-1} d^{-1}) by the volume of a 1 m^2 water column of depth z (m):

(Equation 6) $$In\ situ\ BDOC = BDOC\ * 1000 * z$$

We used BDOC values after one day (derived from the one-reactant multi-G model) to calculate daily rates. The calculation assumes equal biodegradation rates across the entire water column (Maranger et al. 2005). This assumption is supported by the absence of stratification patterns in the vertical temperature and oxygen profiles measured during sampling (also see Ouellet et al. 2014 for evidence of a well-mixed water column during summer). Due to technical limitations, incubation temperature (20°C) was lower than average water temperature measured in the field (24.5 ± 0.6, mean ± SD). Therefore, the results presented in this study are likely a conservative estimate of actual in situ degradation, given that bacterial respiration tend to increase with temperature (Sand-Jensen et al. 2007).

2.6.9 Numerical analyses

Numerical analyses were performed using the [R] graphical and statistical computing environment (version 3.6.1, R Core Team 2019). Linear relationships were investigated through linear regressions using the *lm* function.

In order to identify which compositional and environmental characteristics covaried and explained the greatest variation in biological and photochemical losses across sites, we performed a partial least squares (PLS) regression with ST-BDOC (losses after 1 day), LT-BDOC (losses after 112 days) and Pd as responses variables (Y). Explanatory variables (X) were related to DOM composition and to the reactive environment and included DOC concentration, proportion of total fluorescence attributed to each PARAFAC component, CDOM ($a440$) as compositional variables and total nitrogen, total phosphorus, pH and percentage of dissolved oxygen as environmental variables. For this analysis, we used the ambient values of explanatory variables (i.e. measured before any biological or photochemical treatment). PLS is particularly appropriate for data sets with a large number of predictors relative to a small sample size and for predictors that are correlated (Boulesteix and Strimmer 2007) as is the case in flowing systems such as the SLR. The importance of each explanatory variable was assessed by the variable importance on the projection scores (VIP) and all explanatory variables had VIP scores greater than 0.8. The PLS regression was performed using the statistical analysis software JMP Pro (version 14.0.0, SAS Institute).

2.7 Results

2.7.1 Spatial and hydrological heterogeneity along the studied transect

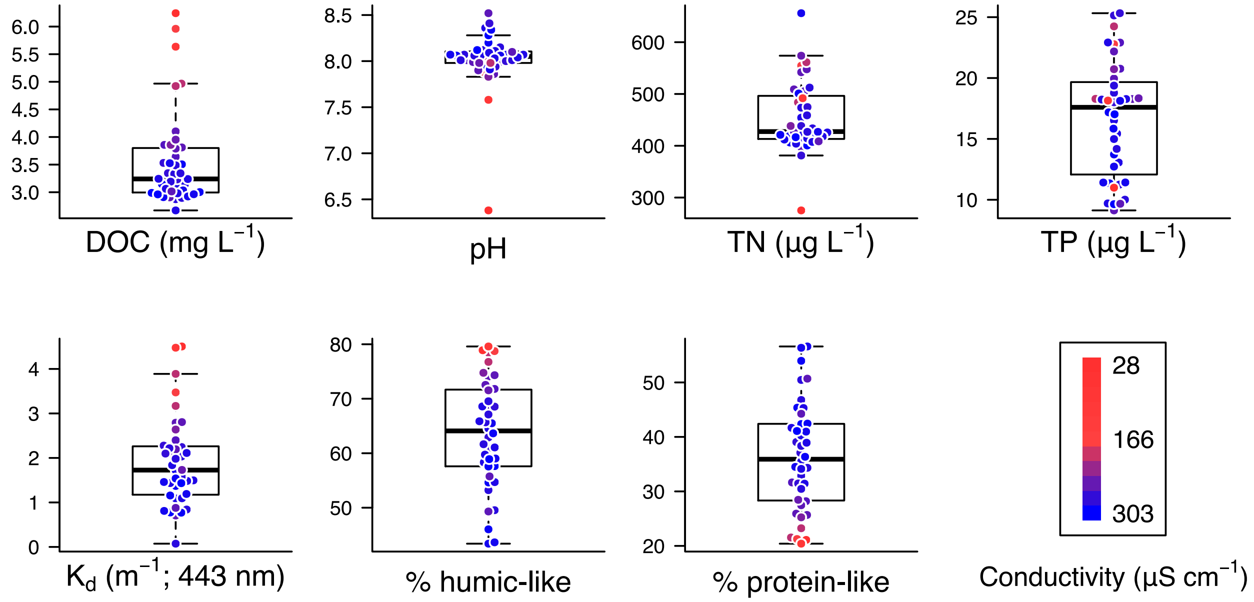

Figure. 2.1 Distribution and range of physical and chemical variables measured in surface waters along the studied transect (DOC: dissolved organic carbon, TN: total nitrogen, TP: total phosphorus, K$_d$: light attenuation coefficient at 443 nm). Percentage of humic-like is calculated as the proportion of total fluorescence associated to PARAFAC components C1, C2 and C3 (see Table

1). Percentage of protein-like is calculated as the proportion of total fluorescence associated to components C4 and C5. Color gradient indicates water conductivity, with high conductivity associated with the blue-green waters from the Great Lakes, low conductivity water originating from typically browner tributaries, and intermediary conductivity representing a combination of both.

The studied sites spanned a wide range in terms of physical and chemical properties that appeared to vary as a function of the origin of the water, namely the Great Lakes water masses with a high conductivity and the St. Lawrence River (SLR) tributaries closer to the shore with lower conductivity (Figs 2.1, 2.2). Most of the upstream sites had high conductivity and were mainly originating from the Great Lakes. The relative contribution of tributaries increased going downstream as conductivity decreased, leading to increases in light attenuation concurrent with increases in concentrations of DOC and humic-like DOM. Water from those tributaries was markedly more colored and had lower pH and proportions of protein-like DOM than the main water mass. Nutrient concentrations varied about three-fold across the studied sites (TN: 275.2-655.9 µg L^{-1}; TP: 9.1-25.3 µg L^{-1}), but there was no clear pattern with conductivity.

2.7.2 Bio- and photo-degradable DOC under standardized conditions

Both biological and photochemical experimental degradation rates showed a wide range of values, which tended to co-vary strongly (for photochemical degradation, Fig. 2.2a) and weakly (for biological degradation, Fig. 2.2bc) with conductivity. The experimental rates cannot be directly compared for bio- and photo-degradation until they are expressed in terms of in-situ losses (below), but the patterns can be compared.

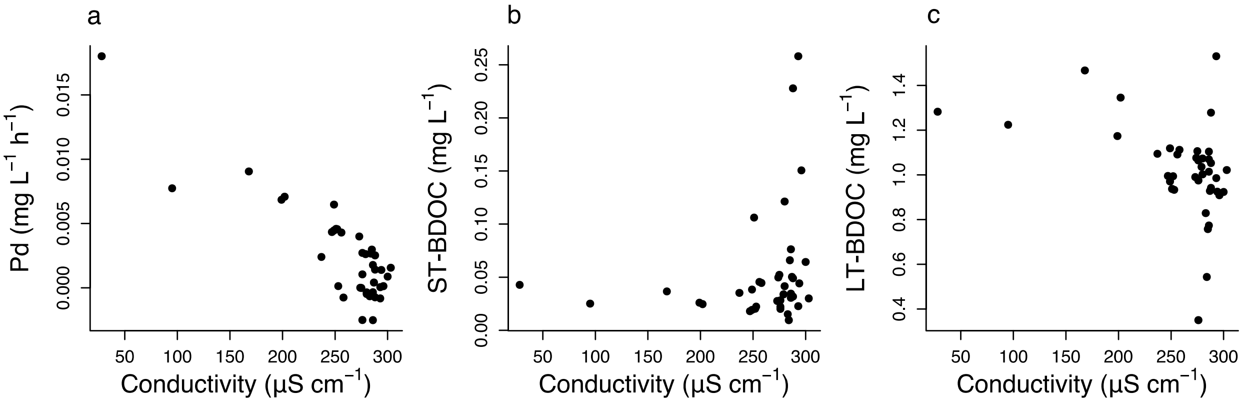

Figure 2.2 Relationships between conductivity and DOC removal following a) light exposure, b) short term biological degradation (ST-BDOC, 1 day) and c) long term biological degradation (LT-BDOC, 112 days)

Overall, photochemical degradation was low as most slopes (thereafter referred to as Pd) were not significantly different from zero (i.e. $p > 0.05$; 0.002 ± 0.0006 mg C L h^{-1}), indicating very low or unquantifiable losses for high conductivity sites originating predominantly from the Great Lakes (GL, Fig. 2.2a). However, we noted higher losses for sites associated with terrestrially impacted tributaries, as Pd appeared to increase with decreasing conductivity in sites with conductivity < 250 µS cm^{-1} (Fig. 2.2a). The proportion of DOC lost after 72 hours of light exposure ranged from unquantifiable to 12% and the highest decrease in absolute concentration was 1.31 mg L^{-1}.

Following short-term incubations (1 day), the proportion of biologically labile DOC (BDOC) ranged from unquantifiable to 7.4% and the highest decrease in absolute concentration was 0.3 mg L^{-1}. For this set of incubations, high concentrations of BDOC were strictly found in a few high conductivity sites, while most sites had BDOC around 0.03-0.04 mg L^{-1} independent of conductivity, hence water origin (Fig. 2.2b). After long term incubations (112 days), between 8.9 and 45.3% was degraded, and the highest decrease was 1.6 mg L^{-1}. The concentrations of BDOC increased with a decreasing proportion of GL water, but there was high variation around the mean trend; clearly, the concentration of BDOC was relatively higher in low conductivity sites compared to other sites after 112 days than after 1 day (Fig. 2.2b, c).

2.7.3 Preferential consumption of specific DOM fractions

Table 2.1 Fluorescence components identified by the PARAFAC analysis

Component no.	Peak name	Peak type	Average proportion of fluorescence in ambient water (% ± SD)
1	A, C	UVC humic-like	18 ± 5
2	M	UVA humic-like	29 ± 3
3	A, C	UVC humic-like	17 ± 2
4	T	Tryptophan-like	8 ± 4
5	B	Tyrosine-like	29 ± 10

In order to better understand the fate of the various DOM fractions, we explored spatial patterns in DOM fluorescence (Fig. 2.1) and compared biological and photochemical daily loss rates for each component identified by the PARAFAC model. Protein-like component 5 (C5), and to a lesser degree C4 and C2, accounted for most of the FDOM biological losses, whereas C1 and C3 typically increased in concentrations following incubations (Fig. 2.3a). Component C1 and C2, which absorb the most in UV-A and UV-B regions, had the highest absolute losses in photochemical experiments, while protein-like C4 and C5, which mostly absorb at wavelengths < 300nm (Fig. S1) had the lowest absolute losses (Fig. 2.3a). This pattern could be due to either, or a combination of these components being highly concentrated in ambient waters, leading to higher losses degradation experiments, or to being highly reactive to one or the other process. The average relative losses of fluorescence components suggest the latter: C4 and C5, and to a lesser extent, C2 had the highest relative losses compared to initial concentrations in biological experiments, and the proportion of C1, C2 and C3 lost in photochemical experiments was about the double of the proportion of C4 and C5 lost (Fig. 2.3b). Moreover, there was a strong negative relationship between relative biological vs photochemical reactivity for the five components (Fig. 2.3b, $R^2 = 0.88$, $p = 0.01$), suggesting that the two processes preferentially target contrasting pools of DOM.

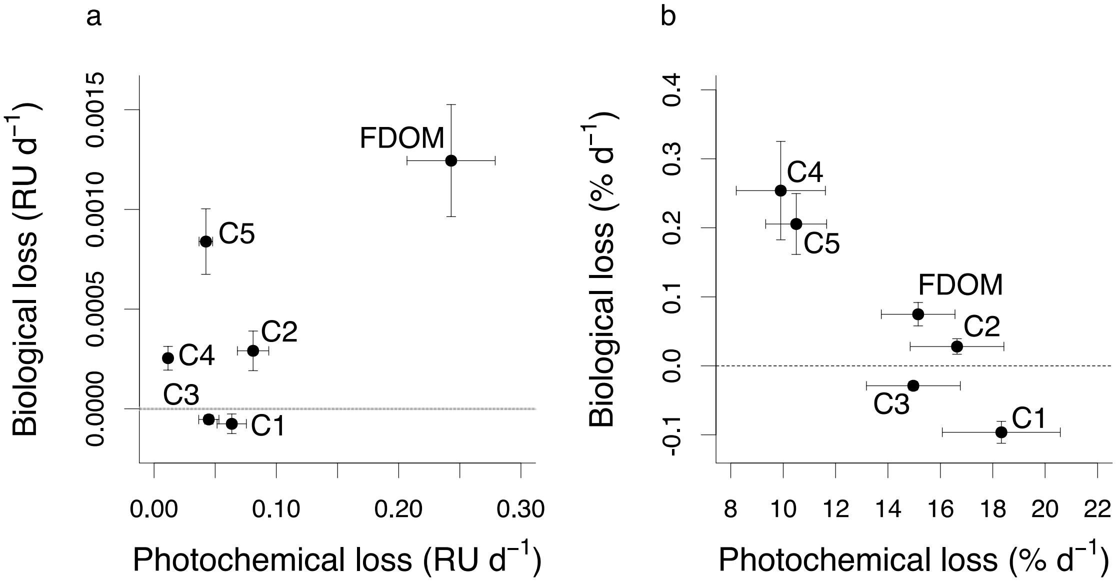

Figure. 2.3 Average a) absolute and b) relative losses of total fluorescence (FDOM) and PARAFAC components (C1-C5) during biological and photochemical degradation experiments. Relative loss rates (%) were obtained by dividing absolute loss rates by ambient concentration in

Raman units. Each point is the average of 40 points and error bars indicate standard error of the mean.

2.7.4 Influence of environmental and compositional factors

Having identified the most bio- and photo-reactive DOM pools in degradation experiments (Fig. 2.3), we aimed to determine what variables allowed us to predict overall DOC losses. To do so, we conducted a partial least square (PLS) regression on a set of explanatory variables either associated to DOM intrinsic composition or to external environmental variables using ST-BDOC, LT-BDOC and Pd as response variables.

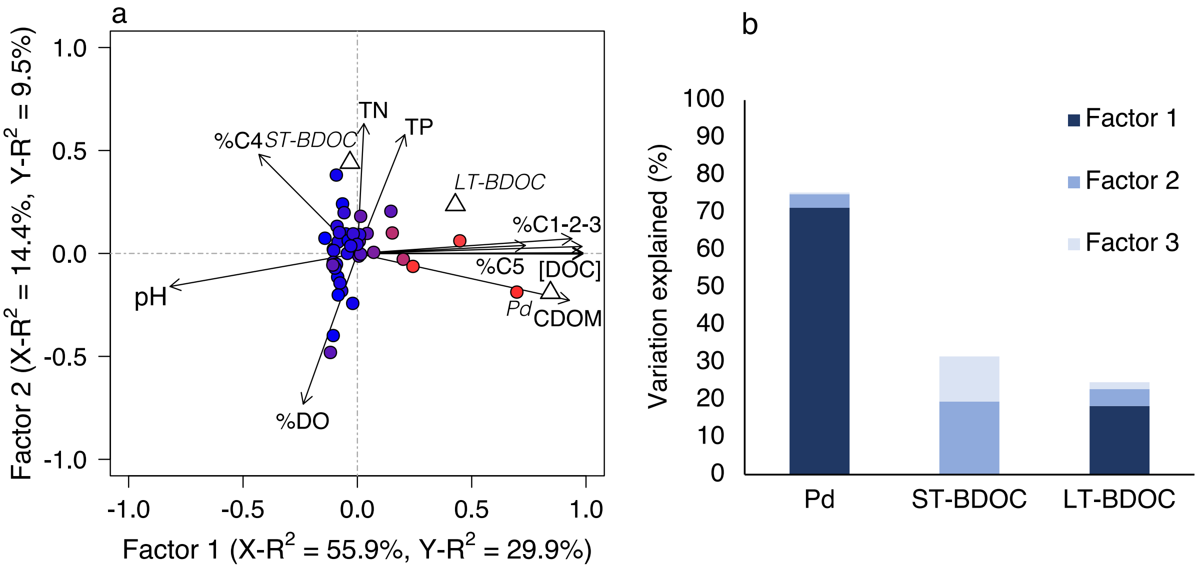

Figure 2.4 Partial least square regression of compositional and environmental variables explaining concentrations of photochemically degradable DOC (Pd), concentrations of short-term biologically degradable DOC (ST-BDOC) and long-term biologically degradable DOC (LT-BDOC). a) Correlation biplot between losses (response variables; triangles), compositional ([DOC]: ambient DOC concentration, %CX: proportion of total ambient fluorescence attributed to component X, CDOM: $a440$) and environmental variables (TN: total nitrogen, TP: total phosphorus, %DO: percentage saturation of dissolved oxygen). Colored dots correspond to sampling sites (n=40). Color gradient indicates water origin based on conductivity (see Fig. 2.1) with values ranging from 28 µS cm^{-1} (reddest, water from terrestrially influenced tributaries) to 303 µS cm^{-1} (bluest, main water mass from the Great Lakes). Only the first two factors are presented in the biplot (see

Supplementary Material for biplot of the first vs third factor). b) Percentage of explained variation in the response variables for the three factors retained.

The first three factors of the PLS (Fig. 2.4b) regression explained 75.4% of the total variation in Pd, 31.5% of ST-BDOC and 24.7% of LT-BDOC. Proportion of humic-like components (C1-C2-C3), as well as concentrations of CDOM and DOC were strongly associated to the first factor (Fig. 2.4a) and explained most variation in Pd (Fig. 2.4b). The effect of composition and concentration on Pd were difficult to disentangle as [DOC] and %C1-C2-C3 strongly covaried along the first factor, but CDOM (positively) and pH (negatively) were the best predictors. Pd was also negatively correlated with the proportion of protein-like components C4. In contrast, ST-BDOC was unrelated to the first factor and was best explained by a combination of factor 2 and 3. In particular, it was positively correlated to nutrient concentrations and proportion of biolabile C4 in ambient waters, but negatively correlated to dissolved oxygen levels. The third factor additionally revealed a positive correlation with bio-labile, protein-like component C5 and a negative relationship with pH. In the case of LT-BDOC, most of the explained variation was along the first factor (Fig. 2.4b, 18.7% of the total variation) and was therefore positively linked to [DOC] and to the proportion of fluorescent components (excluding C4). Iron and nitrates were also considered as explanatory variables but were not included in the final model as their variable importance on the projection scores (VIP) was lower than 0.8.

2.7.5 Estimating in situ DOC processing

Biological degradation rates measured in the lab, expressed as mg C d^{-1}, are presumably transposable in situ given that experiments have been conducted under ambient conditions (except light) and that the water column is well mixed from top to bottom in the SLR. Photochemical degradation, on the other hand depends on the amount of light absorbed by DOM in the water column and the photo-reactivity ($Pd\text{-}E_w$) of DOC i.e. the amount of DOC lost normalized to the amount of light absorbed. Photo-reactivity in the study sites varied from unquantifiable (considered as 0 mg J^{-1} for the purpose of this study) to 2.2×10^{-5} mg C J^{-1} m^{-2}. Combining the photo-reactivity of DOC with irradiance over the study area and light attenuation for each site, we estimated the daily areal rates of in situ photochemical DOC losses (calculated for a typical summer light dose of 36.4 W m^{-2} between 313-450 nm) and compared them to areal rates of biological degradation.

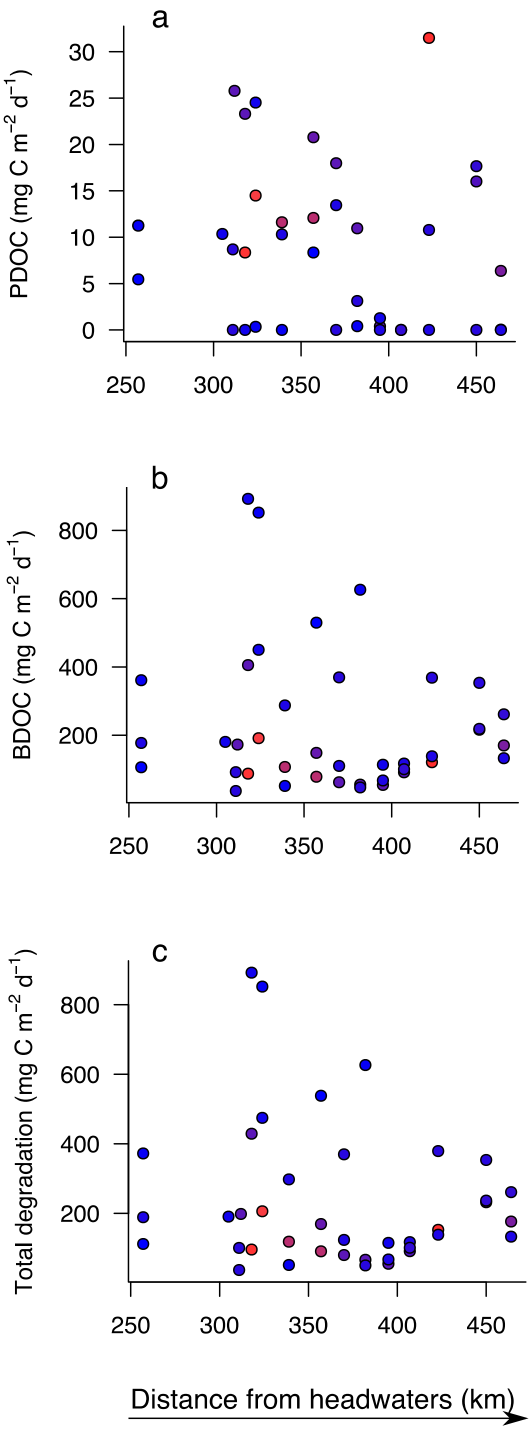

Figure 2.5 Distribution and comparison of daily in situ (a) photochemical, (b) biological and (c) total (sum of photochemical & biological) DOC degradation integrated across the whole water column along the studied transect. Color gradient indicates water origin based on conductivity (see

Fig. 2.1) with values ranging from 28 μS cm^{-1} (reddest, water from terrestrially influenced tributaries) to 303 μS cm^{-1} (bluest, main water mass from the Great Lakes).

In situ photochemical DOC losses ranged from unquantifiable to 31.5 mg C m^{-2} d^{-1} (Fig. 2.5b & 2.6a). In contrast, in situ biological DOC loss rates ranged from 36.7 to 892.1 mg C m^{-2} d^{-1} (Fig. 2.5a & 2.6a). Proportionally, biological degradation accounted for an average of 95.0% of the total daily DOC processing, in part because photochemical reactions were generally concentrated in the first meter of the water column whereas biological degradation was assumed to occur homogeneously up to several meters deep. No significant relationship was found between the in situ rates of photochemical and those of biological processing (Fig. 2.6a), supporting the notion that the two degradation processes not only target different DOM pools (Fig. 2.3), but are also independent in terms of ambient DOC processing along the studied transect as they are not driven by the same physical properties of the river.

Total daily processing (calculated as the sum of photochemical and biological degradation) across the whole water column ranged from 36.7 to 892.1 mg C m^{-2} d^{-1} (Fig. 2.5c). The upper values of this range are associated to a spike present around kilometer 300 and coinciding with the presence of the Montreal wastewater treatment plant (WWTP). The spike gradually disappears downstream. Additionally, a gradient is present in the latitudinal axis of the studied transect, with stations located in browner waters generally expressing lower rates of biological processing (Fig. 2.5b) and consequently, of total processing (Fig. 2.5c).

In situ degradation at sites with greater depth was almost exclusively controlled by biological removal. In fact, at sites where measurable photodegradation is observed, it is between 4 and 100 times less important than biological degradation for a complete water column (Fig. 2.6a). However, the SLR is a dynamic system and the water and the DOM it contains flow across different portions of the river with different depths. To provide an estimate of the in situ importance of both processes in a well-lit environment more typical of shallow, near shore environments that are abundant along the SLR continuum and are under-represented in our sampling, we further estimated the absolute and relative importance of both processes for the first meter of the water column at every site. At this depth, and for sites where PDOC was measurable, photodegradation was of similar order of magnitude, suggesting that in shallow areas with highly colored DOC, photochemical degradation can be as important as biological degradation (Fig. 2.6b, 1:1 line).

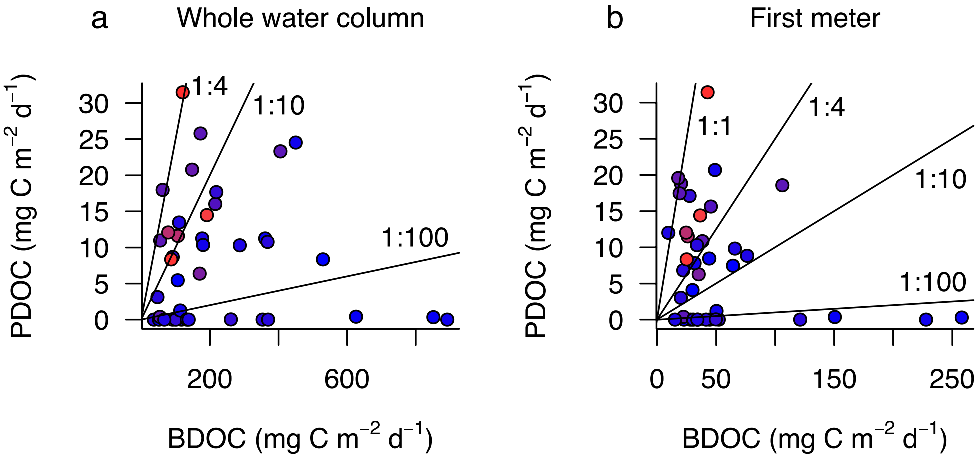

Figure 2.6 Relationship between estimated in situ rates of biological and photochemical processing along the studied transect for a) the whole water column and b) the first meter of the water column. Color gradient indicates water origin based on conductivity (see Fig. 2.1) with values ranging from 28 µS cm^{-1} (reddest, water from terrestrially influenced tributaries) to 303 µS cm^{-1} (bluest, main water mass from the Great Lakes).

The main factor determining daily in situ areal rates of photochemical rates degradation was Pd-E$_w$ (i.e. the amount of DOC lost by unit of energy (Table 2.2, $R^2 = 0.72$), whereas light attenuation coefficients (n.s.), pH (n.s.), depth (Table 2.2, $R^2 = 0.10$) and CDOM ($R^2 = 0.19$) had little to no effect. Daily in situ biological degradation after 1 day was best predicted by the volumetric daily loss rates measured in the laboratory (Table 2.2, $R^2 = 0.77$). This means that, across the studied sites, there was more variation in DOM bioreactivity than in the volume of water in which the processing occurs. However, for prolonged periods of degradation (112 days), the amount of DOC degraded converges toward similar values and site morphometry (i.e. depth) emerges as the main predictor of in situ biological losses (Table 2.2, $R^2 = 0.83$). Total and dissolved phosphorus and nitrogen concentrations, oxygen saturation levels and pH did not correlate significantly with estimated in situ losses, either short or long-term.

Table 2.2 Coefficient of determination (R^2) for linear relationships between estimated in situ areal loss rates and their potential drivers

	In situ areal losses rates		
Potential drivers	PDOC	ST-BDOC (after 1 day)	LT-BDOC (after 112 days)
Pd-E_w	**0.72**	-	-
K_{d-313}	-		**-**
K_{d-320}			
K_{d-340}			
K_{d-443}			
K_{d-550}		0.13	
CDOM ($a440$)	0.18	-	-
Volumetric BDOC (mg C L^{-1} d^{-1})	-	**0.77**	-
Depth	0.10	-	**0.82**
TN	-	-	-
TP	-	-	-
pH	-	-	-
%DO	-	-	-

Regular font: $p < 0.05$

Bold: $p < 0.0001$

(-): non-significant

2.8 Discussion

In this study, we determined how three facets of ecosystem reactivity controlled the in situ degradation rates (mg C m^{-2} d^{-1}) of DOM in a large fluvial system: DOM composition, environmental properties, and system morphometry. DOM composition and environmental properties were important in determining bio- and photo-reactivity during standardized lab experiments, with different DOM pools being particularly bio- or photo-degradable. The resulting biological and photochemical reactivity of DOM, combined, to some extent, with the morphometry of the system modulated the in situ realized degradation rates, which varied from close to zero to almost 900 mg C m^{-2} d^{-1} across the freshwater portion of the St. Lawrence River (SLR) as a function of the origin of the water and the surrounding natural and human features. This allowed us to determine areas of intense DOM processing and to identify underlying control factors, with impacts on our broader understanding of large rivers as transporters vs processors of material transiting from land to oceans.

2.8.1 The role of DOM composition

In any given environment, DOM reactivity will depend on its composition, that is, the degree to which the DOM pool contains molecules that are susceptible to biological or photochemical degradation. Photochemical losses are typically linked to humic-like and aromatic molecules of high molecular weight that strongly absorb in the UVA region of the light spectrum; these conditions represent an optimal combination of oxidative potential and abondance in surface waters (Vähätalo et al. 2000; Spencer et al. 2009; Cory et al. 2014; Lapierre and del Giorgio 2014). This type of DOM tends to be abundant in environments receiving freshly produced DOM that has had little opportunity for photo-oxidative processing, such as headwater streams and wetlands, as opposed to large rivers and coastal zones which are typically more distant from direct terrestrial inputs (Cory et al. 2013; Chupakova et al. 2018). For the same reason, protein-like components, which do not absorb in the visible and UVA region of the spectrum, are more refractory to photodegradation (Cory et al. 2007, Lapierre and del Giorgio, 2014). Our results concur with these general patterns as colored, humic-like components (C1-C2-C3) tended to be preferentially lost over protein-like C4 and C5 (Fig. 2.3b). Overall, color was the best predictor of the concentration of photo-degradable DOC (Pd), the amount of DOC lost by photo-oxidation in lab experiments (Fig. 2.4), suggesting that, in terms of explained variance, the specific compositional properties of

DOM were mostly accounted for by its light absorbing capacity alone. Nonetheless, these results highlight the role of composition on DOM photo-reactivity, and that this reactivity is higher at sites with high color, low pH that receive large proportions of water from the tributaries.

Average rates of experimental DOC loss in our study (0.0024 mg C L^{-1} h^{-1}, Fig. 2.2) were comparable to DIC photoproduction rates (0.0036 mg C L^{-1} h^{-1}) measured under similar exposure conditions near the downstream end of our transect in a previous study (Quebec city, Aarnos et al. 2018). These results place the SLR at the lower end of values reported for 9 other large rivers around the world (0.00053 - 0.013 mg C L^{-1} h^{-1}) (Aarnos et al. 2018). This reflects the overall low absorbance in the system due to the prolonged light exposure history (~260 years, Quinn 1992) of the water mass that has resided within the series of Great Lakes, which contributes to the vast majority of the SLR's discharge. In contrast, the few low conductivity sites receiving more colored DOM from tributaries had rates (0.0068 - 0.018 mg C L^{-1} h^{-1}) closer to -and in one case higher than- the upper range of what has been measured in the world's large rivers. Variation in experimental photochemical degradation rates across the freshwater portion of the SLR was therefore substantial and was likely modulated by prior photochemical degradation opportunities.

DOM biodegradability, on the other hand, is generally associated with freshly produced material (Lapierre and del Giorgio, 2014), which in high order streams and rivers tends to mostly be microbially produced and composed of protein-like compounds (Fellman et al. 2009; Petrone et al. 2009; Kellerman et al. 2015; Casas-Ruiz et al. 2017; Berggren and Al-Kharusi 2018; Khamis et al. 2018). Protein-like components C4 and C5 were indeed removed preferentially following biological incubations (Fig. 2.3b). However, the high degradation rates of these biolabile components do not directly translate into high DOC losses in lab degradation experiments in most cases, suggesting that factors other than intrinsic composition are at play. At the scale of our studied ecosystem, short-term bio-degradable DOC (ST-BDOC) was only weakly related to composition; 31.5% of the variation in ST-BDOC was explained by a combination of factors that include concentration of protein-like components, %DO and nutrients, but these effects were hard to disentangle (Fig. 2.4). Other studies on individual rivers or streams have also reported a similarly limited explanatory power of biodegradability due to DOM composition (Lu et al. 2013; Coble et al. 2016, 2019). We attribute this apparent decoupling to the relatively uniform bioreactivity observed along most of the river. Most ST-BDOC values were clustered around 0.24 mg L^{-1} (SD:

0.16) and this baseline removal appears to be independent from hydrological origin (Fig. 2.2) and therefore from composition. These values could be explained by the presence of a readily bioavailable pool being constantly cycled through the microbial biomass (Hosen et al. 2020; LaBrie et al. 2020), given that DOC concentrations stay relatively constant along the studied transect (Fig. S3). Labrie et al. reported the existence of a surprisingly consistent proportion (on average around 5%) of labile DOC (consumed after 31 days) from wetlands to the open ocean. In our study, on average about 7% of DOC was removed after only 7 days (and 15% after 28 days), suggesting that the DOM in the SLR is highly bioreactive and rapidly cycled in comparison. Still, the proportion removed after 28 days (mean: 15.6%) is in the range reported for the Yangtzee river (12-18%), which has similarly low DOC concentrations (< 5 mg L^{-1}) (Zhou et al. 2021). There were thus no strong relationships between DOM composition and the relatively stable baseline BDOC pool found in most sites, but the PLS analysis suggests that sites with disproportionate degradation rates had distinct DOM composition. In particular, the five most bioreactive sites had values of ST-BDOC 2.5 to 4 times higher than the mean and all had high proportions of protein-like components. These sites were either positioned in shallow environments near islands or in the effluent of wastewater treatment plants (WWTP). Streams affected by inputs of human sewage have been shown to possess a contrasting DOM composition characterized in part by higher proportions of highly labile microbial OM and low aromatic content (Petrone et al. 2009; Williams et al. 2016; Lambert et al. 2017; Khamis et al. 2018; Zhou et al. 2021). Therefore, this compositional shift towards a more protein-rich DOM pool could partly explain the high peaks in the concentrations of BDOC, but our data suggest that it must also be coupled to specific environmental conditions (i.e. nutrients Fig. 2.4) in order for this high bioreactivity to fully be expressed.

We measured the effect of photo- and bio-degradation separately, thus potentially neglecting competitive or synergistic processes that could occur in the water column (Miller and Moran 1997; Obernosterer and Benner 2004; Madsen-Østerbye et al. 2018; Berggren et al. 2020). However, the strong negative relationship between the percent loss, as well as the different absolute losses in concentrations (Fig. 2.3) suggest that photoreactive components tend to be biorefractory, and conversely, that bioreactive components tend to be photorefractory. Moreover, we did not observe photo-production of any bio-reactive components and only measured marginal production (less than 0.1% per day) of photosensitive components C1 and C3 during biological degradation (Fig. 2.2b). Therefore, potential competitive or synergistic effects would likely not alter our main conclusions, as our results suggest that biological and photochemical degradation processes target contrasting pools of DOM found in the SLR.

2.8.2 The role of environmental properties

The potential for environmental conditions to modulate bio- and photo-degradability is well recognized, but their relative role compared to other factors remains under debate as it may vary depending on the type of system considered. Pulses of nutrients or zones of higher photoreactive radiation have been shown to locally increase biological degradation, either directly through stimulation of bacterial metabolism or indirectly through increased primary production of bioreactive OM (Fuß et al. 2017; Soares et al. 2019). Different chemical pathways involving low and high pH as well as high concentrations of iron and nitrates are also known to influence DOM photoreactivity (Anesio and Granéli 2003; Porcal et al. 2014; Panneer Selvam et al. 2019). We found that Pd was strongly and negatively related to pH (Fig. 2.4). At first glance, this could be attributed to an enhancement of DOM photochemical reactivity by lower pH (Porcal et al. 2014) but this effect is hard to disentangle from the effect of CDOM, as both variables were good predictors of Pd and strongly, negatively covaried. This co-variation is specific to our study system and can be attributed to the naturally acidic soils and low buffering capacity of the forested areas on the Canadian shield (Thorp et al. 2005), from which most of the colored DOM in the SLR originates. Calculating Pd-E_w allowed us to partially remove the effect of CDOM (i.e. under the same light dose, the most colored samples absorb more light) through standardization per unit of energy absorbed. Once this effect is accounted for, no significant relationship with pH remains, hence DOM photoreactivity does not appear to be stimulated by pH or the range of pH values was too small to detect an effect. Potential enhancements of photoreactivity by iron and nitrates were also investigated but were undetectable ($p > 0.05$, not shown). Therefore, the role of environmental properties on DOM photochemical reactivity in the SLR appears of secondary importance compared to that of DOM composition.

Relationships between biological processing (short-term (ST-BDOC) or long-term (LT-BDOC) with environmental (and compositional) drivers were weaker than those for Pd. In particular, concentrations of nutrients, and to a lesser extent, of dissolved oxygen saturation (%DO), were related to ST-BDOC (Fig. 2.4), but the low explanatory power of Factor 2 (19.5%) and the absence of significant relationships in simple linear regressions indicate limited predictive ability. In contrast, work conducted in the SLR by Grater et al. (2020) on even shorter time-scale incubations (~24h) revealed a strong positive effect of nutrients concentrations on carbon consumption by bacteria. These combined results spanning a wide range of incubation times together suggest that bacterial metabolism is initially highly responsive to local increases in nutrients concentrations, but that the strength of stimulating effect appears to fade with time, likely as decomposers shift to different DOM compounds (Guillemette et al. 2013). Although our results did not directly measure bacterial respiration (i.e. consumption of O_2) during the incubation, nutrients have been shown to play an important role on bacterial metabolism in several urbanized streams and large rivers (Fuß et al. 2017; Soares et al. 2019). Across the SLR, the rates of biological degradation peaked around the Montreal and Repentigny wastewater treatment plants (WWTP) (Fig. 2.5c), concurrent with the lowest concentrations of dissolved oxygen along the transect. Montreal's WWTP is by far the biggest of the two and only conducts primary treatment, targeting mainly particulate matter and phosphorus. This is reflected by the high TN concentration (1.4x the mean) near the effluent compared to surrounding sites. The specific targeting of phosphorus during wastewater treatment could explain the weaker coupling observed with BDOC compared with nitrogen, as no clear increase in TP was observed near the effluent. Overall, we found that biological degradation rates were fairly stable across most sampled sites and that disproportionately high rates were found at a few shallow sites near islands and in the plume of wastewater effluents and were potentially driven by a combination of elevated concentrations of nitrogen and a shift to a more protein-rich DOM pool.

2.8.3 Implications for in situ processing of DOM in heterogenous large river systems

A combination of DOM composition, environmental properties and ecosystem morphometry resulted in a large range in areal degradation rates of DOM along the SLR, which were typically dominated by biological degradation. As the water column is well mixed and the DOM pool, nutrient concentrations and temperatures are assumed to be homogeneous from surface to bottom, depth would have been expected to be a good predictor of areal biological degradation rates, as has been observed in the Hudson river (Maranger et al. 2005). There was, however, no significant linear relationship between depth and areal rates of short-term biological degradation in our study sites (Table 2). This may be explained in part by the presence of a few shallow, highly reactive sites, and in part because the relationship may be non-linear, presumably because deeper sites are found in the navigation channel, far from main sources of recent DOM production. Shallower zones can stimulate gross primary production (GPP) from phytoplankton and macrophytes through high temperature and light availability, lower quantities of suspended matter and lower water velocities (Hosen et al. 2019). In the SLR, the presence of dense macrophyte beds in the Lac St-Pierre fluvial lake has also been shown to further accentuate this difference in flow between the shallowest and deepest sections of the river (Hudon and Carignan 2008). These contrasting conditions could contribute to shifting the overall DOM pool to newer, smaller, more protein-rich, and likely more microbially bioavailable compounds (Hosen et al. 2020). The increased nutrient concentration induced by urban effluent are also more likely to persist in those shallower and lower current zones. Interestingly, the relationship with depth becomes strong following long-term degradation ($R^2 = 0.82$, Table 2), suggesting that after the rapidly consumed labile pool is consumed, the amount of biodegradable exported to the estuary and to the ocean tends to converge (LaBrie et al. 2020). Hence, areal rates of biological degradation become largely a function of the water volume considered .

There were only weak relationships between areal photochemical degradation rates and the depth of the water column ($R^2 = 0.10$) as well as with CDOM (Table 2., $R^2 = 0.18$) because, at any given site, most photo-oxidative irradiation is absorbed within the first meter; hence all light will be absorbed, mostly by CDOM, regardless of CDOM concentration. This is coherent with Koehler et al. (2014) who have shown that global patterns of photochemical degradation were related to irradiation, not CDOM, for the same reasons. As a result, it is the intrinsic photochemical reactivity of DOC, expressed as Pd-E_w, that had the strongest effect on the calculated in situ areal rates of photodegradation (Table 2, $R^2 = 0.72$). To our knowledge, no similar estimates exist in large rivers, but, in terms of magnitude, our results are similar to other areal rates of carbon processing reported in boreal and temperate lakes (Granéli et al. 1996; Jonsson et al. 2001; Soumis et al. 2007; Vachon et al. 2016). For example, in an oligotrophic headwater lake with comparable $a_{\mathrm{CDOM},440}$ (0.8 m^{-1} *vs* $1.0_{\text{-SLR}}$), DOC (4.0 mg L^{-1} *vs* $3.6_{\text{-SLR}}$), mean depth (5.1 m^{-1} vs $4.8_{\text{-SLR}}$) and located within the SLR watershed, summer photo-degradation was estimated at ~10 mg m^{-2} d^{-1}, compared to 200 mg m^{-2} d^{-1} for pelagic respiration (Vachon et al. 2016). Similarly, across our study sites, the relative importance of the two processes spanned a large range (Fig. 2.6a), and areal photodegradation rates were typically lower than biological degradation by one to two orders of magnitude. This ratio is broadly in line with results in a large arctic river reporting a negligible importance of photodegradation compared to bio-degradation (Chupakova et al. 2018) and with studies attributing only between about 10 to 14% of CO_2 production from inland waters to DOM photo-mineralization (Koehler et al. 2014; Vachon et al. 2016). This suggests that the magnitude and rates of the two processes are relatively well constrained across different types of ecosystems.

The fact that photochemical degradation is constrained in the first meter of the water column, on the other hand, implies that this pathway can be particularly significant for overall DOM processing in shallow environments. In fact, photo-degradation can be just as important as bio-degradation in zones of a meter or less (Fig. 2.6b). Notably, riverine features such as archipelagos and fluvial lakes and seasonal floodplains cover substantial area along the SLR (Frenette et al. 2012) and can also be abundant in other large rivers. Assuming that the patterns observed in the SLR are transposable, this could imply potentially under-estimated sources of DOM processing in the largest rivers of the world such as the Congo river and the Amazon, which both cover vast areas of increasingly deforested floodplains (Renó et al. 2011; Yuan et al. 2017; Becker et al. 2018) and have been shown to contain highly photoreactive DOM in their main channel (Aarnos et al. 2018). Considering areal degradation rates thus renders possible the identification of potentially overlooked areas (e.g. shores, floodplains) and moments (e.g. expansion of water surface beyond the river bed during floods) in terms of DOM processing, and in such areas and moments photochemical degradation may be particularly important.

In this study we have shown how the three main facets behind in situ processing of DOM in riverine environments: composition, environment and morphometry lead to an integrative ecosystem reactivity. Notably, we highlighted that bioreactivity can be disproportionally important in shallower zones within the river itself, but that the reactivity of exported DOM to the estuary and to the ocean is likely more constrained, in line the relative downstream homogenization of DOM reactivity along the freshwater continuum (Creed and McKnight 2015). We also provide rare experimental evidence for the often-assumed dominance of biodegradation over photodegradation in large rivers, but also emphasize that photo-degradation can locally be just as important in shallow environments with high terrestrial influence. These findings have implications for our understanding of rivers as transporters vs processors of material. While the highest areal DOC degradation rates that have been observed in specific sites with large influence of the Great Lakes undoubtedly imply high carbon cycling through the microbial loop, these sites may not contribute meaningfully to a net retention of carbon at the river scale if most of the degraded carbon has been recently produced in situ, or if water retention times are low and a large majority of the DOC pool is exported downstream largely untransformed. On the other hand, shallow sites with longer retention times that may not have the highest areal DOC degradation rates could contribute the most to net carbon retention, especially if they target DOC pools that are not replenished over the river continuum and if areal degradation rates are high compared to lateral exports. These observations hint at the presence of ecosystem control points (Bernhardt et al. 2017) in heterogenous large rivers with contrasting sources and composition of DOM, river morphometry, and hydrology, pointing at promising research perspectives on the role of large rivers in the export and retention of terrestrial matter in a context of increasing climate extremes, human land-use, and human alterations of water level and flow.

2.9 Acknowledgments

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2.10 Supplementary Material

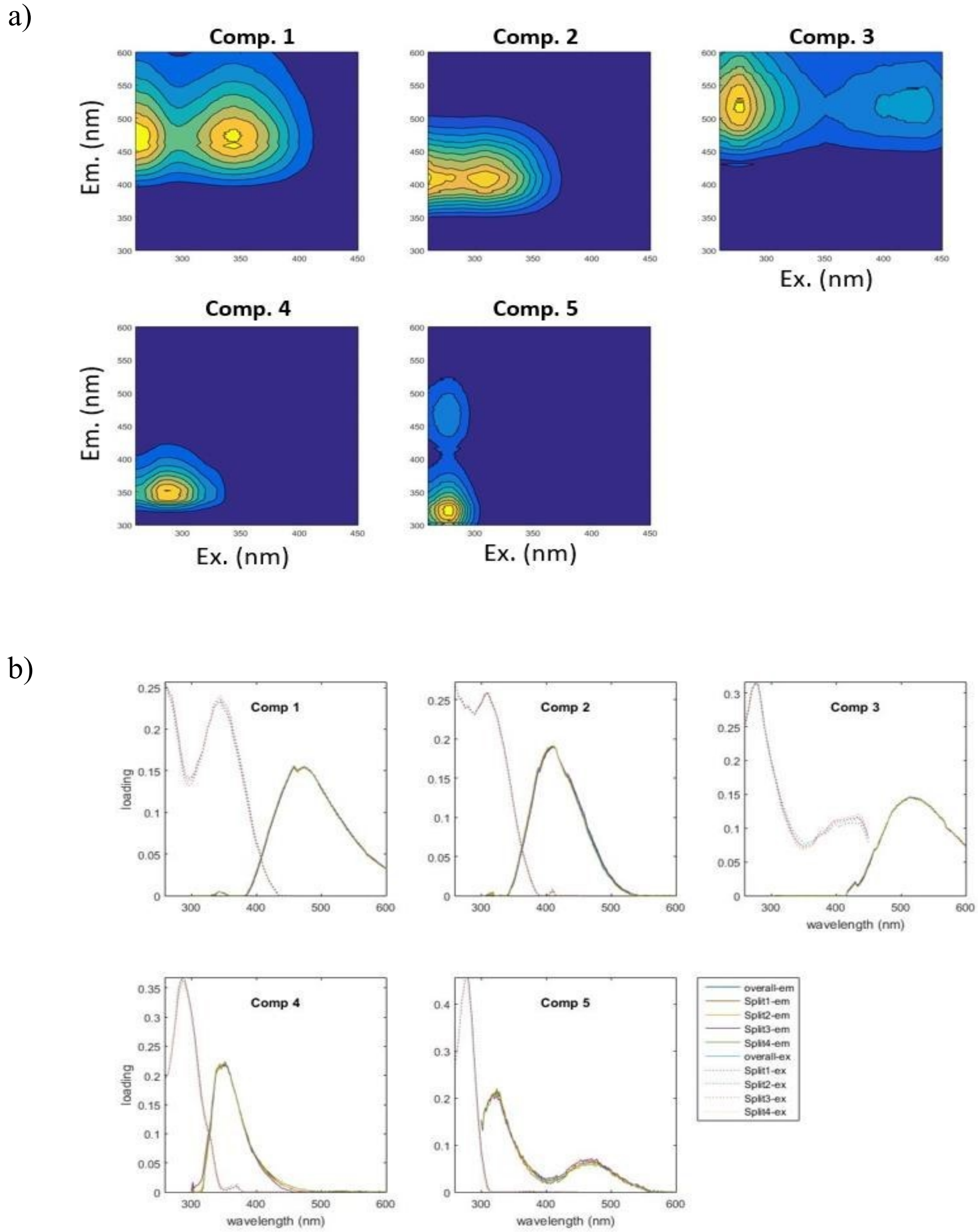

Figure S1. Excitation and emission spectra from the 5 components extracted from the PARAFAC model. a) the loadings of the fluorescence components identified; b) the split half validation plots from the PARAFAC model. Components 1, 2, and 3 are characterized as humic-like peaks, whereas Components 4 and 5 are protein-like peaks.

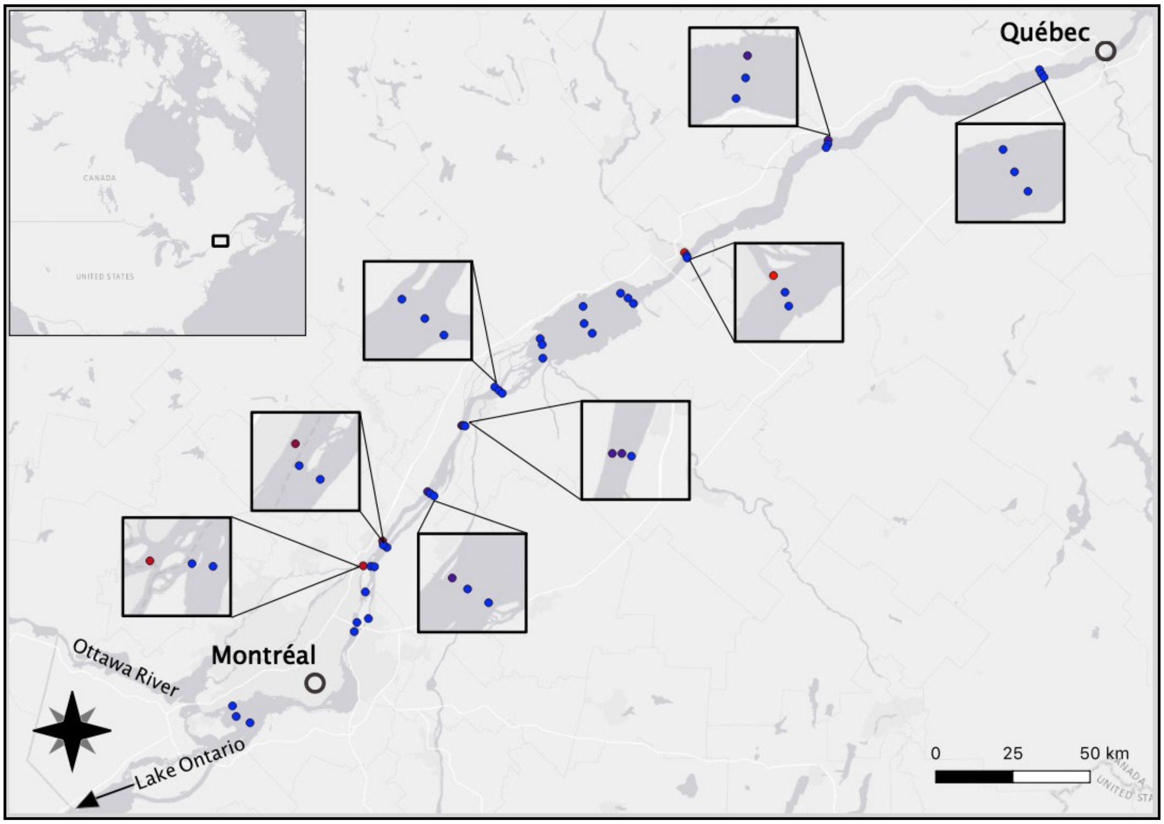

Figure S2. Distribution of the 40 sampled sites during the summer of 2019 on board the R/V *Lampsilis*. Color gradient indicates water origin based on conductivity (see Fig. 2.1) with values ranging from 28 µS cm^{-1} (reddest, water from terrestrially influenced tributaries) to 303 µS cm^{-1} (bluest, main water mass from the Great Lakes).

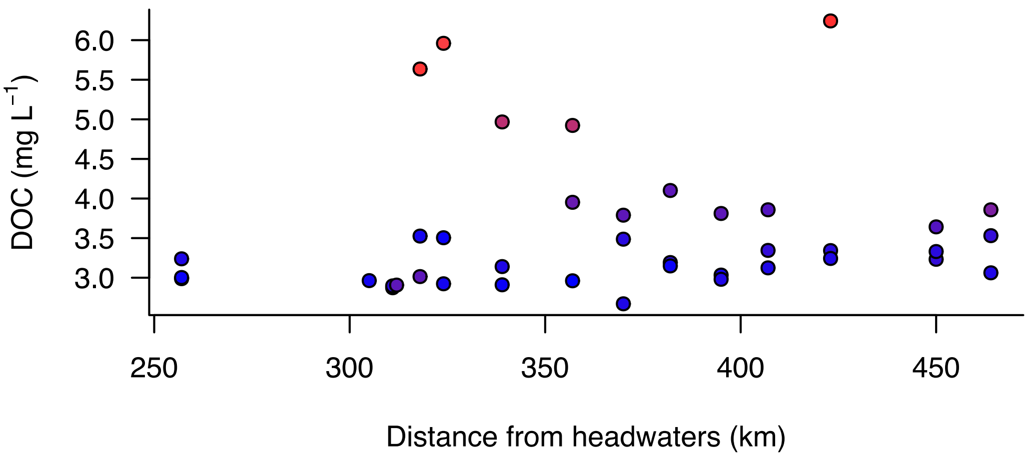

Figure S3. Distribution of ambient DOC concentration along the studied transect. Color gradient indicates water origin based on conductivity values ranging from blue (high conductivity, main water mass from the Great Lakes) to red (low conductivity, water from terrestrially influenced tributaries).

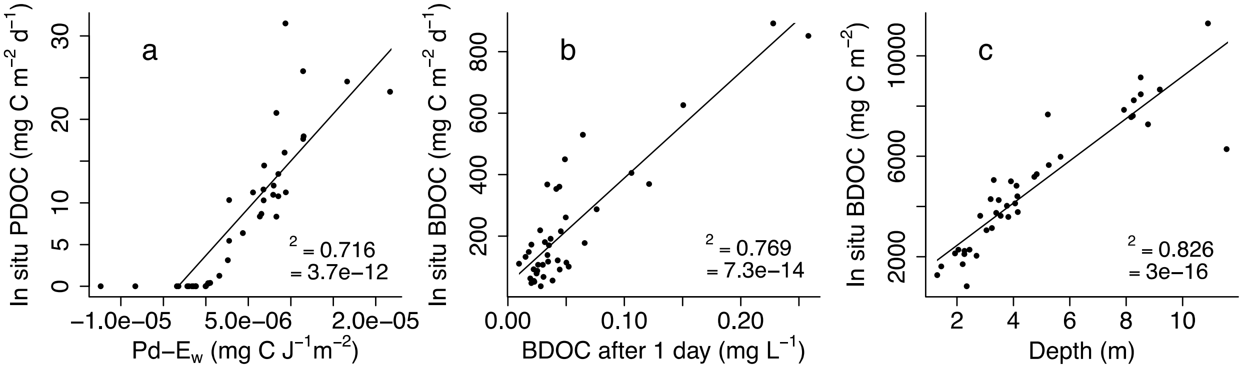

Figure S4. Relationship between estimated in situ loss and their main drivers (as determined by the highest adjusted R^2) for (a) photochemical losses, (b) biological losses after 1 day and c) biological losses after 112 days

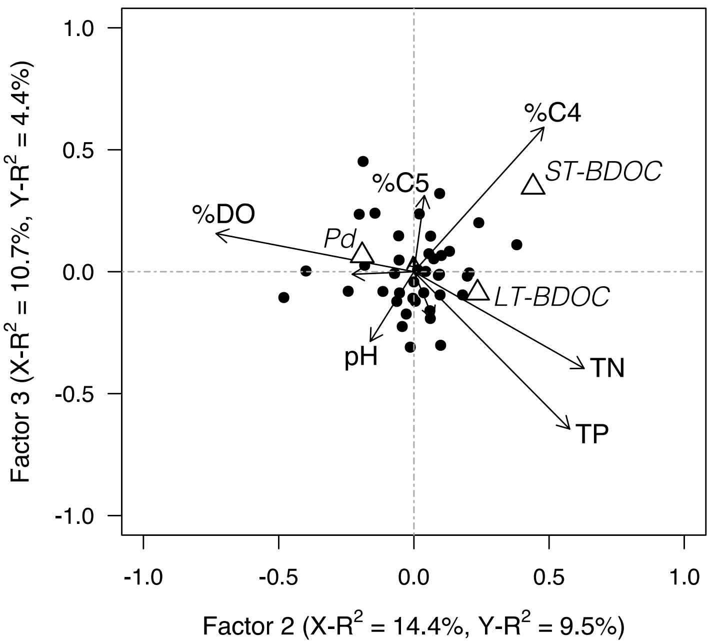

Figure S5. Biplot of the second and third factor of the partial least square regression

Chapitre 3 : Conclusion

3.1 Retour sur les objectifs de l'étude

L'objectif principal de ce projet était de quantifier la réactivité écosystémique de la portion d'eau douce du fleuve Saint-Laurent en évaluant la dégradation biologique et photochimique de la MOD. La réactivité écosystémique a été évaluée dans la portion eaux douces du Saint-Laurent en combinant des approches expérimentale, comparative et de modélisation *in situ*. Ces approches se basent sur des données amassées lors de l'échantillonnage d'un tronçon de 207 km du fleuve Saint-Laurent, au long duquel nous avons caractérisé la concentration et la composition de la matière organique dissoute (MOD) ainsi que l'environnement réactif d'une quarantaine de sites lors d'une mission à bord du navire de recherche Lampsilis. Nous avons par la suite estimé en laboratoire le potentiel de photo- et bio-dégradation de la MOD à partir d'expositions sous un simulateur solaire et d'incubation dans le noir en conditions standardisées. Ces résultats ont par la suite été combinés aux données environnementales (c.-à-d. profondeur et profil d'atténuation de la lumière) afin estimer des taux surfaciques de dégradation *in situ* (c.-à.-d. intégrés à l'ensemble de la colonne d'eau) pour chacun des sites échantillonnés.

3.1.1 Importance relative de la dégradation biologique et photochimique

Le premier sous-objectif était de quantifier et de comparer l'importance et la répartition spatiale des deux principaux processus de dégradation de la MOD. Notre estimation des taux de dégradation *in situ* indiquent que c'est de loin l'activité biologique qui contribue à dégrader le plus de MOD alors que l'activité photochimique est généralement minime et restreinte au premier mètre de la colonne d'eau (Fig. 2.6). Le temps total d'exposition sous la lampe solaire (72 h) s'est révélé suffisant pour observer des pertes photochimiques substantielles et linéaires dans les échantillons hautement colorés provenant des tributaires (Fig. 2.2a). En revanche, pour de nombreux sites à haute conductivité alimentés par les Grands Lacs, les pertes se sont avérées marginales, voire même indétectables, puisque les concentrations oscillaient à l'intérieur de l'incertitude analytique de l'analyseur. Un temps d'exposition plus long combiné à un plus grand nombre de mesures de concentrations permettraient d'améliorer l'exactitude des taux de pertes photochimiques (Pd) dans la masse d'eau principale. Toutefois, il fait peu de toute que ces taux sont extrêmement faibles et les quantifier avec plus de précision aurait peu d'incidences sur nos conclusions. Les courbes de dégradation obtenues suite aux incubations dans le noir étaient quant à elles bien décrites par une équation exponentielle de premier ordre (R^2 : 0,57 - 0,99; moyenne : 0,96). Aucune relation n'a été trouvée entre les pertes engendrées par les deux processus de dégradation, et ce, tant pour les taux de mesurés en laboratoire que pour les taux estimés à l'échelle de l'écosystème. Nous expliquons en partie ce découplage par une consommation contrastée de certains groupes moléculaires par les deux procédés : les composantes fluorescentes de nature humique étaient davantage ciblées par la dégradation photochimique alors que l'activité biologique dégradaient préférentiellement les composantes protéiniques. De plus, les taux de pertes relatives des composantes pour les deux processus étaient corrélés négativement (Figure 2.3b).

La plupart des études comparant la bio- et la photo-réactivité de la MOD dans les écosystèmes fluviaux rapportent uniquement des taux volumétriques de dégradation (Parham 2012; Cory et al. 2014; Lambert et al. 2016; Chupakova et al. 2018; Yang et al. 2019). Ces taux obtenus dans des conditions standardisées permettent une comparaison de la réactivité intrinsèque de la MOD, mais ne permettent pas d'évaluer l'importance relative des 2 processus à l'échelle de l'écosystème. Bien que les études rapportant des taux *in situ* soit rares dans les grandes rivières, l'importance relative des processus dans le Saint-Laurent (Fig. 2.6a) est similaire à celle rapportée par d'études réalisées dans des lacs tempérés et boréaux et desquelles s'inspire notre méthodologie (Granéli et al. 1996; Jonsson et al. 2001; Soumis et al. 2007; Vachon et al. 2016). Cette conclusion semble également se refléter à l'échelle du globe puisqu'on estime qu'environ 10% du CO_2 émis par les écosystèmes d'eau douce peut être attribué à la photo-minéralisation de la MOD (Koehler et al. 2014; Allesson et al. 2020). Pour ce qui est de la répartition spatiale des processus, deux principaux patrons se dégagent de nos résultats. On observe un pic des taux de biodégradation près des effluents urbains de Montréal et de Repentigny, probablement attribuable à des concentrations plus élevées de matière protéinique hautement biolabile. De plus, la distribution des deux processus semble suivre un certain patron longitudinal. Notamment, les eaux à faible conductivité provenant des tributaires de la rive semblent légèrement plus susceptibles à des hauts taux de perte photochimique, mais présentent systématique des taux de perte biologique inférieurs à la moyenne.

3.1.2 Facteurs compositionnels et environnementaux

Le deuxième sous-objectif était d'évaluer l'influence des facteurs compositionnels et environnementaux sur les taux de dégradation de la MOD. Dans le cas de la dégradation biologique, nos résultats indiquent que, pour la plupart des sites, une quantité similaire de MOD (~ 0,03-0,04 mg/L) est dégradée après 1 jour d'incubation, indépendamment de l'origine hydrologique. Nous attribuons cette valeur plancher à un pool de MOD hautement labile et rapidement cyclé à travers la biomasse bactérienne, compte tenu qu'aucun patron d'accumulation n'est observé d'amont en aval (Fig. S2). Additionnellement, une combinaison de facteurs compositionnels et environnementaux semble favoriser une bioréactivité accrue à certains sites. Plus particulièrement, une augmentation des concentrations d'azote et des proportions élevées de composantes protéiniques semblent stimuler une plus grande dégradation pour quelques sites situés près d'effluents urbains ou dans certaines zones de faible profondeur à proximité d'îles. Les pertes photochimiques observées suite aux expositions sous lampe solaire (Pd) sont fortement associées aux proportions de composantes humiques présentes dans la MOD, mais la couleur, un proxy de la concentration en MOD d'origine terrestre, s'avère être un meilleur prédicteur des taux expérimentaux de dégradation par rapport aux autres facteurs intrinsèques et environnementaux.

3.1.3 Réactivité écosystémique

Le troisième sous-objectif était d'évaluer le potentiel total de dégradation *in situ* de la MOD le long du transect étudié grâce à une caractérisation des environnements réactifs. Les taux surfaciques de dégradation totaux se situent entre 36,7 et 892,1 mg C m^{-2} j^{-1} (Fig. 2.4) et sont essentiellement expliqués par les taux *in situ* de biodégradation, qui représentent en moyenne 95% de la dégradation totale. Ces résultats démontrent une grande amplitude dans la réactivité écosystémique le long de la portion d'eau douce du Saint-Laurent. Cette variation n'est étonnamment pas complètement attribuable à la morphométrie du fleuve, c'est-à-dire que les sites présentant les taux *in situ* les plus élevés ne sont pas situés dans les zones les plus profondes de la rivières (Fig. S1). Elles sont plutôt associées à des zones de plus faible profondeur à proximité d'îles ou d'effluents urbains.

Cette évaluation de la réactivité écosystémique présente toutefois certaines limites qui doivent être prises en compte lors de l'interprétation de nos résultats. Nous avions initialement prévu échantillonner le transect au printemps, à l'été et à l'automne 2019, mais des contraintes logistiques et mécaniques ont restreint notre accès au navire de recherche à la saison estivale. Des expériences préliminaires ont aussi été réalisées en 2018, mais les courbes de bio- et de photo-dégradation résultantes étaient inutilisables et ont nécessité un raffinement de la méthode de détermination des concentrations. Notre estimation de la réactivité écosystémique est donc ponctuelle et vraisemblablement représentative de l'été 2019, mais elle ne prend pas en compte les variations saisonnières ou interannuelles. On sait notamment que la MOD humique et terrestre qui intègre abondamment les rivières lors des crues printanières peut être particulièrement fraîche et réactive (Mann et al. 2012; Wang et al. 2012; Coble et al. 2016; Seidel et al. 2016). Par contre, durant cette période, le temps d'exposition aux processus est restreint par le fort courant, la dose lumineuse journalière est réduite et le métabolisme bactérien peut être drastiquement ralenti par les basses températures (Lønborg et al. 2009). Les opportunités de concrétiser cette réactivité sont donc limitées et l'on peut penser que cette matière réactive aura davantage tendance à être exportée en aval du système sans transformation importante (Casas-Ruiz et al. 2020). Notre estimation journalière estivale est donc probablement assez près de la valeur maximale pour l'année échantillonnée. Des données saisonnières de réactivité combinées à des estimations du temps de transit permettraient de confirmer cette affirmation. Mentionnons que le présent projet s'inscrit dans un vaste effort interuniversitaire de caractérisation du fleuve Saint-Laurent et de son état de santé entrepris en 2017. Les données de 3 étés d'échantillonnage ont permis de mettre en évidence que les variations interannuelles du régime hydrologique (Figure 3.1) affectent de façon importante l'influence relative des tributaires et le fonctionnement de la rivière.

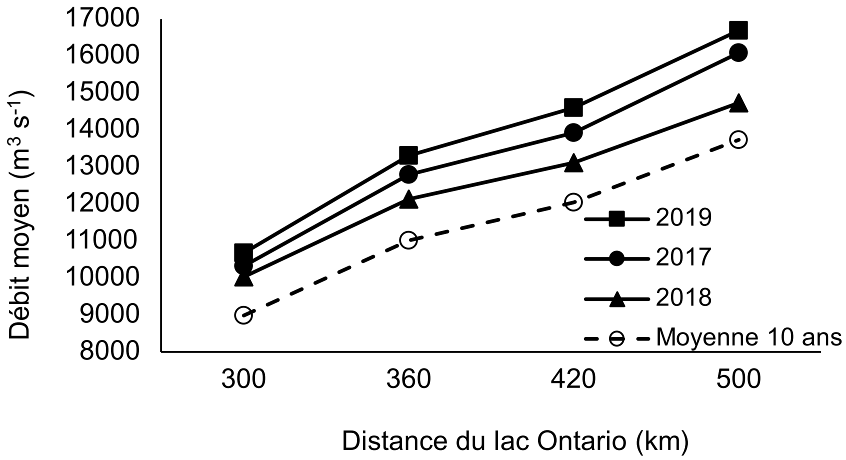

Figure 3.1 Débit moyen du Saint-Laurent mesuré à Lasalle (300 km en aval du lac Ontario), Sorel (357 km), Trois-Rivières (420 km) et Québec (500 km) et calculé entre le 1^er^ janvier et le 8 août (Environnement et Changement climatique Canada, communication personnelle)

Typiquement, la contribution des tributaires à la masse d'eau principale diminue en période de haut débit, ce qui se traduit par des concentrations moyennes plus faibles de nutriments et de composantes humiques photosensibles. Il est donc probable que les taux de dégradation photochimique et biologique soient moins élevés lors de ces périodes. Des expériences mesurant les différentes facettes du métabolisme bactérien effectuées en 2017 et 2018 ont notamment démontré que la consommation bactérienne de carbone est plus faible en période de haut débit (i.e. 2017) (Grater 2020). Bien que l'évaluation détaillée du rôle des variations de régime hydrologique dépasse les objectifs de ce projet, nos résultats obtenus en période de haut débit combinés à ceux de Grater (2020) ainsi qu'à d'autres (Creed and McKnight 2015; Raymond et al. 2016; Casas-Ruiz et al. 2020) contribuent collectivement à renforcer l'idée que les périodes de débit plus élevé inhibent l'expression de la réactivité écosystémique des grandes rivières en limitant le temps d'exposition aux processus de dégradation et favorisant plutôt l'export de matière vers l'aval. Un suivi à long terme permettrait donc de valider cette hypothèse pour le Saint-Laurent. Enfin, il est important de garder à l'esprit que les taux surfaciques que nous avons estimés représentent le potentiel de dégradation journalier d'une colonne d'eau théorique sans nouveaux apports, alors qu'en réalité, la MOD, les nutriments, les bactéries et l'eau qu'elle contient sont constamment renouvelés puis déplacés en aval. Les valeurs rapportées ici demeurent donc une approximation imparfaite, et probablement conservatrice, des taux réels exprimés à chacun des sites. L'intégration de temps de transit et d'une cartographie détaillée du parcours hydrologique pourrait permettre de raffiner cette analyse (ex : Massicotte et Frenette 2011). À ce jour, il demeure toutefois logistiquement impossible de mesurer directement, pour un pixel de rivière donné, les valeurs réelles de dégradation de la MOD au sein même d'un écosystème fluvial en mouvement constant tel que le Saint-Laurent.

3.2 Perspectives d'études

L'étude de la dégradation de la MO en milieu fluvial a connu un essor marqué dans les dernières années avec plusieurs tentatives de conceptualisation de ses dynamiques spatiales et temporelles (Creed and McKnight 2015; von Schiller et al. 2017; Casas-Ruiz et al. 2020;

Kothawala et al. 2020). Malgré l'intérêt croissant pour ces questions, l'enjeu du manque de données concernant la composition et la dégradabilité de la MOD est toujours bien présent (Casas-Ruiz et al. 2020). Les données générées dans le cadre de ce projet permettent donc d'ajouter à cet effort international visant à mieux comprendre les potentiels de transformation et les flux de carbone des grandes rivières du monde (Aufdenkampe et al. 2011; Lauerwald et al. 2012; Butman et al. 2016). Tel que mentionnée précédemment, ce projet s'est principalement concentré sur une caractérisation spatiale de ces processus, mais une caractérisation des variations saisonnières est essentielle si l'on désire en dériver des bilans annuels représentatifs.

La plaine inondable du fleuve représente quant à elle une zone transitoire où se produisent d'importants échanges de MO. Les conclusions de ce projet pourraient d'ailleurs ne pas y être directement transposables puisque cette zone est généralement de très faible profondeur (< 1 m) et contient des concentrations plus importantes de MO particulaire. Elle fait depuis peu l'objet d'un important projet de recherche visant entre autres à caractériser son potentiel de transformation de la MO. Ce type d'environnement hybride brouille la frontière entre le milieu aquatique et le milieu terrestre, mais nous croyons qu'il doit être pris en compte si l'on désire éventuellement dresser un portrait spatio-temporel plus réaliste de la réactivité écosystémique du fleuve.

D'autre part, les changements climatiques apportent déjà et continuerons d'apporter leur lot d'incertitude quant à la compréhension des dynamiques biogéochimiques en milieu fluvial. L'impact de l'augmentation des températures moyennes sur la réactivité et la quantité des apports de MOD en milieu aquatique est encore sujet à débat (Xenopoulos et al. 2021). Dans le cas du Saint-Laurent, on s'attend notamment à ce qu'elle ait une incidence importante sur la contribution hydrologique et sédimentaire des tributaires, particulièrement au printemps et à l'hiver (Boyer et al. 2010a; b). Des apports printaniers enrichis en MO hautement labiles sont susceptibles d'exacerber les problématiques d'hypoxie déjà bien présentes dans la zone estuarienne (Gilbert et al. 2005). Une meilleure compréhension de l'impact de la dégradation de la MO sur l'hypoxie et l'acidification est d'ailleurs l'un des objectifs du plan d'action St-Laurent 2017-2021 (Plan d'action Saint-Laurent 2016). À cet égard, notre projet a permis de mettre en lumière que les zones de faible profondeur à proximité d'îles ou d'effluents urbains sont les lieux disproportionnellement importants de dégradation biologique lorsque l'on tient compte du volume de matière qui y transite. Intégrés à un plan de suivi, ces sites pourraient donc agir à titre de sentinelles de l'activité biologique du fleuve et permettre de détecter rapidement les premiers signes d’une tendance à l’eutrophisation afin d’y faire face plus efficacement.

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