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Dissolved organic matter characterization in a large arctic river : origins and dynamic

Théo Aurélien Le Dantec

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Université
de Toulouse

THÈSE

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*“Sibérie dans la nuit,
Sibérie dans mes yeux,
Sibérie dans ton Coeur,
Sibérie dans la cour,
Sibérie à la mort,
Il fait si froid dehors,
Sibérie, Sibérie, Sibérie nuit et jour.*

*Sibérie mon amour,
Sibérie sous la pluie,
Sibérie c'est mon tour,
Sibérie tout les jours,
Sibérie dans la nuit,
Sibérie dans mes yeux,
Sibérie dans ton Coeur,
Sibérie nuit et jour.”*

“Sibérie”, Manu Chao

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LISTE DES ABRÉVIATIONS ET ACRONYMES

¹³C : Carbon-13

¹⁴C : Radiocarbon

3,5Bd: 3,5-dihydroxybenzoic acid

a350: absorbance at 350 nm

Ad: Acid

Al: Aldehyde

BDOC: Biodegradable Dissolved Organic Carbon

C: Cinnamyl

CDOM: Chromophoric Dissolved Organic Matter

CO₂: Carbon dioxide

CuO: Copper oxide

DIC: Dissolved Inorganic Carbon

DOC: Dissolved Organic Carbon

DOM: Dissolved Organic Matter

DON: Dissolved Organic Nitrogen

EEM: Excitation Emission Matrix

FI: Fluorescence Index

FT-ICR-MS: Fourier Transformed Ion Cyclotron Resonance Mass Spectrometer

GC/MS: Gas Chromatography Mass Spectrometer

HIX: Humification Index

HMW: High Molecular Weight

L8: Lambda 8

LMW: Low Molecular Weight

P: P-hydroxyphenol

PARAFAC: Parallel Factor Analysis

POC: Particulate Organic Carbon

Py/GC/MS: Pyrolysis Gas Chromatography Mass Spectrometer

NMR: Nuclear Magnetic Resonance

S: Syringyl

S₂₇₅₋₂₉₅: Spectral Slope between wavelength 275 and 295 nm

S8: Sigma 8

SUVA₂₅₄: Specific Ultra-Violet Absorbance at 254 nm

TMAH: Tetramethylammonium Hydroxide

V: Vanillyl

RÉSUMÉ

Les projections concernant les changements climatiques dans les régions arctiques annoncent une augmentation disproportionnée des températures de surface pouvant influencer le cycle hydrologique et la fonte des pergélisols. Les hautes latitudes sont donc des environnements potentiellement très sensibles aux modifications du climat. Ces modifications ont la capacité d'impacter les cycles biogéochimiques, en particulier la mobilisation du carbone vers les milieux aquatiques de la zone arctique. Dans les rivières arctiques, la période la plus importante du cycle hydrologique est la crue de printemps qui peut réaliser la majeure partie des transferts annuels de carbone organique vers l'océan dans un temps très court.

L'objectif de cette thèse vise à suivre la dynamique des MOD, au niveau de leur quantité et de leur qualité au cours du cycle hydrologique du fleuve Ienisseï. Diverses techniques de caractérisation des MOD permettant de mettre en évidence les variations saisonnières de leur composition, sources, âge et état de dégradation ont été mise en oeuvre.

La première étape a été d'examiner la large gamme de techniques de caractérisation des MOD dans les rivières du monde afin d'identifier les plus répandues, pertinentes et fiables. Grâce au développement d'une base de données des mesures des qualités des MOD, nous avons pu évaluer la couverture géographique des études de caractérisation des MOD, donner des estimations et gammes de valeurs des principales variables de caractérisation des MOD et observer des tendances générales des qualités des MOD selon un gradient latitudinal.

La seconde étape a porté sur l'étude de la dynamique du COD dans le fleuve Ienisseï concernant les variations de concentrations et les liens avec la chimie de l'eau et l'hydrologie. Nous avons mené des campagnes d'échantillonnage durant trois années consécutives (2014 à 2016), en couvrant avec une haute fréquence de prélèvement la période de la crue de printemps afin d'en capturer la dynamique rapide. Nous avons observé des concentrations en COD qui suivent l'hydro gramme avec les concentrations maximales mesurées quelques jours avant le pic de crue. Le COD a aussi répondu aux variations de débit (augmentation, probablement liée à des précipitations plus intenses) du début d'automne. Nous avons enregistré un flux de COD moyen, durant les trois années de prélèvement, d'environ $4,53 \text{ Tg yr}^{-1}$, ce qui est dans l'ordre de grandeur

rapporté dans la littérature. Nous avons également observé une variabilité interannuelle relativement importante, avec les estimations d'exports annuels variant de 5,45 Tg yr⁻¹ en 2014 à 3,57 Tg yr⁻¹ en 2016, certainement influencée par les variations d'amplitude de débit. Nous avons confirmé le rôle prédominant de la crue de printemps dans les exports de COD avec en moyenne plus de 65% des exportations ayant lieu durant cette période (approximativement mai/juin).

Le troisième point a consisté en l'étude de la qualité des MOD dans les eaux du Ienisseï et de son évolution durant le cycle hydrologique en combinant différents outils de caractérisation. Associer les modes de caractérisation aide à renforcer les observations et à valider les interprétations. La plupart des variables mesurées avec les différentes techniques se sont confirmées les unes les autres. L'utilisation des biomarqueurs de la lignine, des propriétés optiques et de la datation ¹⁴C du MOD ont permis de tracer les sources prédominantes des MOD comme étant principalement dérivées de matières organiques récemment produites lixiviées depuis les litières forestières boréales et des horizons supérieures pendant la crue de printemps et de matières organiques plus anciennes provenant des horizons plus profonds durant la période des basses eaux.

Mots clés : Matières organiques dissoutes, carbone organique dissous, rivières arctiques, Ieniseï, Sibérie, caractérisation, lignine, absorbance, fluorescence, radiocarbon, flux.

ABSTRACT

Arctic regions are expected to be highly sensitive to climate change regarding the prediction of disproportionately large increases in surface temperatures and their related influence over the hydrological cycle and permafrost thaw. These modifications have the potential to impact biogeochemical cycles in these regions and in particular the mobilization of organic carbon into rivers. The most crucial period in arctic rivers hydrological cycle is the spring freshet that can account for most of the annual organic carbon transfers to the ocean in a very short window of time.

The focus of this thesis was to monitor the dynamic of DOM in terms of quantity and quality along the hydrological cycle of the Yenisei river, through DOM characterization approaches to reveal seasonal variations in its composition, sources, age and degradation state.

The first step was to make a review of the full range of existing DOM characterization approaches in worldwide river systems to identify the most widely used, the most relevant and reliable ones. Through the development of a DOM quality measurements database, we have been able to evaluate the geographical coverage of DOM characterization studies, to give estimates and ranges of values of the main reported DOM characterization variables and to observe global trends of DOM quality across latitudinal gradient.

Second stage was to investigate DOC in the Yenisei river with regard to quantity and links with water chemistry and hydrology. We conducted sampling campaigns during three consecutive years (2014 to 2016), covering with a high sampling frequency the spring flood period to capture its very dynamic evolution. We reported DOC concentrations that follow the hydrograph with highest concentrations observed a few days before peak discharge. DOC concentration also responded to discharge variation (increase, likely due to higher precipitation) in early autumn. We reported average DOC flux over the three sampling years of about 4.53 Tg yr^{-1} which is within the range of values reported in the literature. We observed interannual variability with annual export estimates ranging from 5.45 Tg yr^{-1} in 2014 to 3.57 Tg yr^{-1} in 2016, likely driven by discharge amplitude. We confirmed the important role of spring freshet in DOC export with on average more than 65% occurring during this period (roughly May/June).

Third point was to determine DOM quality combining characterization techniques. Combination of approaches helped to strengthen observations and cross validate interpretations. Most of the variables reported from the different characterization techniques confirmed one each other. The use of lignin biomarkers, optical properties and radiocarbon age of DOM allowed us to trace DOM main sources has primarily deriving from recently produced organic matter leached from boreal forest litter and top soil horizon during the spring flood and older organic matter derived from deeper soil horizons during low flow period.

Key words : Dissolved organic matter, dissolved organic carbon, arctic rivers, Yenisei, characterization, lignin, absorbance, fluorescence, radiocarbon, flux.

INTRODUCTION GÉNÉRALE

Enjeux scientifiques en Arctique en lien avec le cycle du carbone

Les régions arctiques présentent une vulnérabilité accrue face au changement climatique avec des augmentations de température plus rapides, disproportionnellement élevées et réparties de façon non uniforme au cours du cycle saisonnier (ACIA, 2004; Serreze et al., 2000; Richter-Menge et al., 2006; Romanovsky et al., 2007). Les impacts du changement climatique incluent également des modifications des cycles hydrologiques, en liens avec la modification des régimes de précipitations, la remonté de la limite forestière vers le nord, l'augmentation de la fréquence des feux de forêt et l'accélération de la fonte des pergélisols (sols restant gelés en permanence durant au moins 2 années consécutives) (ACIA, 2004; Stocker et al., 2013). Ces transformations ont des implications dans la mobilisation des matières organiques vers les milieux aquatiques et de potentielles rétroactions positives sur le climat (Schuur et al., 2008, 2013, 2015; Grosse et al., 2016). Les prédictions actuelles annoncent une contribution importante de la fonte des pergélisols au cycle du carbone global, cependant les multiples devenir de ce carbone restent largement inconnus (Stein et al., 2004; Schuur et al., 2008; Kuhry et al., 2009; Vonk et al., 2013). Les sols gelés préservent les matières organiques des processus de dégradation. Ils ont ainsi une grande capacité de stockage du carbone organique. Les sols des régions arctiques représentent à eux seuls un réservoir de carbone organique équivalent à près de la moitié du carbone organique total présent dans les sols à l'échelle mondiale (Tarnocai et al., 2009; Hugelius et al., 2013, 2014) et près du double du carbone présent actuellement dans l'atmosphère (Kuhry et al., 2009). Ce carbone est actuellement en grande partie « piégé » dans les pergélisols (Schuur et al., 2008). La présence accrue de carbone organique « bio-disponible », remobilisé dans le cycle actif du carbone, résultant de la fonte des pergélisols, pourrait contribuer à alimenter une rétroaction positive sur le climat via l'augmentation de la production de CO₂ et de CH₄ (Kuhry et al., 2010; Schuur et al., 2015; Grosse et al., 2016). Cependant, le degré d'influence de la fonte des pergélisols sur les transferts de matières organiques vers les rivières arctiques et leur composition reste incertain (Vonk et al., 2015).

La saisonnalité extrême et l'éloignement des milieux arctiques compliquent leur échantillonnage. D'octobre à mai, les rivières et les sols sont gelés, la crue de printemps, marquée par la débâcle (période où la glace se brise et est exportée par la rivière) intervient généralement entre mai et juin. Il existe donc encore peu de données publiées sur ces régions et pour des périodes spécifiques comme le dégel de printemps.

Les matières organiques dissoutes

Définition

Les matières organiques dissoutes (MOD), colloïdales et particulaires forment un continuum. Les MOD sont généralement définies de façon opérationnelle. Il s'agit des composées organiques passant à travers la membrane d'un filtre spécifique, le seuil de coupure étant généralement compris entre 0,22 et 0,7 μ m (Thurman, 1985; Zsolnay, 2003). Les MOD comprennent un vaste panel de molécules allant des simples acides et sucres à des substances plus complexes comme la lignine (Stevenson, 1994). La complexité de la composition des MOD provient principalement de la diversité des processus naturels intervenant dans leur synthèse et leur dégradation. Une grande part des molécules constituant les MOD restent encore non identifiées et forment la fraction non caractérisée des matières organiques naturelles, la part des composées spécifiques pouvant être identifiées ne représentant que de 1 à 10% des MOD (Hedges et al., 2000; Leenheer and Croué, 2003; Nebbioso and Piccolo, 2013).

Facteurs de contrôle: quantité et qualité

Les MOD résulte principalement de la décomposition des matières organiques provenant de la végétation, de la litière, des exsudats racinaires et de la biomasse des micro-organismes dans les sols (Kalbitz et al., 2000). Le carbone des sols de surface provenant de la litière peut être incorporé aux horizons minéraux par lixiviation et incorporation biologique ou physique. La consommation microbienne, la décomposition et la minéralisation sont les mécanismes principaux influençant la concentration et la nature des MOD. Les principaux facteurs contrôlant le devenir des MOD sont le climat (quantité et synchronicité des précipitations, températures), la structure et la texture des sols, la disponibilité en nutriments, le pH, la productivité primaire, le type de végétation (distribution racinaire et qualité de la litière) et la nature des communautés microbiennes (Wetzel, 1992; Kalbitz et al., 2000a; Aitkenhead-Peterson et al., 2003; Mulholland, 2003; Cory et al., 2015; Doetterl et al., 2015). Les processus

d'adsorption/désorption et précipitation des MOD sont gouvernés par leurs caractéristiques intrinsèques, leur concentration, mais aussi par la présence d'autres solutés, le pH et le type de matrice (Kalbitz et al., 2005). Les molécules de grande taille ou hydrophobes ont une tendance plus forte à l'adsorption (Kaiser et al., 1996). Dans des sols ayant des surfaces spécifiques élevées, comme les sols argileux, les concentrations en MOD sont maintenues à des niveaux faibles du fait de l'adsorption des molécules organiques sur les surfaces minérales (Nelson et al., 1994). Les quantités et la qualité des MOD dans les milieux aquatiques sont le résultat combiné des processus relargant des MOD (lixiviation des litières, désorption des phases minérales) et de ceux en enlevant (adsorption, décomposition/ minéralisation)(Kalbitz et al., 2000). Ces dernières décennies, il a été observé une augmentation globale des concentrations en Carbone Organique Dissous (COD) mesurées dans les espaces aquatiques, probablement liée aux changements climatiques et aux impacts anthropiques (Evans et al., 2005; Findlay, 2005; Evans et al., 2006, 2007; Lapierre et al., 2013; Butman et al., 2014; Wilson et al., 2016). Il s'agit donc d'un enjeu environnemental majeur motivant l'étude de l'origine, du devenir et des propriétés des MOD dans l'environnement.

Rôle environnemental

A l'échelle globale, le COD représente moins de 1% du stock de carbone total. Il est parmi les formes les plus mobiles et réactives de la matière organique (Cottrell, 2013). Les MOD constituent un vecteur clé entre les sols et le milieu aquatique et jouent un rôle important dans le fonctionnement des écosystèmes. Dans certains cas, les exportations de COD depuis les environnements terrestres peuvent représenter une part importante du bilan carbone d'un écosystème (Kling et al., 1991; Waddington and Roulet, 1997, 2000; Roulet et al., 2007). Les MOD fournissent un substrat et une source de nutriments pour les micro-organismes (Amon and Benner, 1996; Kalbitz et al., 2000b; Del Giorgio and Davis, 2003; Young et al., 2005) et ont donc le potentiel d'influencer la structure des communautés planctoniques et microbiennes (Crump et al., 2003). Les MOD ont également tendance à se complexer avec les polluants, tels que les éléments traces métalliques ou les composés organiques hydrophobes de synthèse, et ainsi influencer leur mobilité dans le système sol-eau (Shiller et al., 2006; Fu et al., 2007; Yamashita and Jaffé, 2008; Aiken et al., 2011; Baken et al., 2011). Les MOD influencent également le fonctionnement des milieux aquatiques de par leur impact sur la pénétration du rayonnement solaire qu'elles atténuent (Foden et al., 2008; Green and

Blough, 1994; Nieke et al., 1997; Vähätalo et al., 2005). Elles peuvent également être partiellement transformées au cours de réactions photochimiques (Wiegner and Seitzinger, 2001; Cory et al., 2007; Osburn et al., 2009; Benner and Kaiser, 2011; Mostofa et al., 2013; Ward and Cory, 2016). Les MOD sont un élément majeur du cycle biogéochimique du carbone. Elles représentent une des formes les plus mobiles de la matière organique. Car l'origine et la structure moléculaire des MOD contribuent à leur réactivité dans les systèmes aquatiques (Wetzel, 1992; Hedges et al., 1997; Findlay and Sinsabaugh, 1999), ces informations sont cruciales pour la compréhension de leur devenir dans l'environnement.

Rôle des rivières (arctiques) dans le cycle du carbone

Les estimations du flux de carbone organique dissous et particulaire (COD et COP) depuis les écosystèmes terrestres vers les océans via les rivières correspondent à des transferts à l'échelle globale de l'ordre de $0,4 \text{ Pg C an}^{-1}$ (Schlesinger and Melack, 1981). Concernant les flux de COD, les estimations varient de $0,17$ à $0,36 \text{ PgC an}^{-1}$ (Meybeck, 1982, 1993; Ludwig et al., 1996; Cauwet, 2002; Aitkenhead and McDowell, 2000; Harrison et al., 2005; Mayorga et al., 2010; Dai et al., 2012). Bien que les estimations des export globaux de COD soient comprises dans une fourchette réduite, elles restent relativement approximatives. Un nombre important d'estimations partagent des jeux de données similaires provenant de l'étude d'un nombre limité de systèmes avec une couverture temporelle également restreinte incluant peu les événements hydrologiques particulier (tempêtes, crues)(Raymond and Spencer, 2015). De plus certaines zones, comme les régions arctiques, sont sous représentées dans les études récentes. Dai et al. (2012) suggèrent une incertitude importante dans le flux annuel autour des 30%. Il existe donc une marge d'amélioration importante dans les estimations des exports de DOM par les rivières à l'échelle globale.

D'un point de vue général, les rivières jouent un rôle important de connecteur entre les écosystèmes terrestres et le milieu marin. Les rivières contribuent au transport latéral de matière en recevant les MOD terrestres mobilisées dans les systèmes aquatiques et en les transférant vers les milieux côtiers. Ainsi, l'étude des MOD transportées par les rivières intéresse également les océanographes, afin de connaître les apports fournis aux milieux estuariens. Les modifications du débit des fleuves peuvent refléter une altération de l'équilibre hydrique terrestre, alors que des

changements de la chimie des eaux sont associés à des perturbations des processus biogéochimiques et des voies d'écoulement des eaux. Il a été suggéré que les exports latéraux de carbone par les rivières pourraient être en mesure d'influencer et de réguler les variations futures des processus de stockage de carbone organiques dans les sols (Dawson and Smith, 2007; Doetterl et al., 2015). Les concentrations en COD mesurées dans les systèmes lotiques varient globalement de 0.5 mg/L à 50 mg/L (Mulholland, 2003). Dans les petits cours d'eau de tête de bassin, la majeure partie du COD est d'origine terrestre (allochtone)(Aufdenkampe et al., 2007; Longworth et al., 2007; Semiletov et al., 2011).

La majeure partie de ce COD provient de la dégradation des résidus de plantes terrestres et de leurs exsudats qui sont transférés des sols vers les cours d'eau par des écoulements souterrains ou de surface. Les MOD peuvent subir diverses transformations au cours de leur transport : dégradation par des hétérotrophes (R. M. Amon and Benner, 1996; Meon and Amon, 2004; Berggren et al., 2009; Logue et al., 2015; Roiha et al., 2016), photo-oxydation (Wiegner and Seitzinger, 2001; Cory et al., 2007; Osburn et al., 2009; Stubbins et al., 2010; Benner and Kaiser, 2011; Hansen et al., 2016; Ward and Cory, 2016), et floculation (Helms et al., 2013; Asmala et al., 2014). La vision du rôle des rivières a largement évolué au cours de la dernière décennie, passant d'un conduit neutre à un réacteur capable de transformer de façon significative les MOD (Cole et al., 2007; Bauer and Bianchi, 2011; Creed et al., 2015; Riedel et al., 2016). En plus des MOD naturelles d'origine terrestre, des MOD autochtones peuvent s'ajouter, elles proviennent généralement des algues et autres micro-organismes (Baines and Pace, 1991) et de la végétation submergée (Raymond and Hopkinson, 2003); et des MOD d'origines anthropiques provenant de sources ponctuelles comme les rejets d'eaux usées (Ma et al., 2001; Guo et al., 2010, 2011).

Les rivières arctiques transfèrent près de 10% de l'eau douce globale vers l'Océan Arctique qui représente à peine 1% du volume global des océans (Opsahl et al., 1999; McClelland et al., 2012). L'influence terrestre sur cet écosystème marin est donc particulièrement forte. Les rivières arctiques exportent, sous forme de COD, de 18 à 26 Tg C an⁻¹ (flux similaire à celui de l'Amazone) vers l'océan arctique. Le flux de carbone organique particulaire est bien inférieur avec de 4 à 6 Tg C an⁻¹ (Dittmar and Kattner, 2003). Dans les régions arctiques, alors que les petits cours d'eau gèlent en totalité, les fleuves arctiques gèlent uniquement en surface. Le débit de base est donc

principalement alimenté par les eaux souterraines. Avec le réchauffement printanier, la neige et la glace fondent déclenchant la débâcle. De la mi-mai à la mi-juillet les fleuves arctiques transfèrent près de 70% du débit annuel (McClelland et al., 2006; Ågren et al., 2010; Stuefer et al., 2011; Wagner et al., 2011; Whitefield et al., 2015). C'est donc une période clé dans les transferts de matière depuis les écosystèmes terrestres vers les écosystèmes aquatiques et *in fine* vers l'Océan Arctique. La période de la crue de printemps (mai-juin) peut contribuer à plus de 60% des exports annuels de carbone organique dissous (Dittmar and Kattner, 2003; Buffam et al., 2007; Raymond et al., 2007; Spencer et al., 2009a; Amon et al., 2012; Holmes et al., 2012; Mann et al., 2012). Dans les bassins versants arctiques, les flux de carbone organique dissous sont principalement contrôlés par le cycle hydrologique.

Caractérisation des matières organiques dissoutes dans les rivières arctiques

Les approches de caractérisation des MOD sont variées et diffèrent selon les propriétés étudiées. Les principales méthodes incluent l'étude des propriétés optiques (absorbance et fluorescence), qui renseignent sur les grands groupes chimiques composant la MOD (aromatique, humique/fulvique, protéique)(Weishaar et al., 2003; Fellman et al., 2010). Les indicateurs optiques peuvent également donner des informations sur la taille des molécules (Low Molecular Weight/Height Molecular weight) (Helms et al., 2008), servir de « proxies » moléculaire (Hernes et al., 2009; Osburn et al., 2016) et différencier leur origine, plutôt allochtone ou autochtone (terrestre /aquatique). Un autre outil de caractérisation correspond à l'identification de molécules bio-marqueurs (composés organiques retrouvés dans les eaux, les sols ou les sédiments permettant d'établir un lien avec des molécules synthétisées par des organismes vivants spécifiques, par exemple un type de végétation ou des micro-organismes particuliers) permettant de tracer les sources et l'état de dégradation de la MOD, la lignine est un des plus utilisés (Canuel and Hardison, 2016). L'isotopie du carbone est également employé dans la caractérisation des matières organiques, l'étude du ^{13}C permettant d'évaluer leurs sources (grand type de végétation)(Thornton and McManus, 1994; Gandhi et al., 2004; Hood et al., 2005; Guo and Macdonald, 2006; Nagel et al., 2009; Kohn, 2010) et la mesure du ^{14}C , leur âge (Neff et al., 2006; Raymond et al., 2007; Tipping et al., 2010; Vonk et al., 2010; Hulatt et al., 2014; Marwick et al., 2015;

Canuel and Hardison, 2016). Les techniques analytiques à haute résolution telles que le *Fourier transform ion cyclotron resonance mass spectrometer* (FT-ICR-MS)(Kujawinski et al., 2002; Sleighter et al., 2009; D'Andrilli et al., 2010; Hertkorn et al., 2013; Cao et al., 2015; Podgorski, 2016) et la résonance magnétique nucléaire (RMN)(Kaiser et al., 2003; Conte et al., 2004; Simpson et al., 2004; Lam and Simpson, 2008; Simpson et al., 2011; Hertkorn et al., 2013; Cao et al., 2016) commencent à être utilisées en routine pour l'étude des MOD dans les rivières. Elles permettent l'élucidation d'un grand nombre de formules moléculaires rattachées aux principaux groupes fonctionnels comme les carbohydrates, les protéines, les lipides, la lignine et les tannins. Des études des MOD se sont également spécifiquement intéressées à leur dégradabilité (photochimique et biologique) à travers des incubations in-situ ou en laboratoire couplées à des méthodes d'analyses (optiques, moléculaires ou isotopiques) (Buffam et al., 2001; Wiegner and Seitzinger, 2001; Del Giorgio and Davis, 2003; Young et al., 2005; Balcarczyk et al., 2009; Mann et al., 2012; Vonk et al., 2013; Logue et al., 2015; Vonk et al., 2015; Hansen et al., 2016).

La connaissance des caractéristiques des MOD peut permettre de prédire son devenir potentiel dans l'environnement (propension à être dégradé ou relative stabilité) (Young et al., 2005; Bauer and Bianchi, 2011; Cory et al., 2015; Riedel et al., 2016; Moody and Worrall, 2017) en intégrant les conditions spécifiques du milieu (Marín-Spiotta et al., 2014; Ward et al., 2017). De nombreuses études ont montré que le COD est généralement moderne, par rapport au COP, et dérive principalement de la production récente de la végétation (Raymond and Spencer, 2015 et références associées). Concernant les rivières arctiques, il est généralement rapporté que la crue de printemps est caractérisée par des exports de MOD fraîches et jeunes, dérivées de la végétation boréale alors que la période de débit de base (dominée par les apports d'eaux souterraines) est marquée par des exports de MOD plus âgées provenant majoritairement des sols profonds, tourbières et zones humides des bassins versants(Neff et al., 2006; Raymond et al., 2007; Amon et al., 2012; Mann et al., 2012, 2016).

Les informations sur la composition chimiques des matières organiques dissoutes dans les rivières arctiques restent relativement limitées. De plus, du fait d'un biais d'échantillonnage où la période estivale est sur représentée, il y a également peu de données sur sa dynamique saisonnière globale. Quelques études ont documenté la

qualité des matières organiques dissoutes dans les fleuves arctiques de façon détaillée, elles concernent en particulier le Yukon (Guéguen et al., 2006; Guo and Macdonald, 2006; Spencer et al., 2008, 2009b, O'Donnell et al., 2010a, 2012; Cao et al., 2016), la Kolyma (Mann et al., 2012; Frey et al., 2015), et la Lena (Lara et al., 1998; Dubinenkov et al., 2015; Gonçalves-Araujo et al., 2015).

Mise à part les grands projets de recherche (PARTNERS, Arctic-GRO) englobant les principaux fleuves arctiques (Lobbés et al., 2000; Amon et al., 2012; Holmes et al., 2012; Walker et al., 2013; McClelland et al., 2015; Mann et al., 2016), peu de recherches ont spécifiquement étudié la qualité des matières organiques du Iénisseï qui est pourtant l'un des plus importants, de par sa surface drainée ($2,54 \cdot 10^6 \text{ km}^2$), de débit ($636 \text{ km}^3 \text{ an}^{-1}$) et ses transferts de carbone organique dissous ($5,08 \text{ Tg an}^{-1}$ soit 27,8 % du COD exporté par les fleuves arctiques)(Amon et al., 2012). L'avantage des projets de recherches comme PARTNERS est qu'ils offrent la possibilité d'évaluer l'ensemble des plus grands fleuves arctiques et de comparer leurs caractéristiques, cependant les campagnes d'échantillonnages restent limitées avec au maximum quelques dizaines de points de prélèvement pour un cycle hydrologique complet capturant rarement la dynamique de la crue de printemps. Spécifiquement au Iénisseï, Kawahigashi et al, (2004) ont étudié la qualité (Fractionnement par résine XAD-8, sucres, lignine, acides aminés, protéines, spectroscopie UV et fluorescence) et la biodégradabilité des MOD transférées dans les petits cours d'eau du bassin versant suivant un gradient de pergélisols, mettant en évidence leur influence sur la qualité des MOD transférées. Roth et al, (2013) ont également étudié les changements de composition des MOD, par extraction sur phase solide et FT-ICR-MS, au long d'un transect suivant le cours du Iénisseï. Prokushkin et al., (2007;2011) ont également étudié les sources des MOD (via absorbance UV et Pyrolyse/GC/MS), dans des tributaires importants du Iénisseï (Kochechum et Nizhnyaya Tunguska principalement) drainant le plateau de Sibérie centrale. Le Iénisseï a un rôle important dans le cycle biogéochimique des MOD dans la zone arctique et est encore à ce jour relativement peu étudié. C'est pour ces raisons que nous nous sommes intéressés à ce fleuve.

Objectifs de la thèse

Cette thèse a pour objectif d'améliorer notre compréhension du rôle des rivières arctiques dans le cycle du carbone, dans le contexte du changement climatique. Dans cette optique, nous avons quantifié et caractérisé les matières organiques dissoutes terrigènes transportées par l'un des plus grands fleuves arctiques. Nous avons plus particulièrement étudié les sources, l'état de dégradation et l'âge des MOD. Ceci tout au long du cycle hydrologique et durant trois années consécutives, avec une attention particulière accordée à une période clé : la crue de printemps. L'originalité de ses travaux réside dans la haute fréquence d'échantillonnage au moment de la crue, permettant de capturer la dynamique des MOD durant cette période cruciale, la large gamme des variables de qualité des MOD mesurées et l'étude d'un des plus grands bassins versants arctiques encore peu documenté sur ces sujets. Les conditions climatiques extrêmes et les défis logistiques de ses zones reculées offrent des opportunités rares d'effectuer des campagnes d'échantillonnages proches des embouchures des grandes rivières arctiques. L'étude du cycle du carbone dans ces régions est donc un défi scientifique et humain important, et l'acquisition de données dans ces espaces méconnus est cruciale afin d'évaluer son évolution dans le contexte du changement climatique actuel.

Les principales questions de recherche posées:

- Quelle est la variabilité temporelle des concentrations et flux de matières organiques dissoutes au cours d'un cycle hydrologique ?
- Quelle est la variabilité temporelle de la composition chimique des matières organiques dissoutes dans les rivières arctique ?
- Quelles sont les différentes sources des matières organiques dissoutes au cours du cycle hydrologique ?
- Quels liens existe-t-il entre la quantité et la qualité des matières organiques dissoutes et les variables hydrologiques et physico-chimiques des eaux?
- Quels liens existe-t-il entre la quantité et la qualité des matières organiques dissoutes exportées et les caractéristiques du bassin versant ?

Notre approche pour répondre à ces interrogations:

Le Ienisseï, notre fleuve d'étude, draine l'un des plus grand bassin versant de l'Arctique. C'est l'un des plus importants contributeurs en termes de flux d'eau et de COD vers l'océan arctique. Il a pour particularité de posséder dans sa zone nord des pergélisols continus et discontinus. La modification de ces écosystèmes, sensibles au changement climatique, est susceptible d'impacter les transferts de carbone.

L'approche choisie dans cette étude est l'observation de séries temporelles à proximité de l'exutoire du Ienisseï. Un échantillonnage intensif au niveau temporel permet de rendre compte des variations saisonnières des variables étudiées. Cette variabilité est particulièrement prononcée dans les rivières arctiques. Elle est principalement liée à un cycle hydrologique fortement contrasté. On observe d'une part la crue de printemps présentant des débits extrêmement élevés (provenant de la fonte des neiges) durant un court laps de temps (moins de 2 mois) et d'autre part une longue période (plus de 6 mois) où le fleuve est totalement gelé en surface et les débits très faibles. Les variations de température et de débit vont avoir tendance à influencer les chemins d'écoulement des eaux et l'activité biologique générale, tout ceci impactant les concentrations et la nature des éléments transportés dans le fleuve au cours du temps. La localisation de la zone d'échantillonnage à proximité de l'exutoire permet de mesurer un signal qui intègre l'ensemble du bassin versant en termes de flux et de processus biogéochimiques et ainsi avoir une vision globale du fonctionnement de ce vaste écosystème. L'observation de variables spécifiques, telles que les caractéristiques des matières organiques, à l'exutoire d'une rivière renseigne sur les processus en cours et la nature du bassin versant drainé. En effet, toutes les matières transportées par l'eau dans cette zone et n'étant pas transformées auparavant, finissent par transiter par ce point précis, apportant avec elles des informations mesurables et interprétables sur leur parcours. Les MOD ainsi transportées par les rivières reflètent les caractéristiques des paysages environnant et tout changement au sein du bassin versant finira par impacter le signal de la rivière. Cette étude utilise donc la signature particulière des MOD transportées dans les rivières pour obtenir des informations sur les processus en cours à l'échelle du bassin versant.

Les outils de caractérisation employés comprennent :

- Les propriétés optiques des MOD, fluorescence et absorbance, permettant d'identifier certaines grandes classes chimiques composants les MOD (aromatiques, type humique ou protéique, proxy de la lignine etc...) et de différencier des apports terrigènes ou autochtone et microbiens. Certains indicateurs renseignent également sur le poids moléculaire de constituants de MOD.
- les biomarqueurs de la lignine qui fournissent des indicateurs sur les sources des MOD provenant des plantes supérieures.
- la datation au ^{14}C du COD, qui informe sur la source et le devenir de MOD. L'analyse ^{14}C du COD permet de révéler les contributions relatives de différents réservoirs de carbone dont les âges varient. Elle peut par exemple révéler le contraste entre des MOD fraîches et jeunes provenant des litières végétales et des horizons de surfaces et des MOD plus anciennes provenant d'horizons de sols profonds voir des MOD très anciennes provenant des pergélisols.

Une particularité de nos campagnes d'échantillonnage, lié à la nécessité d'obtenir d'importantes quantités de MOD afin de réaliser les analyses moléculaires et isotopiques envisagées, réside dans le prélèvement de grande quantité d'eau brute, de l'ordre d'une centaine de litres, que nous concentrons par la suite grâce à un système constitué d'une filtration tangentielle couplée à un dispositif d'osmose inverse.

Contenu de la thèse :

Cette thèse est organisée en trois chapitres présentés sous forme d'articles :

Le chapitre 1 intitulé « Dissolved organic matter characterization in lotic ecosystems at a global scale: a review » présente une synthèse des techniques actuelles de caractérisation des MOD et dresse un état des lieux de leur application pour l'étude de la biogéochimie du carbone dans les rivières à l'échelle mondiale. Il repose sur la création d'une base de données rassemblant les mesures des principales variables de caractérisation des MOD dans les rivières de la planète. Cet outil a permis d'identifier les grandes tendances et les gammes de valeurs des différentes variables observées en fonction des régions du globe (classes de latitudes). Ce chapitre met également en avant les évolutions récentes des techniques de caractérisation de la matière organique et les futures directions de recherche.

Le chapitre 2 intitulé « Dissolved organic carbon dynamic, hydrology and water chemistry in the Yenisei river » porte sur la dynamique et les flux de COD dans le Ienisseï au cours des trois années d'observation et leurs relations avec les variables environnementales (hydrologie, climat) et la physico-chimie de l'eau.

Le chapitre 3 intitulé « Dissolved organic matter quality and its dynamic in the Yenisei river: composition, sources, age and degradation state » s'intéresse à la qualité des MOD et à l'évolution de leur composition en relation avec la dynamique hydrologique du Ienisseï via l'étude combinée des biomarqueurs de la lignine, des propriétés optiques des MOD et de l'isotopie du ^{14}C du COD.

Contributions:

Durant ma thèse, j'ai participé à une première campagne de reconnaissance de terrain en octobre 2014. Durant cette mission j'ai pu découvrir Igarka et ses alentours, le laboratoire de géocryologie qui nous y accueille, la zone d'échantillonnage et être formé au protocole de prélèvement et de filtration. J'ai ensuite participé à la préparation et la réalisation des campagnes d'échantillonnage des crues de printemps de 2015 (sur le terrain de début mai à fin juillet) et 2016 (sur le terrain de fin avril à mi juin). Durant les campagnes d'échantillonnage, j'ai réalisé les prélèvements et les mesures in-situ accompagné par nos collègues russes (Anatoli Pimov et Sergueï), les étapes de filtration/concentration des échantillons et leur conditionnement préalable avant rapatriement à Toulouse. La campagne d'échantillonnage 2014 a été menée par Roman Teisserenc et Allison Myers-Pigg avec la contribution de Nikita Tananaev pour les échantillons de fin d'été et d'hiver. En 2015, les échantillons précédant la crue de printemps ont été prélevé par Nikita Tananaev et Laure Gandois a réalisé les prélèvements estivaux (juillet/août). En 2016, les prélèvements de mi juin à mi juillet ont été assuré par Pierre-Alexis Herrault puis par Maxime Deschuyteneer de mi-juillet à mi-août. Roman Teisserenc a également participé aux prélèvements au moment des pics de crue de 2015 et 2016 autour de la mi-mai.

Chapitre 1 : J'ai réalisé la revue systématique de la littérature, créé et alimenté la base de données sur laquelle se base l'article. Les co-auteurs ont participé à l'interprétation et à la discussion des résultats, m'ont aidé à organiser la trame de l'article et m'ont orienté dans le traitement des données.

Chapitre 2 : J'ai réalisé la majeure partie de la préparation des échantillons. La plupart des mesures (concentration en COD, anions-cations) ont été conduites par Frédéric Julien sur la plateforme d'analyse physico-chimique de EcoLab à Toulouse. La mise en forme et le traitement des données ont été réalisés par mes soins ainsi que la majeure partie du processus de rédaction. Les co-auteurs m'ont orienté dans la sélection de variables clés et dans la structuration de l'article.

Chapitre 3 : J'ai réalisé la majeure partie des mesures d'absorbance sur la plateforme d'analyse physico-chimique de EcoLab à Toulouse, les mesures complémentaires ont été assurées par Frédéric Julien. J'ai effectué les mesures de fluorescence à l'iC2MP de Poitiers avec l'aide de Jérôme Labanowski et Leslie Mondamert qui ont également réalisé les traitements PARAFAC des matrices d'excitation/émission. Les analyses de biomarqueurs de la lignine de 2014 ont été conduites par Allison Myers-Pigg au Texas A&M à Galveston. J'ai réalisé les analyses des biomarqueurs de la lignine pour les échantillons de 2015 et 2016 à AWI à Bremerhaven en Allemagne, avec l'aide de l'équipe de Gésine Mollenhauer et en particulier de Maria Winterfeld qui m'a formé aux manipulations et au traitement des sorties GC/MS. La préparation des échantillons et les analyses ^{14}C ont été réalisées à AWI à Bremerhaven par l'équipe de Gésine Mollenhauer. La mise en forme et le traitement des données ont été réalisés par mes soins ainsi que la majeure partie du processus de rédaction. Les co-auteurs m'ont orienté dans la sélection de variables clés et dans la structuration de l'article.

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CHAPITRE I

DISSOLVED ORGANIC MATTER CHARACTERIZATION IN LOTIC ECOSYSTEMS AT A GLOBAL SCALE: A REVIEW

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*« Quel jour sommes-nous
Nous sommes tous les jours
Mon amie
Nous sommes toute la vie
Mon amour
Nous nous aimons et nous vivons
Nous vivons et nous nous aimons
Et nous ne savons pas ce que c'est que la vie
Et nous ne savons pas ce que c'est que le jour
Et nous ne savons pas ce que c'est que l'amour. »*

« Chanson » Jacques Prévert

RÉSUMÉ

Le cycle global du carbone organique comprend diverses composantes (réservoirs et flux) qui subissent l'influence des changements globaux. Le compartiment rivière, où domine généralement le Carbone Organique Dissous (COD), est un des plus réactifs et dynamiques. Bien que les flux de COD soient relativement bien contraints, les caractéristiques du COD (en particulier source et réactivité) sont encore mal connues. Depuis la dernière décennie, on note tout de même un essor significatif de ce domaine de recherche.

Les matières organiques dissoutes (MOD), sont considérées comme une des substances naturelles les plus complexes et jouent un rôle majeur dans la biogéochimie et la photochimie des eaux naturelles. Identifier l'origine des MOD, telle que le type de végétation ou l'horizon de sol desquels elles découlent, ainsi que son état de dégradation est crucial pour une meilleure compréhension des processus du cycle du carbone liant les milieux terrestres aux milieux aquatiques et leurs apports aux océans. De plus, la dynamique des MOD donne un aperçu de la réponse de l'écosystème aux changements climatiques et aux perturbations anthropiques, et de sa potentielle rétroaction sur le climat général. La qualité des MOD a été bien moins étudiée que celle des matières organiques particulaires. Ceci est probablement dû aux limitations techniques associées avec l'isolation des MOD et les méthodes d'analyses. Le développement et l'amélioration constante des techniques analytiques et l'intensité des échantillonnages permettent de décrire les MOD de plus en plus précisément. Cependant, aujourd'hui, jusqu'à 75% des MOD restent non caractérisées. Cet article de revue se concentre sur les études caractérisant les MOD dans les rivières du monde, il dresse un bilan des méthodes et approches employées, souligne les progrès récents et discute leur pertinence et perspectives de recherche. Les résultats acquis à l'échelle globale ont été synthétisés pour évaluer leur couverture géographique et déterminer les statistiques basiques des principales variables de caractérisation selon un gradient de latitude à l'échelle globale.

Les principales observations que l'on peut tirer de ces travaux sont qu'à une échelle globale, peu de jeux de données sont disponibles, que leur représentativité spatiale et temporelle est encore limitée et est accompagnée d'un manque de standardisation des méthodes. Néanmoins, la dynamique scientifique actuelle sur le sujet est prometteuse.

Mots clés: MOD, techniques de caractérisation, écosystèmes lotiques, propriétés optiques, isotopie du carbone, composition moléculaire, biomarqueurs

ABSTRACT

Global organic carbon cycle comprises several components (reservoirs and fluxes) that are influenced by global change. The riverine component dominated by dissolved organic carbon (DOC) is one of the most reactive and dynamic. Although DOC fluxes estimation are relatively well constrained, the DOC characteristics (source and reactivity) are still poorly understood. Since last decade, an increase of scientific effort in this field of research has been noticed.

Dissolved Organic Matter (DOM) is considered as one of the most complex naturally occurring mixtures and plays a major role in the biogeochemistry and photochemistry of natural waters. Identify the origin of DOM, such as vegetation type or soil horizon and its degradation state is critical to better understand carbon cycling processes linking terrestrial and aquatic ecosystems, and their inputs to oceans. Moreover, DOM dynamics provides insight on ecosystem's response and potential carbon feedback to climate change associated with anthropogenic disturbances. DOM quality has been much less investigated than particulate organic matter. This is related to technical limitation in DOM recovery and analytical methods. Constant improvement and development of analytical techniques and sampling resolution allow describing DOM in an increasingly detailed way. However, to date, up to 75% of DOM remains uncharacterized. This review focuses on DOM characterization studies in lotic ecosystems, summarizing methods and approaches applied, highlighting recent progresses, discussing their suitability and research perspectives. Relevant results acquired at a global scale have been synthesized to report geographical coverage, sampling effort and basic statistics of the main characterization variables across a global latitudinal gradient.

The main conclusions drawn from this work are that at a global scale few datasets are available, that the temporal and spatial representativeness is still poor along with a lack of methods standardization. However, the current scientific advances on this topic are promising.

Keywords: DOM, characterization techniques, optical properties, isotopy, molecular composition, biomarkers, lotic ecosystems

1.1 INTRODUCTION

Riverine dissolved organic matter (DOM) characterization: issues and challenges

Riverine carbon comprises Dissolved Inorganic Carbon (DIC), Particulate Organic Carbon (POC) and Dissolved Organic Carbon (DOC). The riverine carbon inputs to estuaries and ocean margins are approximately 1 Gt annually (Ludwig et al., 1996), with around 40% as DIC and the remaining as DOC and POC. On average the organic carbon discharge is dominated by DOC by a factor of 4 (Bauer and Bianchi, 2011 and references therein).

In the past few decades, scientific interest for the study of dissolved organic matter (DOM) has drastically increased, along with the comprehension of its biogeochemical significance. The role of inland aquatic system has evolved from being considered as neutral pipes to active DOM reactors (Cole et al., 2007). Dissolved organic matter is extremely mobile in the environment and has important roles in river ecosystem as a nutrient source influencing food webs structure and function (Findlay and Sinsabaugh, 2003) and as it can influence light penetration through the water column (Foden et al., 2008). Dissolved organic matter can also interact with other chemical elements such as metals (Yamashita and Jaffé, 2008) and organic pollutants (Haitzer et al., 1998). Riverine dissolved organic matter has strong implications for global carbon budgets as net carbon fluxes in aquatic systems tend to be greater per unit area than in the surrounding land (Cole et al., 2007).

The complexity of DOM is related to its numerous sources within terrestrial and aquatic ecosystems (vegetation, microorganism, soil organic matter), transformation processes (light and microbial related) and interaction with natural and anthropogenic phases (oxydes, clays, plastics...). As a consequence, a wide range of molecular composition, ages, degradation states and reactivity can be measured in aquatic ecosystems (Raymond and Bauer, 2001). The nature of DOM influences its fate along the land to ocean continuum, controlling the extent to which the C will either be retained in the fluvial network, released to the atmosphere via biotic or abiotic degradation, or transported downstream (Moody and Worrall, 2017 and references therein). Riverine DOM can originate from a variety of sources, including autochthonous sources resulting from in situ processes and allochthonous sources resulting from terrestrial or

atmospheric deposit inputs. Autochthonous sources may include leachates from dead aquatic organisms, phytoplankton, zooplankton, macrophytes and bacterial exudates etc., whereas allochthonous sources comprise leachates from watershed soils and vegetation (Aitkenhead-Peterson et al., 2003) and atmospheric deposits (Willey et al., 2000).

When evaluating the significance of a carbon input to aquatic ecosystems, the quality (composition, physico-chemical properties, reactivity) and quantity (concentration and fluxes) of organic matter must be considered. The term “organic matter quality” refers on one hand it can define the organic matter biodegradability, i.e. its ability to support microbial growth (labile versus refractory fractions) (Hopkinson et al., 1998) and on the other hand it also relates to DOM chemical composition that can allow to infer its behavior and origin. Therefore major biogeochemical interests concern how much C is exported from catchments, in what form and in which conditions, i.e. when and where these exports occur. The comprehension of the mechanisms governing the mobilization and transfer of organic matter from watersheds to riverine networks has strong implications for soil conservation, water quality and ecosystem health management.

Detailed DOM characterization can be extremely challenging because DOM comprises a huge diversity of organic compounds and is highly variable at spatio-temporal scales. However, great progress has been made during the last three decades toward identifying the structure of DOM and the role that it plays in the biogeochemistry of aquatic ecosystems. Current trends in DOM studies, supported by improvements in DOM isolation, characterization techniques and molecular biology, tend to more combined analytical methods to investigate DOM complexity.

The present review proposes an assessment of the current abilities to describe riverine DOM characteristics. We made an inventory of studies reporting riverine DOM characterization data through the constitution of a global database of DOM variable measurements and studies conducted in lotic systems. To explore the contribution of DOM characterization methods to the understanding of DOM quality evolution in rivers, we provide a synthesis of the data available along with range of values of specific characterization parameters across a global latitudinal gradient, evaluation of the spatial coverage of past sampling campaigns and trends in the use and development of DOM analytical techniques.

1.2 DATABASE PRESENTATION

We selected scientific papers reporting DOM characterization specifically in lotic systems, i.e streams and rivers. Our focus was on global DOM characterization, studies investigating specific DOM fractions such as high molecular weight (HMW) or low molecular weight (LMW) DOM or fulvic and humic acids were not included. DOM variables were included only if they were related to unique spatio-temporal information, i.e corresponding to one sampling point and representing a time period from day to season (regionally or yearly averaged data were not included). To be included, sampling sites must have freshwater salinity (threshold <1 psu to include data originating from river area with limited marine influence) to reflect the river “end-member” signature. Studies were selected when they presented bulk DOC information along with at least one characterization variable. We retrieved numerical data when they were directly available from a table in the paper or in supplementary information. Main information gathered includes paper reference, sampling location, time of sampling, list of characterization variable reported and when available measured DOC concentration, DOC/DON, bioavailable dissolved organic carbon (BDOC), main lignin phenols parameters, absorbance at specific wavelength and ratios, fluorescence indicators and stable and radiocarbon isotopic ratios. The compilation represents our best attempt to integrate the available information, yet nomenclature for study sites varies considerably and in some occasion, little or no information is provided in the literature (i.e. site names, sampling dates and conditions etc.). In the future, some basic information should be systematically associated with DOC characterization data: precise sampling location (longitude, latitude), precise time of sampling (full date), discharge or hydrological stage, and has much as possible provide raw data when presenting averaged information. Other data that could be included in an improved database but are not systematically reported: Watershed area, % Land cover type, Stream order, residence time (days) and other ancillary data (environmental parameters). This would facilitate incorporation in synthesis work, improving contextualization and comparability. Our database consists in the evaluation of 227 DOM characterization studies representing around 2830 unique entries comprising either data points or study description.

Since the oldest study we reviewed (Larson, 1978) conducted in White Clay Creek (Pennsylvania, U.S.A.) and presenting DOM content of phenol, carbohydrate, lipid, amino

acid and protein (determined by compound classification analysis and GC), riverine DOM characterization studies have known an exponential increase especially in the past five years. As shown on figure 1, riverine DOM characterization measurements have been acquired across all continents with an higher spatial coverage in USA including Alaska. For tropical regions most of the data have been reported for two main watersheds, the Amazon (Seidel et al., 2015) and Congo rivers (Stubbins et al., 2010; Spencer et al., 2016) with sampling campaigns going from small headwaters catchments to river mouth. A new growing pool of riverine DOM characterization studies is originating from Chinese research with most of the studies focusing on anthropic influences on DOM in rivers flowing through urbanized areas (Jiang et al., 2017). In Arctic regions, the majority of the sampling sites is within the great arctic river watersheds in Alaska, Canada and Siberia (Amon et al., 2012). Spectroscopic techniques relying on fluorescence and absorbance DOM properties are by far the most widespread technique with more than 50% of the evaluated studies presenting absorbance or fluorescence data (Figure 1.1). This over representation of spectroscopic techniques is probably due to their lower cost and the fact that large number of samples can be processed easily and fast.

1.3 DOM CHARACTERIZATION APPROACHES FOR RIVERINE SYSTEM STUDY WORLDWIDE

DOM characterization can be divided in two main complementary categories. On one hand, analytical approaches aiming at describing DOM constituents, focusing on elucidating specific functional groups and molecular structures and on the other hand holistic approaches aiming at interpreting molecular trends with regards to ecological processes and DOM fate. Early methods for DOM characterization have been primarily developed for seawater studies (Bauer and Bianchi, 2011). First developments of riverine DOM characterization approaches consisted in the identification of measurable characteristics of DOM providing indicators of the “quality” of organic material entering estuaries (Hopkinson et al., 1998).

At a spatial level, different sampling approaches exist. Sampling sites located close to river mouth, aiming at describing terrestrial export from land to ocean and general watershed processes, river transects investigating in situ DOM transformation across

environmental gradients and research conducted in headwater catchment focusing on DOM transfers from soils to aquatic systems. Differences arise between DOM in headwaters, middle reach or at river mouth in relation to the intensity and duration of transformation processes (Jaffé et al., 2008 ; Marín-Spiotta et al., 2014). A variety of tools exists to characterize riverine DOM including bulk DOM properties such as DOC:DON ratios, stable ($\delta^{13}\text{C}$) and radiocarbon isotopes ($\Delta^{14}\text{C}$) determined by Isotope Ratio Mass Spectrometry (IRMS) and Accelerator Mass Spectrometry (AMS), optical properties (CDOM absorbance and fluorescence) derived from excitation/emission fluorescence measured by spectro(fluoro)meters, various biomarkers such as amino acids, carbohydrates, lipids, black carbon and lignin phenols generally determined through Gas- or Liquid Chromatography Mass Spectrometry (GC-MS/LC-MS). New perspectives in DOM molecular description are given by high-resolution analytical techniques, such as Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) and advanced Nuclear Magnetic Resonance (NMR) spectroscopy which are now routinely used to investigate riverine DOM. Global DOM characterization approaches in freshwater and marine environments have been extensively reviewed (Leenheer and Croué, 2003; Nebbioso and Piccolo, 2013; Minor et al., 2014).

1.3.1 Spectroscopy

The optically active fraction of DOM can provide compositional information and allow to track DOM change during degradation and consumption processes (Weishaar et al., 2003; Osburn and Bianchi, 2016). The widespread use of spectroscopic techniques has been supported by recent advances in optical technology and the development and validation of specific DOM optical proxies (Fellman et al., 2010a). These methods are now relatively easy to handle, precise, rapid and cost effective, thus representing an excellent tool to monitor DOM dynamics at high spatio-temporal resolution that can be incorporated to long term monitoring studies (Jaffé et al., 2008).

Evaluation of DOM properties mainly relies on Ultraviolet-visible spectroscopy at specific wavelengths (a254, a350 etc...). Spectral slope coefficients (S275-295, SR) also provide DOM quality information (Molecular weight and aromaticity) (Helms et al., 2008; Li and Hur, 2017). Specific Ultraviolet Absorbance at 254 nm (SUVA254) has

been validated by Weishaar et al. (2003) relating this indicator to chemical composition (aromaticity) and reactivity of DOM via correlation with DOM ^{13}C NMR analysis.

Detailed review of fluorescence DOM techniques have been made by Hudson et al. (2007) with focus on the study of natural, waste and polluted waters. Fellman et al. (2010) have also reviewed DOM fluorescence with emphasis on the novel perspectives offered by this technique to study DOM dynamics in freshwater ecosystems. A large panel of indicators has been developed to characterize DOM fluorescence properties. Among the most common indicators is the fluorescence index (FI), which provide source (microbial vs. terrestrial higher plant material) and degree of degradation information (reflecting contribution of aromatic vs. non aromatic DOM) (Cory and McKnight, 2005). DOM fluorescence analysis is also commonly reported as excitation-emission matrices (EEMs) analyzed by parallel factor analysis (PARAFAC) to identify specific fluorescence components related to DOM properties, mainly humic like, fulvic-like and protein-like corresponding to specific peaks of fluorescence intensities (Jaffé et al., 2014). Specific indices also derive from EEMs such as humification index (HIX) or freshness index ($\beta:\alpha$). Summary and detailed description of existing fluorescence components and optical indices can be found in Fellman et al. (2010), Singh et al. (2010) and Hansen et al., (2016).

Fluorescence characterization of DOM provides information about source, redox state and biological reactivity of DOM (Fellman et al., 2010 and references therein). However, only a fraction of the total DOM pool likely contributes to its overall fluorescence and the technique does not provide definitive information on biochemical structure of DOM or actual concentration of organic compounds. Fluorescence measurements can be affected by factors such as pH variations, quenching by chelation with metal ions (Reynolds and Ahmad, 1995), changes in temperature, oxygen concentration and spectral interference due to highly absorbing sample inducing inner filter effect (Fellman et al., 2010 and references therein). For a critical analysis of commonly used fluorescence metrics and special considerations for analysis and data interpretation see Korak et al. (2014).

One concern in DOM study, in particular as most of the investigations are based on spectroscopic measurements, is the existence of an invisible DOM (iDOM) pool. This fraction is not detected by spectroscopic approaches as suggested by Pereira et

al.(2014). It could represent a substantial fraction of the total DOM, in particular during extreme events such as rainstorm or floods.

We identified 129 studies applying spectroscopic techniques for DOM characterization from which 1057 data points could be extracted. The study of optical properties of organic matter is now the most applied characterization approach in riverine DOM studies. As shown on figure 2, the number of studies reporting measurements of DOM optical properties has almost doubled between 2015 and 2016. This approach has been deployed worldwide, with most of the data acquired in the U.S.A. In most cases, absorbance and fluorescence measurements are reported conjointly as they allow describing different fractions of Chromophoric Dissolved Organic Matter (CDOM), respectively chromophores and fluorophores components (Lakowicz, 2010). The most reported indicators in the identified literature were FI with a total of 810 data points and SUVA₂₅₄ with 906 measurements. For latitudes (0°-30°S), FI values ranged from 1.21 to 1.76 with a mean of 1.49 and a standard deviation of 0.12 (n=29). For latitudes (0°-30°N), FI values ranged from 1.08 to 2.09 with a mean of 1.54 and a standard deviation of 0.26 (n=108). For latitudes (30°-60°N), FI values ranged from 1.09 to 2.14 with a mean of 1.49 and a standard deviation of 0.22 (n=475). For latitudes (60°-90°N), FI values ranged from 1.22 to 1.84 with a mean of 1.40 and a standard deviation of 0.09 (n=198). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 9.294e-08). Latitudes (0°-30°S) and (60°-90°N) seems to have a more terrestrially derived signature (Low FI ~1.2) compare to (0°-30°N) and (30°-60°N) which present both terrestrially and microbially (High FI ~1.8) derived signatures. For latitudes (0°-30°S), SUVA values ranged from 0.50 to 4.93 with a mean of 2.66 and a standard deviation of 0.1 (n=37). For latitudes (0°-30°N), SUVA values ranged from 0.1 to 11.18 with a mean of 3.0 and a standard deviation of 1.9 (n=62). For latitudes (30°-60°N), SUVA values ranged from 0.02 to 11.0 with a mean of 3.89 and a standard deviation of 2.23 (n=479). For latitudes (60°-90°N), SUVA values ranged from 0.1 to 8.24 with a mean of 2.73 and a standard deviation of 1.04 (n=328). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 4.2e-13). High SUVA values typically indicate greater aromatic content, highest values were found for (0°-30°N) and (30°-60°N) latitudes. Density distribution of the values of these indicators among latitudinal classes are shown on figure 2 and reveal more specific fingerprint for FI and

SUVA values of low Southern (0°-30°S) and high Northern (60°-90°N) latitude classes with a narrow range of values compared to those of low (0°-30°N) and middle (30°-60°N) Northern latitude classes with values spanning a much larger range.

1.3.2 Isotopy

The use of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ indicators to identify DOC sources and cycling in aquatic systems have been reviewed by Raymond and Bauer (2001). $\delta^{13}\text{C}$ is recognized as a reliable tracer for DOC sources allowing to decipher between general vegetation types (C3,C4 plants), algal inputs and microbially processed OM (Kohn, 2010) . However, caution should be given as major DOM sources $\delta^{13}\text{C}$ signatures present significant overlap (recent vegetation vs soil organic matter etc.) (Marwick et al., 2015). Thus, it is recommended to use in combination $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ indicators. The $\Delta^{14}\text{C}$ of river DOM gives insight into its sources as well as information about its residence time in the different carbon reservoirs. In some cases, there is a direct link between DOM reactivity and its age; the young DOM being made of OM of high nutritional interest that is quickly consumed, while the older DOM fraction is considered to be highly oxidized and thus resistant to further degradation (Loh et al., 2008). However, physical processes can contribute to remove part of the reactive DOM fraction from short term cycling, inducing old signature in reactive preserved DOM. They include soil freezing mechanisms, water saturation, and protection through interactions with the mineral layers in soils (Raymond and Spencer, 2015 and reference therein). Major controls on DOC age have been highlighted by studies investigating contrasted river basins. Undisturbed small watershed mostly export young DOM (Evans et al., 2007). Discharge appears to have an influence on DOC age, with older DOC exported during base flow (Neff et al., 2006). Other phenomenon inducing old C release include rivers that are rapidly eroding old soil profiles and systems with thawing permafrost or glacier inputs (Vonk et al., 2013).

First Raymond and Bauer (2001), then Butman et al. (2014) and Marwick et al. (2015) have gathered large dataset of paired $\delta^{13}\text{C}/\Delta^{14}\text{C}$ measurements for DIC, DOC and POC to evaluate the sources and global transfer of aged carbon to rivers. They have formulated one of the first responses to the lack of synthesis of the growing number of ^{14}C measurements and derived regional or global patterns. Raymond and Bauer (2001)

only reported a few studies from the 80s in addition to their own study of 2001, covering only the Amazon basin and the Chesapeake Bay tributaries, whereas Marwick et al. (2015) reported about 60 studies (for both DIC, DOC and POC isotopy) conducted worldwide. This illustrates the growing dynamic of the field since the 2000s (figure 3). Marwick et al. (2015) have especially contributed to reduce the gap existing in the coverage of African rivers, adding to the existing pool of worldwide ^{14}C data, measurements from the Congo, Zambezi, Tana, Betsiboka and Rianila river basins.

We identified 55 studies reporting $\delta^{13}\text{C}$ and/or $\Delta^{14}\text{C}$ for DOM in rivers from which 979 data points could be extracted. In the majority of studies stable and radiocarbon isotope data are reported simultaneously offering a better identification of DOM origin crossing vegetation source and age indications. DOM isotopic studies have been conducted worldwide, but still remain scarce in regions such as central Asia and South America. Since the study of Marwick et al. (2015), as shown on figure 3, we identified 10 studies investigating riverine DOM through isotopic approaches. Most of them have been conducted in tropical region where there was a lack of data (mainly Amazonian and African rivers) (Seidel et al., 2015; Spencer et al., 2016). For latitudes (0° - 30°S), $\delta^{13}\text{C}$ (‰) values ranged from -30.4 to -15.0 with a mean of -26.3 and a standard deviation of 3.1 (n=146). For latitudes (0° - 30°N), $\delta^{13}\text{C}$ values ranged from -32.0 to -19.3 with a mean of -27.58 and a standard deviation of 2.34 (n=112). For latitudes (30° - 60°N), $\delta^{13}\text{C}$ values ranged from -33.2 to -15.1 with a mean of -26.9 and a standard deviation of 1.8 (n=370). For latitudes (60° - 90°N), $\delta^{13}\text{C}$ values ranged from -32.2 to -16.0 with a mean of -26.7 and a standard deviation of 2.0 (n=168). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 0.0005486). For latitudes (0° - 30°S), $\Delta^{14}\text{C}$ (‰) values ranged from -452 to 154.0 with a mean of 30.4 and a standard deviation of 100.2 (n=50). For latitudes (0° - 30°N), $\Delta^{14}\text{C}$ values ranged from -257.7 to 336 with a mean of 68.8 and a standard deviation of 123.35 (n=69). For latitudes (30° - 60°N), $\Delta^{14}\text{C}$ values ranged from -361 to 257 with a mean of 26.1 and a standard deviation of 101.3 (n=406). For latitudes (60° - 90°N), $\Delta^{14}\text{C}$ values ranged from -463 to 307 with a mean of 5.6 and a standard deviation of 117.6 (n=198). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 0.0067). $\Delta^{14}\text{C}$ density plot (Figure 3) shows that the riverine DOM signatures are relatively similar across latitudinal classes with higher $\Delta^{14}\text{C}$ (Younger signature) reported for the 0° - 30°N region and lower (Older signature) for (60° - 90°N). On a global

scale, riverine DOC appears to have a modern $\Delta^{14}\text{C}$ signature (>0). $\delta^{13}\text{C}$ signatures of riverine DOM worldwide are mostly in the range of C3 plants signatures (-31 to -23 ‰) (Kohn, 2010) with differences linked to specific influence of the vegetation of each regions. Lower values are observed for tropical-equatorial latitudes (0° - 30°S and 0° - 30°N) probably linked with the contribution of a specific vegetation in this region. For instance, values below -31.5‰ could reflect canopy effects in low-light tropical forest (Kohn, 2010). However 0° - 30°S region also presents some higher $\delta^{13}\text{C}$ (around -23‰) values that could correspond to algae signatures (-12 to -23‰) (Smith and Epstein, 1971).

1.3.3 Molecular level

Investigating the composition of riverine DOM can give insight into its origin, degradation state and environmental fate. A popular approach is the use of specific biomarkers that allow tracing its sources (vegetation type, soil horizon, microorganism activity etc...). An organic biomarker is a compound that characterizes specific biotic sources and processes (Simoneit, 2005). To be relevant, a biomarker should preserve the information even after some alteration during its transfer in the environment (Meyers, 2003). Commonly used source tracers are lignin biomarkers that allow to identify material of terrestrial origin and vegetation source contributions (Hedges and Mann, 1979; Hernes et al., 2007a). Before being analyzed on GC/MS to quantify lignin phenols, samples need to be prepared to make the huge polymers of lignin analyzable. Traditional technique consist in CuO oxidation of lignin macromolecules to produce a serie of lignin-derived CuO oxidation products (Hedges and Ertel, 1982; Kaiser and Benner, 2012). An alternative technique for the analysis of lignin is the thermochemolysis with tetramethylammonium hydroxide (TMAH) at elevated temperature that yields methylated lignin monomers (Hatcher et al., 1995; Shadkami and Helleur, 2010). Resulting lignin-derived phenols are classified into three structural groups: vanillyl, syringyl and cinnamyl. Specific ratios of these phenols can be used to gain insight into plant origins: vanillyl species (V) are ubiquitous to every lignin types, syringyl phenols (S) are unique to angiosperms, and cinnamyl phenols (C) are derived from non woody plant tissues (Hedges and Mann, 1979); thus C/V versus S/V plots can be used to describe OM origin. Information about the degradation state of OM can also

be obtained from the proportion of oxidized species of each group (Opsahl and Benner, 1995) and insight into diagenetic state can be inferred from acid to aldehyde ratios (Thevenot et al., 2010).

Amon et al. (2012), have applied lignin biomarkers approach to trace DOM sources and degradation state in large arctic rivers. Arctic spring flood is characterized by high lignin concentrations, implying high terrigenous inputs. Specific lignin phenol ratios associated with ^{14}C ages indicated that DOM was also young, fresh and originating primarily from boreal forest vegetation. In contrast, low flow conditions corresponded to older, soil, peat, and wetland derived DOM. The author observed strong seasonal and spatial patterns (differences between seasons and arctic watersheds) with lignin concentrations strongly related to discharge.

Some limitations exist in the use of lignin biomarkers and results should be interpreted with caution. The majority of the end-members currently used to describe riverine DOM origin are derived from pure plants, such as the regions corresponding to vegetation type sources in property property plots (C/V versus S/V) (Hedges and Mann, 1979). However, shift in the lignin monomer ratios has been observed during leaching and sorption (Hernes et al., 2007a), processes undergone by most of riverine DOM. In addition, significant differences in lignin composition have been reported between soil organic matter and its corresponding DOM fraction, as well as differences between leachates from litter, surface soils and subsurface soils (Kaiser et al., 2004a). Thus there is a need to develop a better understanding of the influence of leaching, sorption, desorption, and degradation on the lignin phenol composition of DOM in different watersheds to improve the interpretation of lignin based indicators (Marín-Spiotta et al., 2014). Moreover, define specific reference standard for lignin phenols signature of soils and pure vegetation sources taking into account biome differences would be beneficial (Moingt et al., 2016). Finally, attention should be given to the fact that overall terrestrial contribution and especially terrestrial microbial derived OM may be underestimated by the only use of plant biomarkers (Marín-Spiotta et al., 2014).

DOM comprises many other compounds that provide information on DOM sources, processes, fate and reactivity, such as carbohydrates, proteins and amino acids, lipids (fatty acids, sterols, photosynthetic pigments), black carbon and fossil organic carbon (ancient organic matter stored in sedimentary rocks) (Bauer and Bianchi, 2011 and references therein). Monitor DOM composition at temporal or spatial scales can help

identify specific dynamic patterns that trace environmental processes influencing DOM quality (for example removal of specific compounds along the river network or specific seasonal inputs).

Classical techniques for the analysis of OM composition are based on GC/MS, HPLC/MS or Pyrolysis Py/GC/MS (Simoneit, 2005). However, DOM comprises very complex biomolecular mixtures unrelated to known biochemical groups and thus poorly suitable to common target analysis (Hertkorn et al., 2007). To date, the Electrospray Ionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (ESI-FTICR-MS) is the most advanced instrumentation available for detection of ionized organic compounds (ultra high resolution, resolving power capable of revealing thousands of empirical formulas) and has been used for DOM studies (Gonsior et al., 2016). Results from FTICR experiments are generally observed through Van Krevelen diagrams (Kim et al., 2003) plotting O/C and H/C ratios of individual molecular formulas. It defines specific compound class graphical regions (lignin, proteins, lipids, cellulose etc...) and allows comparing global molecular fingerprints among aquatic DOM samples of differing origins. The resolution power of FTICR technique has allowed to study the chemodiversity of riverine DOM and introduced the concept of river acting as “chemostat”. Changes of DOM composition across stream orders have been studied by FTICR. Creed et al. (2015) showed attenuation of DOM diversity down the river network accompanied with a shift from a dominance of aromatic DOM in headwaters to a dominance of aliphatic DOM downstream. Using FT-ICR-MS analysis, Wagner et al. (2015) established links between molecular heteroatomic (i.e. containing atoms of N, S, P etc.) DOM signature and watershed characteristics.

The extreme heterogeneity of DOM samples, the mutual interferences occurring between different classes of compound or the tendency to form complex superstructures can affect the performance of DOM MS analysis (Nebbioso and Piccolo, 2013 and references therein) inducing irreproducible results in the ionization of DOM. Thus, this limitation and the fact that non-ionizable compounds cannot be characterized by MS prevent to rely on MS methods alone to achieve definitive structural identification of complex DOM molecules.

A powerful and complementary tool (ionization not required) for the molecular level characterization of DOM is the Nuclear Magnetic Resonance (NMR) spectroscopy (Hertkorn et al., 2013). This technique allows to elucidate molecular functional groups

and specific molecular structures based on the magnetic resonance of specific atoms such as ^1H or ^{13}C for the study of OM. NMR and FTICR can be complementary methods as they rely on different properties of matter and thus reveal different information (Hertkorn et al., 2013). Cao et al. (2016) have applied NMR to give insight into seasonal changes in the composition of DOM exported by the Yukon River. They highlighted contrasting DOM composition with specific export of reactive (bio- and photo-labile) DOM enriched in carbohydrates and aromatic structures during spring freshet.

Although they have a powerful resolution, most of the current molecular characterization methods are relatively complex and time consuming and have high analytical cost that prevent their inclusion in routine long-term or spatially extensive studies (Leenheer and Croué, 2003; Fellman et al., 2010a). These techniques generally require large sample volume and pre-concentration to recover enough material. This pre-concentration step is critical, depending on its recovery efficiency, it may only capture a fraction of total DOM (Bauer and Bianchi, 2011; Minor et al., 2014). To date reverse osmosis is considered as the most effective DOM concentration method (DOM recoveries >90%) (Bauer and Bianchi, 2011; Minor et al., 2014). Solid phase extraction methods (XAD resins, C18 stationary phases etc.) recover DOM compounds according to their specific affinity for the stationary phase (Spencer et al., 2010). Ultrafiltration techniques use DOM restrictive membranes that can be affected by incomplete recovery (Wilding et al., 2005). To overcome the issue of recovering efficiency, Lam and Simpson (2008) developed an improved water suppression technique to apply ^1H NMR on intact sample (i.e. without pre-concentration).

66 studies investigating riverine DOM at the compound level have been identified among which 32 lignin biomarkers studies, 10 NMR studies, 19 FTICR studies, 11 studies using other compound level analysis (mostly Py/GC/MS) with 4 studies combining either NMR, FTICR, lignin biomarker approach or other compound level analysis. We extracted 337 data points for lignin data (figure 4). We only reported results from lignin studies as data from NMR or FTICR experiences are difficult to transpose in a database and data from other approaches were too scarce or poorly standardized among studies.

For latitudes (0° - 30°S), Lambda 8 (the sum of the eight main lignin phenols in organic carbon (OC), expressed as mg/100mg OC) values ranged from 0.053 to 2.24 with a mean of 0.55 and a standard deviation of 0.43 (n=71). For latitudes (0° - 30°N),

Lambda 8 values ranged from 0.18 to 2.30 with a mean of 0.81 and a standard deviation of 0.39 (n=85). For latitudes (30°-60°N), Lambda 8 values ranged from 0.12 to 8.13 with a mean of 1.5 and a standard deviation of 1.41 (n=62). For latitudes (60°-90°N), Lambda 8 values ranged from 0.11 to 1.03 with a mean of 0.45 and a standard deviation of 0.25 (n=37). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 1.247e-09).

For latitudes (0°-30°S), S/V values ranged from 0.20 to 1.89 with a mean of 0.73 and a standard deviation of 0.31 (n=54). For latitudes (0°-30°N), S/V values ranged from 0.71 to 1.44 with a mean of 0.85 and a standard deviation of 0.12 (n=62). For latitudes (30°-60°N), S/V values ranged from 0.19 to 2.47 with a mean of 1.04 and a standard deviation of 0.56 (n=40). For latitudes (60°-90°N), S/V values ranged from 0.11 to 2.48 with a mean of 0.73 and a standard deviation of 0.61 (n=168). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 1.381e-07).

For latitudes (0°-30°S), C/V values ranged from 0.04 to 0.49 with a mean of 0.18 and a standard deviation of 0.10 (n=146). For latitudes (0°-30°N), C/V values ranged from 0.10 to 0.72 with a mean of 0.19 and a standard deviation of 0.12 (n=62). For latitudes (30°-60°N), C/V values ranged from 0.07 to 0.97 with a mean of 0.37 and a standard deviation of 0.20 (n=55). For latitudes (60°-90°N), C/V values ranged from 0.04 to 1.23 with a mean of 0.31 and a standard deviation of 0.30 (n=168). Differences between latitude classes were significant (Kruskall Wallis Rank Sum Test (R software), p-value= 2.245e-08).

1.3.4 DOM lability

Studies of DOM turnover in river system differ from ocean and lakes (on which most studies have been focusing), as rivers have much shorter DOM residence time (time of DOM transfert from land to estuary) (Moody et al., 2013). The two main pathways, acting conjointly, for DOM degradation in the environment are photodegradation (i.e. light induced degradation) and biodegradation (i.e. intervention of microorganisms mainly bacteria and fungi) (Riedel et al., 2016).

Incubation experiments have been developed to evaluate DOM sensitivity to these processes. These set ups provide estimates of the photolabile or bioavailable DOC fractions (BDOC) or of total BDOC loss (% of total DOC) and in other cases C consumption rates. In literature, DOC pools are generally classified with regard to their degree of reactivity : « labile », « semi-labile » and « recalcitrant », though, DOC probably comprises a continuum of reactivity influenced by environmental conditions (Guillemette and del Giorgio, 2011 and reference therein). Important methodological variables for incubation experiments are the duration of the experiment, the physico-chemical conditions (temperature, pH, O₂ availability, light (specific wavelength or dark incubation), etc...), the filter pore size used to filter water prior to incubation, the bottle size or plug flow bioreactor type, the shacking of the incubation media, the eventual nutrient and specific inoculum addition (Vonk et al., 2015).

To date no real standard exist for incubation experiment set up. Vonk et al. (2015) conducted a meta-analysis of the biodegradability of dissolved organic carbon in permafrost soils and aquatic systems. They reported a pronounced variability in incubation set up and thus proposed a standardized protocol for future experiments. The apparent lability of DOC greatly depends on the experimental conditions, thus standardization of incubation set up becomes critical when it comes to compare studies (Guillemette and del Giorgio, 2011). Vonk et al. (2015) also recommend to associate DOM incubation experiments to DOM molecular measurements allowing tracing changes in DOM composition during experiment.

Guillemette and del Giorgio (2011) have studied DOC bioavailability in freshwater ecosystems of Canada and determined both short-term bacterial C consumption (STCC, <2 days) and long-term C consumption (LTCC, 28 days) along with a first order decay constant (k). STCC specifically targets a highly reactive DOC pool with very short turn over and LTCC targets a DOC pool that is decreasingly reactive (Del Giorgio and Davis, 2003). McLaughlin and Kaplan (2013) have evaluated the biological lability of DOC in a southern Pennsylvania stream during various hydrological conditions using plug-flow bioreactor (residence time between 0.5 min to 150 min). Their results show that storms deliver increased BDOC loads and highlight the temporal variability of labile and semi-labile BDOC. Moody et al. (2013) assessed the rate of DOC loss through a catchment of northern England. The authors aimed an experimental design that reproduces as much as possible natural conditions. They conducted degradation experiments (10 days, in

relation with water residence time scale) each month within a year for different locations from source to downstream reach. Measurements were made in ambient light and temperature conditions, considering both light and dark degradation to distinguish the photo-induced degradation component. Samples were not pre-filtered to consider the net fate of DOC including its potential production from POC or its adsorption onto particles. During the experiment they also monitor the solar radiation and temperature and were able to estimate the activation energy necessary for DOC photo-degradation. Stubbins et al. (2010) investigated the photochemical alteration of DOM in the Congo River using a solar simulator for a 57 days irradiation experiment of filtered water. Analysis of pre- and post-irradiation DOM by FT-ICR-MS revealed three pools of DOM of differing photoreactivity: photo-resistant, photo-labile and photo-produced.

We gathered 42 studies that evaluated riverine DOM lability (figure 5). Most of them are recent; about 45% of riverine DOM lability studies have been conducted since 2013. Although riverine DOM photolability evaluation is growing (Riedel et al., 2016), the majority of lability studies focuses on DOM biodegradability. Studies investigating the composition of BDOC are still scarce. FT-ICR-MS is generally used to analyze DOM before and after incubation in order to identify masses that are degraded or produced (Stubbins et al., 2010). The geographical coverage and temporal representativeness of lability studies is still limited with very few studies evaluating riverine DOM lability across the full hydrological cycle (Moody et al., 2013).

We have been able to extract 46 unique values reported for BDOC (mg/L), all of which have been measured in the northern hemisphere. Only one value of 0.12 mg/L is reported for the region 0°-30°N, from the Rio Tempisque in Costa Rica sampled during baseflow (Kim et al., 2006). For latitudes (30°-60°N), BDOC values ranged from 0.30 to 35.0 mg/L with a mean of 4.44 mg/L and a standard deviation of 6.69 (n=30). For latitudes (60°-90°N), BDOC values ranged from 0.48 to 2.14 mg/L with a mean of 1.32 mg/L and a standard deviation of 0.50 (n=15).

We extracted 84 measurements of total BDOC loss (%). For latitudes (0°-30°S), values ranged from 11.1 to 37.2 with a mean of 21.4 and a standard deviation of 6.2 (n=28), this data are from a single publication conducted in North West of Australia (Fellman et al., 2014). A single value of 22 % of total BDOC loss is reported for the region 0°-30°N from the study of Kim et al., (2006). For latitudes (30°-60°N), values ranged from 2.4 to 42.0 % with a mean of 14.7 % and a standard deviation of 11.4 (n=26). For

latitudes (60°-90°N), values ranged from 0.1 to 45.5 % with a mean of 14.07 % and a standard deviation of 11.3 (n=29). The highest values for total BDOC loss were observed in middle (30°-60°N) and high northern latitudes (60°-90°N), during summer or storm event (Kim et al., 2006; Casas-Ruiz et al., 2016). Mann et al., (2012) reported higher total BDOC loss during Kolyma spring flood, with values ranging from 0.1 before flood to 20.4 % at peak discharge and decreasing to 1.2 % after the flood.

1.3.5 Combination of techniques:

Combining DOM characterization techniques can be useful to develop and validate DOM proxies and indicators such as the ones based on DOM optical properties (SUVA₂₅₄ and FI for instance) that reflect some aspects of DOM composition. Weishaar et al. (2003) combined ¹³C NMR and Absorbance techniques to relate SUVA₂₅₄ to aromatic DOM content. Hernes et al. (2009) proposed fluorescence-based proxies for lignin in freshwater DOM. Lignin biomarkers are powerful tool in DOM studies but the complexity of lignin analysis limits the number of samples processed and thus spatial and temporal coverage. Hernes et al. (2009) developed partial least square models to predict lignin parameters. They obtained relatively good agreement for lignin concentration, carbon-normalized lignin yields and phenols ratios (S/V, C/V) whereas the acids to aldehydes ratio of vanillyl (Ad/Al)_v (indicator of diagenetic state of lignin) was poorly explained by fluorescence. Studies on Swedish lakes (Kellerman et al., 2015) and subtropical wetland (Wagner et al., 2015) have drawn links between fluorescence PARAFAC components to individual molecular formula identified by FT-ICR-MS. Butman et al. (2012) have investigated the relationships between $\Delta^{14}\text{C}$ and molecular quality of DOC determined through its optical properties, finding significant correlation of $\Delta^{14}\text{C}$ to aromaticity indices of DOC measured by SUVA₂₅₄ ($r^2 = 0.87$, $p < 0.001$), and FI ($r^2 = 0.6$; $p < 0.001$). Osburn et al. (2016) have implemented single linear regression models to relate DOC and lignin concentrations to CDOM (a_{350}). Compiling data from various regions, they observed a wide variability suggesting that optical models should be developed at local or regional scales and include seasonal variations.

We found 69 studies that combined at least two characterization techniques to describe riverine DOM. Spectroscopic techniques appear in most of the associations. The simultaneous study of different variables allows looking for correlations and could help to identify interesting proxies for method substitution. However, reported pairwise variables from different approaches are scarce. From our dataset we have identified

relevant correlation arising from data originating from various publications for SUVA₂₅₄ and $\delta^{13}\text{C}$ ($r=-0.64, p=3.3\text{e-}05, n=35$), SUVA and $\Delta^{14}\text{C}$ ($r=0.84, p=9.1\text{e-}08, n=27$), a_{350} and Lambda_8 ($r=0.8, p=8.6\text{e-}08, n=31$). Sanderman et al., (2009) reported similar correlation for SUVA₂₅₄ and $\delta^{13}\text{C}$ ($r=-0.67$), $\Delta^{14}\text{C}$ ($r=0.96$) with their own data from a small coastal watershed ($n=23$). Walker et al., (2013) present relationships between fluorescence components and discharge, DOC concentration, lignin biomarkers and $\Delta^{14}\text{C}$ in Arctic rivers.

Another aim of combining characterization approaches is to take advantage of their complementarity to gain a more comprehensive chemical representation of DOM, improve the interpretation of data and strengthen the reliability of the results. Evaluation of DOM lability via incubation experiments is often associated with DOM composition analysis to relate DOM fractions of varying lability to DOM molecular properties. DOM photo-transformation evaluation have been associated with NMR (Dutta Majumdar et al., 2017) and FT-ICR-MS (Stubbins et al., 2010). Dutta Majumdar et al. (2017) observed that photo-transformation mainly affect the aromatics and unsaturated structures (in particular lignin derived) and Stubbins et al. (2010) identified DOM pools of differing photoreactivity, i.e. photo-resistant, photo-labile and photo-produced. Seitzinger et al. (2005) investigated bioavailability of DOM in stream water and its molecular level characterization via electrospray-ionization mass spectrometry (ESI-MS), giving insight into which specific masses are used by bacteria and in which amount. Hulatt et al. (2014) have combined bioavailability and radiocarbon age to study the potential effect of land-use change on DOM in a Northern Finland river system. Raymond and Bauer (2001) conducted long-term, dark incubations (2-12 months) with York River water to investigate how bacterial utilization of DOC in rivers may affect the $\Delta^{14}\text{C}$ signature of riverine DOC prior to discharge in marine environments. They observed decreasing $\Delta^{14}\text{C}$ values for all their incubations, indicating a preferential removal of ^{14}C -enriched (i.e. young) labile DOC by heterotrophic bacteria. Guillemette and del Giorgio, (2011) used fluorescent DOM EEMs analyzed by PARAFAC to identify distinct DOC components supporting STCC and LTCC.

As they are reliable, rapid and simple, spectroscopic techniques are very often associated with other approaches. Classical technique associations include stable and radiocarbon isotopy with lignin biomarkers (Spencer et al., 2016) and more occasionally with NMR or FT-ICR-MS (Seidel et al., 2015). Improvement in the coupling of

characterization techniques (GC/MS and IRMS or AMS) allow for compound specific isotopy study. Prokushkin et al. (2007) have used this technique in central Siberia watershed highlighting the advantage of this method to identify differences between DOM of similar chemical composition but with distinct $\delta^{13}\text{C}$ signature implying unexpected source or process changes. Neff et al. (2006) recommend the combination of structural and age-related signature of DOM in boreal ecosystems as it may reveal the mobilization of specific DOM pools and in particular old carbon formerly trapped in permafrost soils.

1.4 EMERGING IDEAS AND NEW VIEWS

The last decade has seen the consideration of rivers shifting from neutral pipes for carbon transfer to efficient bioreactors rapidly processing organic matter (Cole et al., 2007). Many studies have explored the detailed composition and character of DOM using a range of powerful analytical tools. However, fewer have investigated the link between DOM composition and its behavior in aquatic environments. A current challenge concerns the evaluation of DOM turnover in fluvial networks, especially the reactivity of freshet material as it leaves the soil for the river channel (Moody and Worrall, 2017). Therefore focus must be given to DOM in headwater catchments as lower reach and river mouth DOM could already be considered as processed, “old” carbon (Raymond and Bauer, 2001).

Recent studies suggest that the fate of DOM is not only predetermined by its chemical structure but also by the environmental settings including microbial community composition, redox state and sorption/desorption to particles (Marín-Spiotta et al., 2014; Ward et al., 2017). As pointed out by Marín-Spiotta et al., (2014), paradigm shifts in soil organic matter research may influence the perceptions of aquatic carbon cycling. Riverine DOM view has progressively evolved from considering terrestrial DOM as both chemically and biologically refractory to DOM as potentially reactive. Therefore, microbiological and photolytic processes play a major role in its fate. This new view implies that chemical recalcitrance is not the primary control of DOM turnover. Thus, radiocarbon ages should be re-interpreted in terms of reactivity

("old" does not necessary imply long-term persistence). It is important to account that most of soil derived DOM entering aquatic systems has already been microbially processed.

Recent findings question the reliability of lignin as a conservative tracer due to the environmental influence on lignin decomposition and the ability of microbes to degrade these compounds given accessibility and favorable conditions (Marín-Spiotta et al., 2014 and references therein). This suggests that plant biomarkers alone may underestimate terrigenous OM inputs missing the microbial derived OM that can make up a large proportion of soil OM.

A growing field of research is the study of the influence between microbial communities and OM that shape one each other (Meunier et al., 2017).

Creed et al. (2015) proposed the concept of river as a "chemostat". The conjunction of biogeochemical processes occurring in the river tends to homogenize DOC concentrations and DOM composition downstream. This view corresponds to a higher chemical diversity with a predominance of aromatic DOM in headwaters followed by preferential losses of labile compounds during transport and specific gains of aliphatic DOM downstream along with a decreasing chemical diversity.

Ejarque et al. (2017) have investigated the quality and reactivity of DOM in a Mediterranean river across hydrological and spatial gradients. Their results show that river hydrology has a significant control on DOM variability influencing its residence time in aquatic systems. Floods correspond to conservative DOM transport and low flow to reactive DOM transport. These findings stress the importance of accounting for the full range of hydrological (including extreme events) and spatial variability to fully understand the role of rivers in the global carbon cycle. A solution to better capture the DOM temporal variability could arise from the development of high temporal resolution monitoring tools for DOM quantity and quality. Spencer et al. (2007) have observed diurnal variability of DOM in a Californian river using in situ optical measurements. The potential of in situ optical sensors to study riverine DOM dynamics has been reviewed by Blaen et al., (2016) and Ruhala and Zarnetske, (2017).

Only a few river systems have been studied in an integrated and systemic way. The Amazon and Congo rivers are examples of systems where recent research focuses on evaluating OM along the whole soil, river, ocean continuum (Seidel et al., 2015; Lambert et al., 2016).

1.5 CONCLUSION AND PERSPECTIVES

The evaluation of the gathered data set showed differences (in distribution and average reported values of main quality indicators) in the characteristics of DOM sampled at different latitudes corresponding to contrasted ecosystems. This suggests the potential influence of climate, vegetation, geology and ecosystem structure on DOM exported to rivers and the importance of the watershed characteristics in shaping riverine DOM both qualitatively and quantitatively.

The aim of this study was to give a comprehensive evaluation of what have been done and where, with regard to DOM characterization in rivers worldwide. This is in connection with the observation of Creed et al. (2015), that few datasets are available to analyze the spatial heterogeneity and temporal variability of DOC concentration and DOM composition across continents. Despite recent increase in the number of publications investigating riverine DOM characterization, various challenges remain. Few rivers have been studied combining DOM characterization approaches. Standardization of methods allowing for reliable comparisons between studies worldwide is not already achieved. Recent sampling efforts have extended the spatial coverage but on a global perspective it is still limited. The temporal representativeness of the sampling campaigns needs to be improved, monitoring the full hydrological cycle including extreme events. This stresses the need for high temporal resolution measurements. Therefore new in situ sensors need to be developed implying the research and validation of reliable proxies for DOM quality. This will require the production of specific datasets allowing building strong relationships between DOM characterization variables. Path has been open with the recent development of fluorescence and absorbance based DOM quality proxies.

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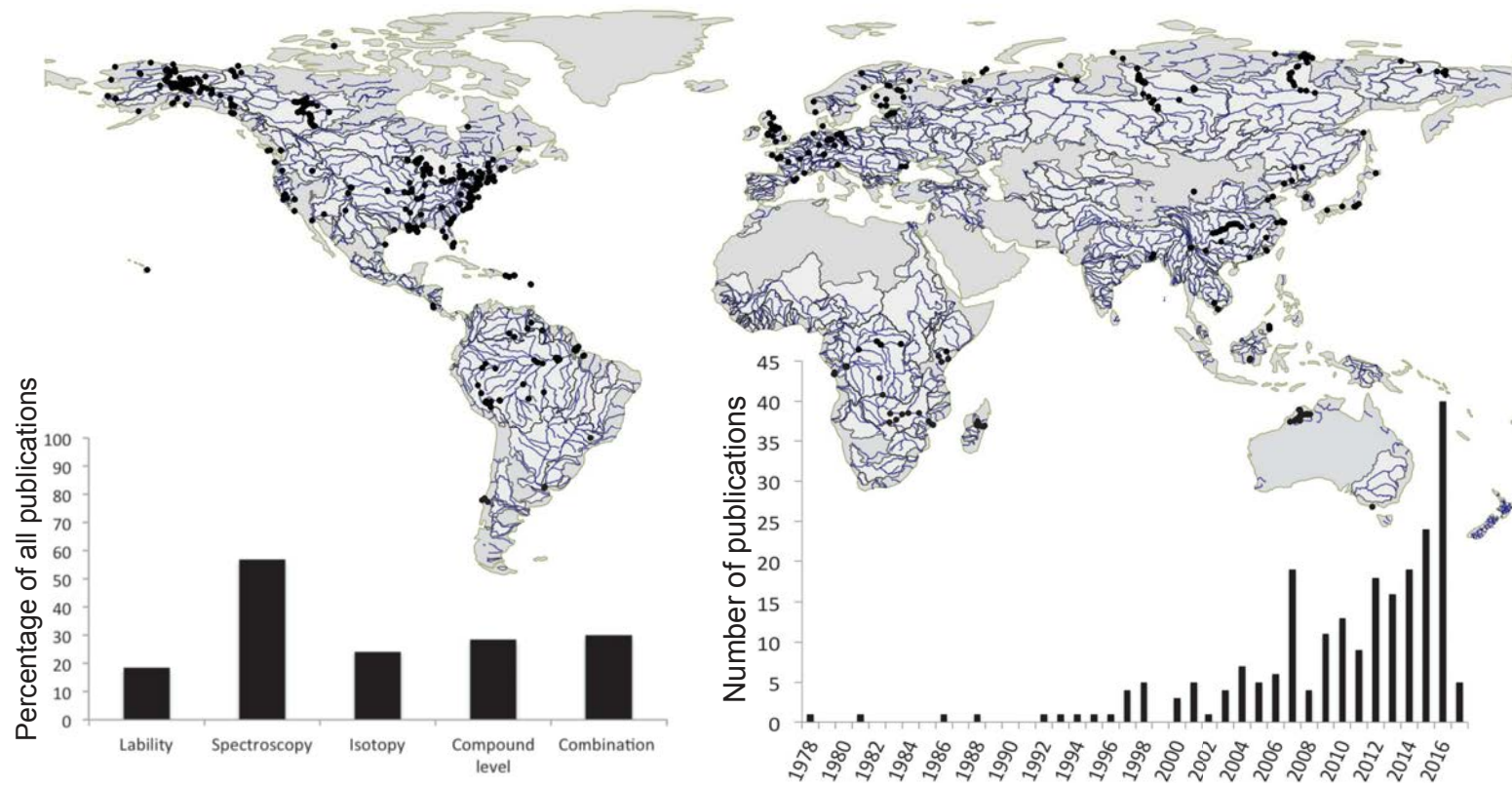


Figure 1. 1 World map repartition of riverine DOM characterization studies included in the database. Each black dot represents a single sampling site. On the left, proportion of each characterization approach used in the reviewed publications, “combination” refers to the use of multiple methods. On the right, evolution of the number of publications reporting DOM characterization in rivers.

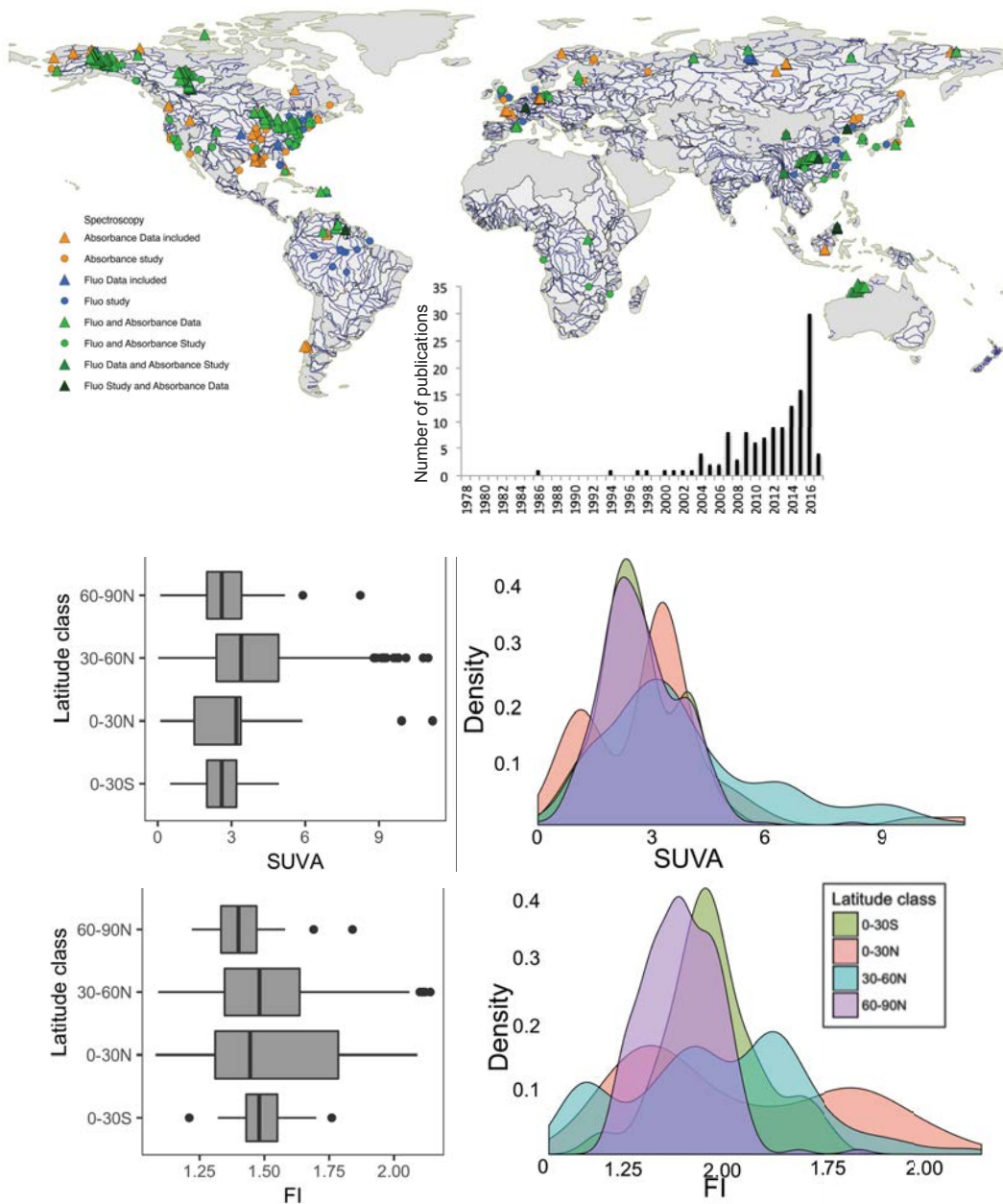


Figure 1. 2 World map repartition of spectroscopic (both absorbance and fluorescence) studies included in the database. The bar chart represents the evolution of the number of publication using this method for riverine DOM characterization. Box plots and density plots represent the distribution of values of the main indicators for absorbance (SUVA) and Fluorescence (FI) measurements by latitude classes.

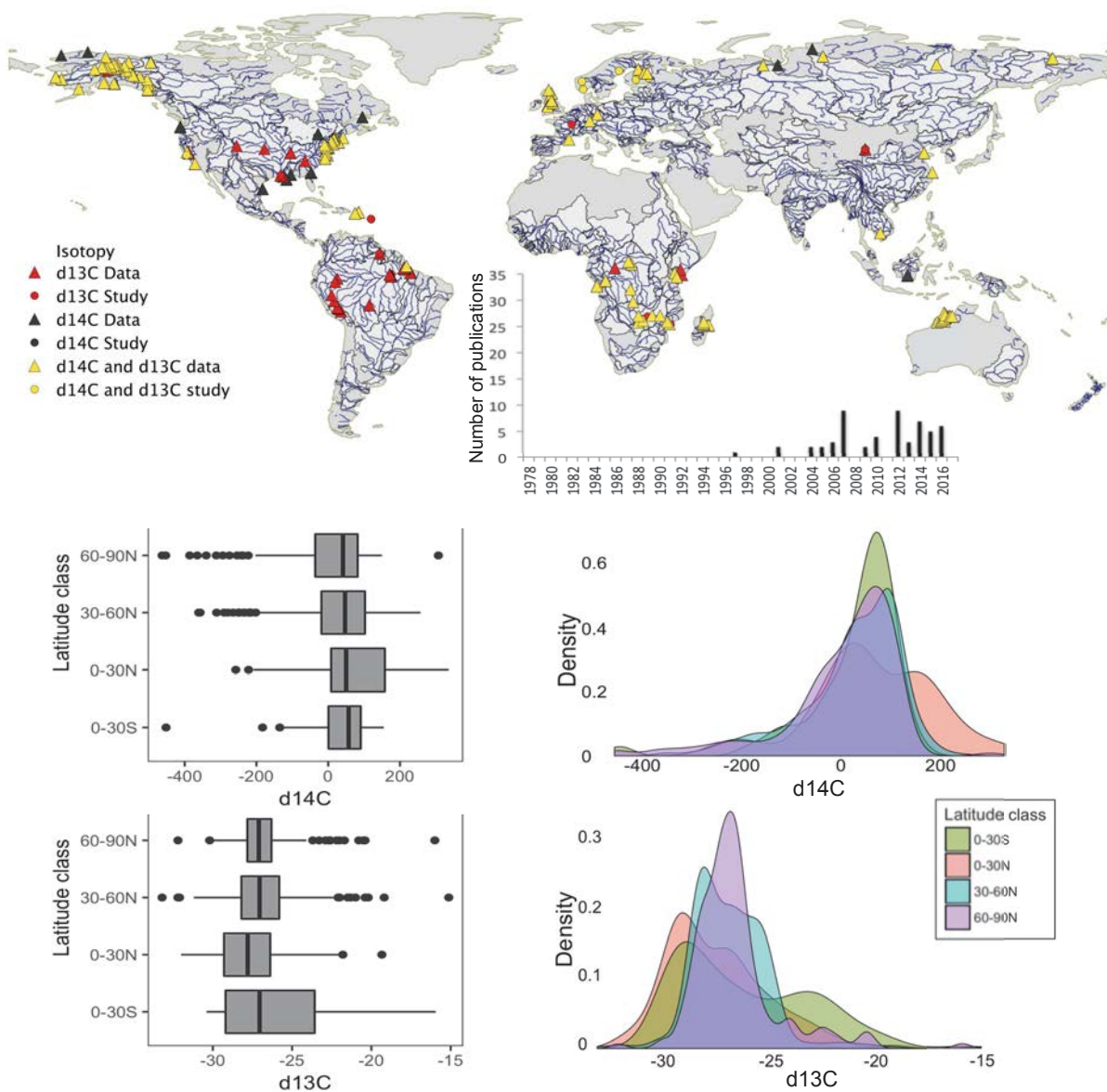


Figure 1. 3 World map repartition of isotopic of ^{13}C and ^{14}C included in the database. Bar chart represents the evolution of the number of publications using carbon isotopy for the characterization of riverine DOM. Box plots and density plots represent the distribution of values by latitude classes for $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$.

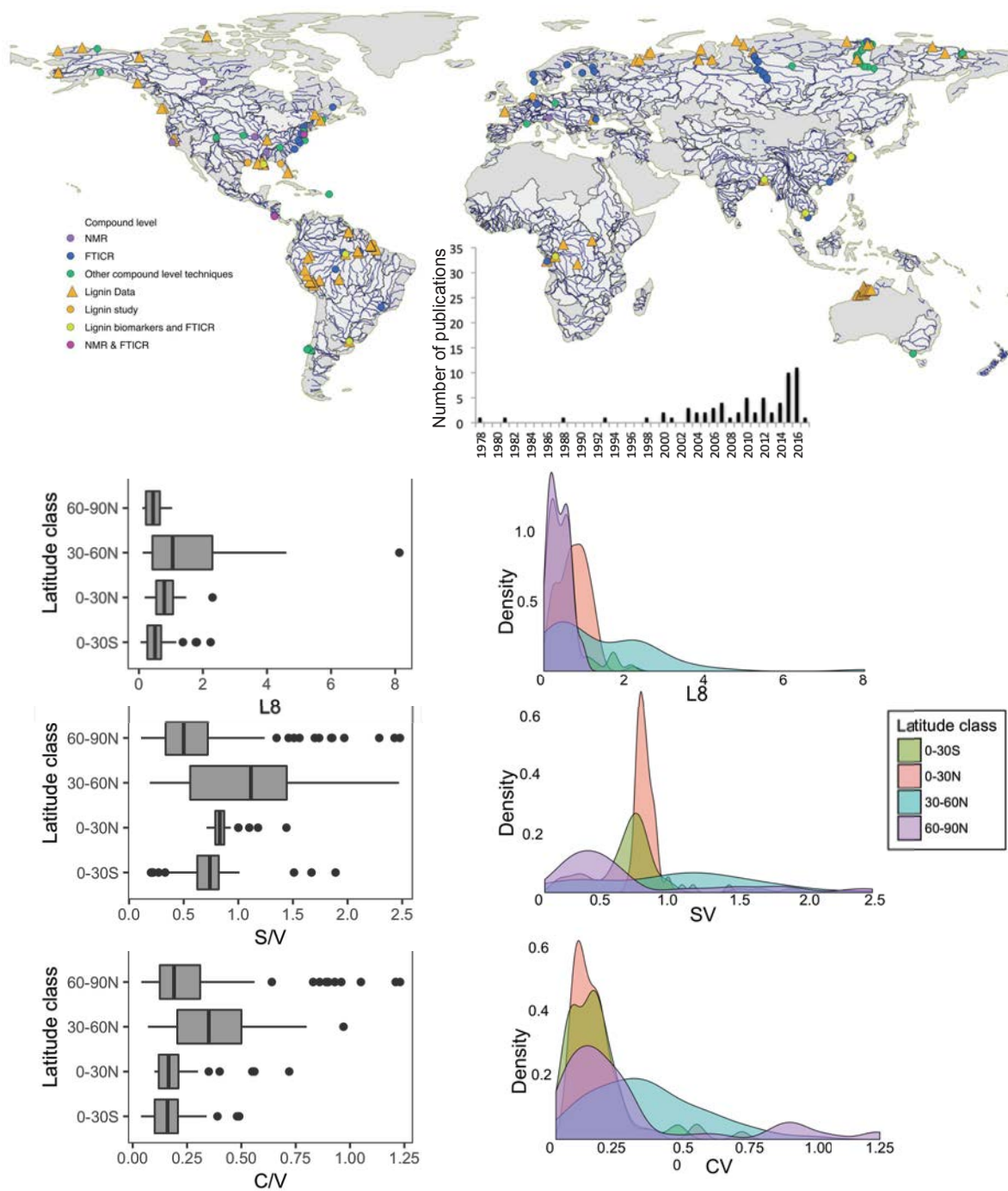


Figure 1. 4 World map repartition of studies characterizing riverine DOM at the molecular level. Bar chart represents the evolution of the number of publications using molecular level approaches for the characterization of riverine DOM. Box plots and density plots represent the distribution of values by latitude classes for main lignin indicators.

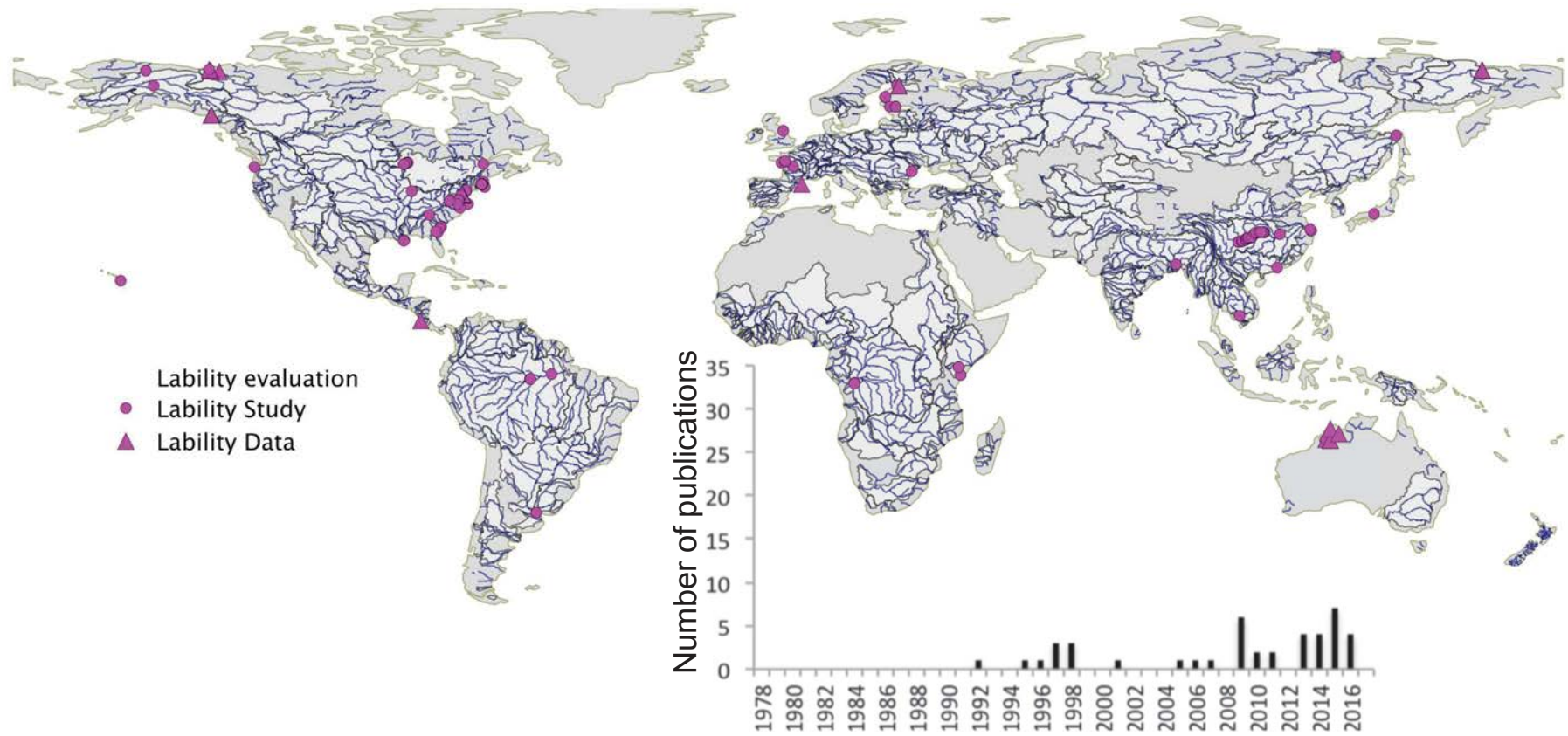


Figure 1. 5 World map repartition of lability based studies on riverine DOM included in the Database. The bar chart shows the evolution of the number of studies using lability experiments for riverine DOM characterization.

CHAPITRE II

DISSOLVED ORGANIC CARBON DYNAMIC, HYDROLOGY AND WATER CHEMISTRY IN THE YENISEI RIVER

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« La vodka est bonne, la neige tombe et Oleg a apporté des concombres. On les coupe en lamelles, et on en croque une à chaque rasade. Oleg n'a pas parlé depuis longtemps. »

« Dans les forêts de Sibérie » Sylvain Tesson

RÉSUMÉ

Les sols des régions arctiques, en particulier les pergélisols, abritent de grandes quantités de carbone organique. Les changements climatiques actuels sont susceptibles de modifier les cycles biogéochimiques dans ces régions, avec une influence marquée sur les transferts de matières des milieux terrestres vers les milieux aquatiques et marins. Les fleuves arctiques jouent un rôle significatif dans les transferts de matières organiques dissoutes vers l'océan arctique. La crue de printemps étant la période où la majeure partie des exports a lieu.

Notre étude vise à mettre en évidence la variabilité saisonnière des matières organiques dissoutes transportées par le Ienisseï afin d'identifier les périodes clés et les facteurs d'influences majeurs. Nous avons donc étudié la dynamique du carbone organique dissous (COD) dans le fleuve Ienisseï, du point de vue des variations de concentrations et des liens avec la chimie de l'eau et l'hydrologie.

Nous avons mené des campagnes d'échantillonnage durant trois années consécutives (2014 à 2016), en couvrant avec une haute fréquence de prélèvement la période de la crue de printemps afin d'en capturer la dynamique. Des échantillons d'eau ont été prélevés au centre du fleuve, pendant la période où le fleuve est gelé, à travers la glace (hiver et début de printemps), jusqu'à quelques jours avant la débâcle (mi-mai), puis pendant la saison d'eau libre durant l'été depuis un bateau (juin-octobre).

Les concentrations en COD suivent l'hydrogramme, avec les concentrations maximales mesurées quelques jours avant le pic de crue. Le COD a aussi répondu aux variations de débit du début d'automne (augmentation probablement liée à des précipitations plus intenses). Le flux de COD moyen, durant les trois années de prélèvement, a été d'environ $4,53 \text{ Tg yr}^{-1}$, ce qui est de l'ordre de grandeur rapporté dans la littérature. Il y a une variabilité interannuelle relativement importante avec les estimations d'exports annuels variant de $5,45 \text{ Tg yr}^{-1}$ en 2014 à $3,57 \text{ Tg yr}^{-1}$ en 2016, influencé par l'amplitude de débit. Le rôle prédominant de la crue de printemps dans les exports de COD a été confirmé, avec en moyenne plus de 65% des exportations ayant lieu durant cette période (mai/juin).

Mots clés: COD, rivières arctiques, Yeniseï, Sibérie, chimie de l'eau, sonde multi-paramètres

ABSTRACT

Arctic soils, in particular permafrost, comprise large amounts of organic carbon. Current climate change could modify biogeochemical cycles in these regions, with a specific influence on the transfers of material from terrestrial to aquatic and marine ecosystems. Arctic rivers play an important role in dissolved organic matter transfers to the Arctic Ocean, the key being the spring freshet when most of the export occurs.

Our study focuses on the seasonal variability of dissolved organic matter transferred by the Yenisei River to identify key periods and main controlling factors. DOC dynamic has been investigated in the Yenisei River with regard to quantity and links with water chemistry and hydrology.

We conducted sampling campaigns during three consecutive years (2014 to 2016), covering with a high sampling frequency the spring flood period to capture its dynamic evolution. Water samples have been taken from the middle of the Yenisei channel, during the winter and early spring through ice, until a few days before icebreak (mid-May), and during the ice free season from a boat (June-October).

DOC concentrations followed the hydrograph with highest concentrations observed a few days before peak discharge. DOC concentration also responded to discharge variation (increase, likely due to higher precipitation) in early autumn. Average DOC flux over the three sampling years was about 4.53 Tg yr^{-1} which is within the range of values reported in the literature. We observed interannual variability with annual export estimates ranging from 5.45 Tg yr^{-1} in 2014 to 3.57 Tg yr^{-1} in 2016, likely driven by discharge amplitude. We confirmed the important role of spring freshet in DOC export with on average more than 65% occurring during this period (roughly May/June).

Keywords: DOC, arctic rivers, spring flood, Yenisei, Siberia, water chemistry, multi-parameter probe

2.1 INTRODUCTION

Arctic soils represent about half of the world's terrestrial organic carbon pool. The top 3 meters of Northern Circumpolar soils contain about 1024 Pg of organic carbon and on a larger scale, permafrost regions are estimated to account for an organic carbon pool of 1672 Pg, with 88% found in permanently frozen ground and deposits (Tarnocai et al., 2009; Hugelius et al., 2013).

Arctic regions experience faster and more intense climate change than elsewhere in the world (Stocker et al., 2013). Recent warming at high latitudes has accelerated rates of permafrost thaw (Jorgenson et al., 2006). This thawing permafrost and the resulting microbial decomposition of previously frozen organic carbon is potentially one of the most significant carbon-climate feedbacks, because of the size of the carbon pools and the intensity of climate forcing at high latitudes (Schuur et al., 2008; Koven et al., 2011; der von Deimling et al., 2012; MacDougall et al., 2012; Schuur et al., 2013, 2015).

Several research studies indicate that permafrost thaw, apart from enhancing soil atmosphere gas exchange (CO_2 , CH_4), is also driving changes to the lateral flux of C from soils to freshwater and marine ecosystems (Frey and McClelland, 2009; Tank et al., 2012; Vonk and Gustafsson, 2013). Climate change has the potential to influence hydrological and biogeochemical cycles in arctic regions (Bring et al., 2016) with Climate models predicting ground warming, increased precipitation, higher riverine discharge and decreasing snow cover duration and extent in the High Arctic (McGuire et al., 2009; Grosse et al., 2016). These changes will likely affect the transfers of elements from terrestrial to aquatic ecosystems and dissolved organic carbon is particularly concerned (Guo et al., 2007; Schuur et al., 2008; McGuire et al., 2010; Feng et al., 2013; Holmes et al., 2013). Climate change has the potential to modify flux, composition and fate of exported DOC. Although the magnitude and direction of the response appear to differ regionally across the circum-arctic (Tank et al., 2012), in most of the great arctic river watersheds, mobilization of organic C from soils to riverine systems has increased by 3 to 6% between 1985 and 2004 according to the estimates of Feng et al., (2013), and this trend is predicted to continue with a warming climate (Amon et al., 2012).

Dissolved organic matter transported and processed in inland waters is an important component of the global carbon cycle (Cole et al., 2007; Battin et al., 2008). Organic matter concentrations in the Arctic rivers are among the highest reported in

world's rivers (Dittmar and Kattner, 2003). Arctic freshwater ecosystems process and transport substantial amount of dissolved organic carbon (DOC), delivering 34–38 Tg yr⁻¹ to the Arctic Ocean, and mineralizing or immobilizing another 37–84 Tg yr⁻¹ (McGuire et al., 2009; Holmes et al., 2012). The Arctic Ocean represents only 1% of the total world oceanic volume and receives about 10% of the global run off (Opsahl et al., 1999); thus the river runoff is proportionally very important (Anderson et al., 1998; Cooper et al., 2005; Hansell et al., 2004; Stein and Macdonald, 2004) and in combination with the current Arctic ocean changes, including rising temperature and sea ice decrease (Screen and Simmonds, 2010; Anderson and Macdonald, 2015; Whitefield et al., 2015; Carmack et al., 2016), this area may become a huge and powerfull biogeochemical reactor in the future.

In Arctic rivers, spring floods are key features for the transfer of DOM. This specific period is relatively short (May-June) driven by the spring snow-melt (Opsahl et al., 1999; Dittmar and Kattner, 2003; Holmes et al., 2012; Mann et al., 2012; Bring et al., 2016). Elevated discharge associated to high DOC concentrations can lead up to 90% of the annual DOC flux during this short period of time (Dittmar and Kattner, 2003; Raymond et al., 2007; Spencer et al., 2008, 2009a; Amon et al., 2012; Holmes et al., 2012). The Arctic rivers spring flood (freshet) is a relatively understudied period mainly due to remoteness and harsh sampling conditions during this season (icebreak, ice jam, changing weather), thus to date, very few studies captured the whole dynamic of the spring flood period at a high temporal resolution. Studies that encompass a large range of hydrological conditions, including in particular spring flood period, are valuable to provide a more complete picture of the amounts of organic carbon delivered by Arctic rivers (Rember and Trefry, 2004; Finlay et al., 2006).

The Yenisei is one of the world largest rivers and delivers the highest supply to the Arctic Ocean in terms of water volume and annual input of carbon and nitrogen (Amon et al., 2012; Dittmar and Kattner, 2003; Lobbes et al., 2000). It thus plays a significant role in the Arctic carbon cycle with one of the highest flux of DOC to the Arctic Ocean estimated around 4.1 – 4.9 Tg (Dittmar and Kattner, 2003). Although organic carbon fluxes of the Yenisei have been covered in some publications (Lobbes et al., 2000; Dittmar and Kattner, 2003; Amon and Meon, 2004; Amon et al., 2012; Holmes et al., 2012) an understanding of the detailed DOC temporal variations along with hydrology and ancillary variables is lacking.

Our study focuses on DOC dynamic in term of concentration and flux along the hydrological cycle of the Yenisei River with a special attention given to the spring flood. Sampling campaigns have been conducted during three consecutive years from 2014 to 2016. To improve our comprehension of the impact of the spring flood on DOC cycling we monitored DOC concentration at the river mouth at a high temporal resolution (close to daily sampling) during this crucial period with a few samples also taken during low flow periods (Winter and Summer). To give insight into the processes occurring along with DOC cycling, we also monitored water physico-chemical variables such as pH, ion concentration and water isotopy. DOC export from the Yenisei watershed will be compared to previous estimates and discussed along with its potential drivers.

2.2 MATERIAL AND METHOD

2.2.1 General description of the Yenisei Basin:

The Yenisei is the longest of the Arctic rivers and has the largest watershed ($2.5 \cdot 10^6 \text{ km}^2$) (Figure 2.1), showing the largest annual discharge with 673 km^3 for the total watershed (1999-2008) (world's sixth largest annual discharge). 32% of the basin is underlain by continuous permafrost, 12% is discontinuous permafrost, and 45% is sporadic isolated permafrost (Serreze et al., 2003). The Yenisei watershed embodies three geographically distinct regions: mountainous headwater area of Southern Siberia, a relatively flat area of boreal forest in its central and northern parts, and the central siberian plateau corresponding to its northernmost large tributaries basin. The mean elevation is 670m and the average basin slope is 0.2% (Fabre et al., 2017). The high flow period lasts from mid-May to mid-July, with peak daily discharges occurring in two weeks in late May and early June and generally exceeding $100\,000 \text{ m}^3 \cdot \text{s}^{-1}$. The streamflow is altered by the presence of large hydroelectrical dams on the main channel and its largest tributary, the Angara (Stuefer et al., 2011). Discharge dataset used is from Roshydromet for 2014 to 2016 and from Arctic GRO for the mean daily discharge calculation (period 1999-2014) (Figure 2.2).

2.2.2 Sampling site:

Our sampling site is located at the river mouth, at Igarka (67°28'19"N, 86°33'31"E, Figure 2.1), northern Krasnoyarsk Krai, Russian Federation. This specific location allows us to monitor an integrated signal of most of the watershed without tidal and marine influence inducing salinity increase and water chemistry perturbation. The watershed area at this point covers 2.44 million km². The region of Igarka corresponds to the forest tundra ecotone with vegetation characterized by mixed forest dominated by *Larix siberica*, *Picea obovata*, *Betula pubescens* and *Pinus Siberica*. Climate is a transition between moderately continental western Siberian climate to strongly continental eastern Siberian climate. The average annual temperature is -7.4°C and the mean annual precipitation is around 510 mm with about 50% occurring during summer months. Snow cover and ice pack usually extends from early October to late May (Vuglinsky, 2002; Rodionov et al., 2006). The area is situated within the continuous permafrost belt although presenting discontinuous features on a local scale (Ershov, 1996; Rodionov et al., 2007).

2.2.3 Sampling and analysis protocols:

We collected water samples daily (except when safety was not guaranteed, in particular during ice flow) during the spring flood and at lower temporal scale during lowflow period to capture the seasonal variability of DOM exports from the Yenisei watershed. Samples were collected with different means of transport depending on the time of the season. For winter and early spring samples, they were taken from a hole made into the ice and we reached the sampling site by snowmobile or overcraft for the last sampling before icebreak. When open waters reappeared sampling continued from small fisherman boat. Samples were pumped in an integrated manner from 1 to 5m depth. A total of 117 samples have been collected over a 3 years period (2014-2016). Sampling times are reported on Figure 2.2 along with Yenisei daily discharge, ice break dates and mean daily discharge.

To recover dissolved organic matter, water samples were filtered immediately after collection in Igarka Geocryology Laboratory laboratory through GF/F (0.7µm) glass fiber filters (Whatman, United States) (precombusted for 5h at 450°C) on glasswire filtration system (Sartorius, Germany).

For isotopic analysis ($\delta^{18}\text{O}$, $\delta^2\text{H}$), unfiltered samples were taken on the field in 10 mL glass vials (precombusted for 2h30 at 530°C), vials were filled and closed under water to avoid the presence of air bubble. Isotopic ratios were determined with Isoprime 100 (Elementar, Germany) coupled to a geo-multiflow equilibration system.

For ions analysis, filtered samples were transferred in 30 mL nalgene bottles. Measurements were made on a DIONEX Ics-5000+ (ThermoFischer scientific, United States) for Anions and on a DIONEX DX-120 (ThermoFischer scientific, United States) for cations. Reference materials used were ION 915 and ION 96.4.

All samples were stored refrigerated at 4°C in the dark prior to analysis. All of the organic and isotopic measurements were conducted at the physico chemical and isotopic platforms of Ecolab in Toulouse, France.

Ancillary in-situ measurements of pH, Temperature, Dissolved Oxygen, Turbidity, fDOM, Total Dissolved Solids and Conductivity were made with the EXO2 multiparameter sonde (YSI inc., Xylem inc., United States).

For DOC analysis, filtered samples were transferred in precombusted 10 mL glass vials (precombusted for 2h30 at 530°C) and spiked with HCl 6N for degassing DIC. Analysis was conducted on a TOC analyzer, Shimadzu TOC-5000A (Shimadzu, Japan) by catalytic oxidation at 680 °C and infrared measurement of CO₂. Standard used was Coal NCS FC 28010h.

2.2.4 Flux estimates calculation:

DOC fluxes were estimated using the USGS LoadEstimator software (LOADEST) similar as in Holmes et al. (2012). LOADEST uses time series of paired streamflow and DOC concentration data to construct a calibration regression, which is then applied to a daily discharge record to obtain daily DOC loads. Daily discharge data used were obtained from Roshydromet.

2.3 RESULTS

2.3.1 Yenisei discharge during the sampling years 2014-2016:

As most of the great Arctic rivers the Yenisei present hydrological cycle characterised by an intense spring flood driven by snowmelt (Figure 2.2). On average (1999-2014) the Yenisei river at Igarka exports 613 km³ annually, with the freshet period representing on average 56% of the annual export of water (from 25 April to 1 August). In 2014, the freshet period started on the 21 April, ice break occurred on the 20 May, discharge peaked on the 25 May at 118 000 m³.s⁻¹ and freshet ended on the 1 August. In 2014 the daily discharge during the freshet was higher than the daily mean discharge. The 2014 annual water flux was 634 km³ with 61% of the annual water export occurring during the freshet. The 2014 falling limb present a different pattern than the mean discharge with a slight rebound of the discharge in the second half of June. In 2015, discharge started to rise on the 24 April, icebreak occurred on the 19 May, peak discharge was reached on the 27 May at 105 000 m³.s⁻¹ and the freshet lasted until the 08 August. Annual water flux in 2015 was 618 km³ with 59% of the water flow occurring during the freshet. The general trend of the discharge in 2015 is very close to the mean discharge. In 2016, discharge rose from the 25 August, icebreak occurred on the 30 May, discharge was maximum on the 11 June at 77 000 m³.s⁻¹ and freshet ended on the 26 July. The annual water flux in 2016 was 482 km³ with 51% of the annual export occurring during the freshet. The 2016 discharge is lower than the mean discharge with an attenuated peak flood occurring later in the season.

2.3.2 Yenisei water physico-chemical context:

The main water physico-chemical variables are shown on Figure 2.3. General trends were similar across the sampling years. Water temperatures vary from close to 0°C in winter to a maximum around 20°C generally reached in late July. The Dissolved oxygen (mg/L) trend is slightly offset compared to discharge. It generally rises and peaks earlier than discharge. Lowest values are observed during low flow, on average 9.4 mg/L, and highest values are reached during high flow with dissolved oxygen concentration exceeding 10.5 mg/L. Dissolved oxygen (mg/L) and dissolved oxygen (% sat) have different trends with dissolved oxygen concentration decreasing with decreasing discharge in summer whereas percent saturation leveled off after peak discharge. Conductivity tends to drop during spring flood period from on average 129

$\mu\text{S}/\text{cm}$ during low flow to 49 $\mu\text{S}/\text{cm}$ during high flow. Total dissolved solids concentration drastically decreases during freshet period dropping from an average of 137 mg/L during low flow period (winter concentrations are slightly higher than summer ones) to 48 mg/L during high flow. Turbidity (FNU) dynamic is slightly offset compared to discharge, peaking earlier; it drastically increases during the spring flood from an average of 1.6 during winter and summer low flow up to 29 for maximum values before peak flood. It seems that there is a specific pattern with 2 local maximum for turbidity, a first one prior to peak flood and a second one more synchronized with the maximum discharge (particularly visible for 2015 and 2016). pH generally tends to decrease during the flood period (particularly visible in 2015 and 2016). Annual pH average is around 7.6, with higher values during low flow around 8.2 and lower pH during high flow around 7 or slightly below (2015-2016).

Variations of major ions concentrations in the Yenisei during the three sampling years (2014-2016) are shown in Figure 2.4 . Major ions concentrations tend to drastically decrease during the spring flood, this tendency is similar across the sampling years. Cl^- concentration has an average of 10.7 mg/L during winter and summer low flow and drops to an average of 2.7 mg/L for high flow period with lowest values down to 1.4 mg/L. SO_4^{2-} concentration has an average of 2.3 mg/L during winter and summer low flow and drops to an average of 0.9 mg/L for high flow period with lowest value down to 0.4 mg/L. Na^+ concentration has an average of 8.4 mg/L during winter and summer low flow and drops to an average of 2.6 mg/L for high flow period with lowest value down to 1.2 mg/L. K^+ concentration has an average of 0.8 mg/L during winter and summer low flow and drops to an average of 0.5 mg/L for high flow period with lowest value down to 0.3 mg/L. Mg^{2+} concentration has an average of 5.5 mg/L during winter and summer low flow and drops to an average of 2.1 mg/L for high flow period with lowest value down to 1 mg/L. Ca^{2+} concentration has an average of 22.7 mg/L during winter and summer low flow and drops to an average of 8.5 mg/L for high flow period with lowest value down to 3.8 mg/L. Figure 2.5 shows the evolution of the ratio $(\text{K}^+ + \text{Na}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+})$ indicating the relative contribution of silicate versus carbonate rocks to the water chemistry. The low flow signal is mainly reflecting the dominant contribution of carbonate, with a rapid and ephemeral shift toward silicate contribution (high ratio value) peaking prior to peak flood (reported in 2014 and 2015, peak was not recorded in 2016). The Piper diagram associated (proportions of $\text{Ca}^{2+}, \text{Mg}^{2+}$

and Na⁺+ K⁺) in Figure 2.5 indicates water chemical composition as calcium type, except for peak flood samples of 2014 and 2015 showing a shift toward a slightly more sodium/potassium type chemical composition. According to the Piper diagram, the water chemical composition was relatively constant across seasons and years, with most of the samples plotting in a restricted area. Figure 2.6 displays the relationship between the sum of calcium and magnesium ions and alkalinity. Samples mostly fall within the equilibrium relationship of calcium and carbonates dissolution except spring flood samples. Piper diagram associated (proportions of HCO₃⁻, SO₄²⁻ and Cl⁻ + NO₃⁻) indicates a water chemical composition of bicarbonate type, with a tendency toward higher proportion of alkalinity for spring flood samples.

2.3.3 Yenisei water isotopic signature:

The $\delta^{18}\text{O}$, $\delta^2\text{H}$ signals of the Yenisei water (Figure 2.7, 2.8) tend to be higher during low flow periods (winter and late summer), on average about -17‰ for $\delta^{18}\text{O}$ and -128‰ for $\delta^2\text{H}$, whereas high flow (when discharge is higher than half of the peak discharge) signal is lower with on average a signal around -21.5‰ for $\delta^{18}\text{O}$ and -153‰ for $\delta^2\text{H}$.

2.3.4 DOC dynamic and export from the Yenisei watershed at Igarka:

DOC concentration variations and correlation with discharge across the hydrological cycles from 2014 to 2016 are shown on Figure 2.9. DOC dynamic is close to the discharge variations with strong linear correlation between DOC and discharge (R^2 of 0.73, 0.75 and 0.92 for 2014, 2015 and 2016 respectively, 0.78 over the 3 years $n=117$). DOC appears to be more correlated to discharge during winter low flow and during the onset of the spring flood whereas there is a slight discrepancy during the recession limb and around the peak flood. In 2014, discharge presents a rebound in mid-june, however DOC concentrations seem not to respond to this particular variation. Contrary, in 2015, DOC concentrations show a rebound in late June/early July whereas discharge does not show any specific change. DOC mean over the 3 sampling years measured is 7 mg/L (Standard deviation= 3.9, $n=117$). DOC concentrations are low during winter and summer low flow, on average around 4.1 mg/L (Standard deviation= 1.5, $n=61$) and significantly increase with discharge during spring flood with an average during high flow of 10.3 mg/L (Standard deviation= 3.0, $n=56$). DOC concentrations

peak during spring freshet reaching maximums of 19 mg/L in 2014 (18 May 2014, discharge= 53 700 m³.s⁻¹), 15.6 mg/L in 2015 (22 May 2015, discharge= 76 000 m³.s⁻¹) and 12.8 mg/L in 2016 (2 June 2016, discharge= 70 300 m³.s⁻¹). Our measurements show that maximum DOC concentrations occur about 5-7 days prior to peak discharge (25 May 2014 - 118 000 m³.s⁻¹, 27 May 2015 - 105 000 m³.s⁻¹, 9 June 2016 - 77 200 m³.s⁻¹), our DOC measurements at (or closest to) peak discharge are 15.3 mg/L (27 May 2014, discharge= 110 000 m³.s⁻¹), 13.33 mg/L (27 May 2015, discharge= 105 000m³.s⁻¹). DOC concentration peak close to ice break and start to decline even if discharge is still rising. DOC concentration changes are extremely rapid in the middle of the rising limb, around the ice break period. In 2014, DOC concentrations jumped from 7.32 mg/L on the 12 May 2014 to 19mg/L on the 18 May 2014 just before ice break. In 2015, DOC concentrations almost doubled after the ice break, increasing from 8.2 mg/L on the 15 May 2015 to 15.6 mg/L on the 22 May 2015. In 2016, DOC concentrations also almost doubled after the ice break, rising from 6.4 mg/L on the 28 May 2016 before ice break to 12.8 mg/L on the 2 June 2016.

fDOM (RFU) measured in situ across the 3 sampling years with the EXO2 sonde shows good correlation with DOC concentration ($R^2=0.94$, $n=100$, Figure 2.10). fDOM dynamic is close to the discharge one ($R^2=0.87$, $n=100$). fDOM values are low during winter and summer low flow with an average of 10.8 and increase during high flow period with an average of 44.8 and maxima recorded in 2014 of 63.3, 56.2 in 2015 and 45.1 in 2016 occurring close to the peak discharge.

Over the period 2014 to 2016, the Yenisei basin exported on average 4.53 Tg .yr⁻¹ of DOC, with average export during Spring flood of 3.11 Tg representing 68.8% of the total mean annual export. The Yenisei watershed average DOC yields were 1.86 ton.km⁻².yr⁻¹. In 2014 total annual export was 5.45 Tg, with spring flood contributing up to 3.85 Tg, accounting for 70.7% of annual export. DOC yields were 2.23 ton.km⁻².yr⁻¹. In 2015 total annual export was 4.86 Tg, with spring flood contributing up to 3.28 Tg, accounting for 67.5% of annual export. DOC yields were 1.99 ton.km⁻².yr⁻¹. In 2016 total annual export was 3.27 Tg, with spring flood contributing up to 2.2 Tg, accounting for 67.4% of annual export. DOC yields were 1.34 ton.km⁻².yr⁻¹.

2.4 DISCUSSION

2.4.1 Hydrology

Discharge trends

Discharge observed during our sampling years (2014-2016) show inter-annual variations, with 2014 being higher than average in term of water export, 2015 within the average and 2016 being within the lower range. Inter-annual variation in snowmelt dynamic and precipitation regime with Yenisei tributaries contributing at different times may explain these variations (Finlay et al., 2006; Bagard et al., 2011; Prokushkin et al., 2011; Kuzmin et al., 2014; Zscheischler et al., 2016). Another factor can be the presence in the southern part of the Yenisei basin of massive dam infrastructures that can have the ability to influence the hydrological regime of the river (McClelland et al., 2004; Yang et al., 2004; Shiklomanov and Lammers, 2009). However, we may consider that the three hydrological years studied are representative of the different hydrological conditions that can occur in the Yenisei. Discharge variation is very rapid and difficult to capture. During the period between the ice break and the total open water, it is impossible to sample water due to drifting ice, but hydrological changes are tremendous over a daily scale. In 2014, discharge jumped from $53\,700\text{ m}^3\cdot\text{s}^{-1}$ (18/05/014) on our last sampling on ice to $110\,000\text{ m}^3\cdot\text{s}^{-1}$ (27/05/2014) on our first open water sampling. Studies on the Yenisei river hydrology and factors of change, in particular through the investigation of historical discharge records have been conducted by McClelland et al., (2004); Yang et al., (2004); Shiklomanov and Lammers, (2009) and recently Fabre et al., (2017).

In Arctic watersheds, permafrost has a great influence on water flow. The active layer dynamic (depth and extent) induces a wide range of surface and subsurface processes and drives runoff generation. In addition, topographic variations from mountainous environments to lowlands along with vegetation and soil type strongly influence water flowpath, soil moisture, ground freeze-thaw dynamic and evaporation processes (Bring et al., 2016 and reference therein).

Main impacts of climate change in the Arctic will involve terrestrial freshwater with decreasing extent and duration of snow cover and increasing discharge of large Siberian rivers (Bring et al., 2016 and reference therein). Modifications of the hydrological cycle will be combined to changes in the cryosphere with alteration of the permafrost magnitude and extent and active layer deepening. These changes will impact

water flow volumes, timing and pathways through terrestrial ecosystems and quality and duration of river ice cover (Wrona et al., 2016).

Water chemistry and isotopy

Preflood waters characterized by high conductivity, linked to the presence of soluble salts (confirmed by corresponding high TDS values and elevated ions concentrations) (Figures 2.3, 2.4), suggest a significant contribution of ground water to the global discharge during winter low flow. Ions specific composition indicators (Figure 2.5, 2.6) indicate contrasting water mass origins between low flow and Spring flood periods. According to lithologic composition maps (Amiotte Suchet et al., 2003; Dürr et al., 2005), the silicate signal of the peak flood likely originate from the basaltic volcanic formation located in the northern part of the watershed whereas carbonates formations influencing the low flow signal are located in southern parts of the watershed.

The trend in isotopic signature observed during the hydrological cycle may correspond to the winter contribution of low latitudes (Southern/warmer region of the watershed) with higher isotopic values and the spring contribution of high latitude (colder region of the watershed) characterized by lower isotopic values (Rozanski et al., 1993) (Figure 2.8). This reflects the “rain-out” phenomenon affecting water isotopic ratio along latitudinal gradient (Gat, 1996). Isotopic signal of water is variable during the hydrological cycle, suggesting the contribution of different water sources and appear to be related to variability in river discharge (inverse relationship) (Figure 2.7). This trend has been previously observed through the PARTNERS data set (Yi et al., 2012) where isotopic variation in the Yenisey as in the Kolyma, Mackenzie and Yukon responds to discharge in a linear way. This phenomenon is expected in snowmelt-driven watersheds like the Yenisei. The melting snowpack being isotope-depleted contributes to Spring flood whereas groundwater with more heavy isotope-enriched signature supplies low flows (St Amour et al., 2005; Stadnyk et al., 2005; Yi et al., 2010). Yi et al., (2012) have reported water isotopic values for Major Arctic Rivers, including the Yenisei at Dudinka. Our data falls within the range of previously recorded values, from -16.41 ‰ to -21.09 ‰ for $\delta^{18}\text{O}$ and -139.4 ‰ for $\delta^2\text{H}$ (flow-weighted). Local snow isotopic signature is comprised between -26 ‰ and -27.8 ‰ for $\delta^{18}\text{O}$ and between -200 ‰ and -212 ‰ for $\delta^2\text{H}$ (Streletskiy et al., 2015). Lower values ($\delta^{18}\text{O} < -20$ ‰ and $\delta^2\text{H} < -160$ ‰) during the peak flow period (late May/early June) may thus indicate the

contribution of local snowmelt to the global discharge, spring flood of local rivers being characterized by lighter isotopic composition (Streletskiy et al., 2015).

2.4.2 Dissolved organic matter dynamic

Temporal trends in DOC

Arctic watershed features include snowmelt dominated hydrological cycle, supplying more than half of annual run off within 4-6 weeks, shallow water flow path due to permafrost, limiting soil drainage, and large area of organic-rich soils, providing large quantities of DOC potentially mobilizable to riverine systems (Prokushkin et al., 2011 and reference therein).

DOC concentration is highly variable during the freshet period, relatively stable during wintertime and shows limited variation during late summer early autumn. The ice break period seems to be the most dynamic time of the spring freshet but is very difficult (if not impossible) to sample because of the ice jams and represents a gap (about one week generally) in the record of the DOC dynamic. Increased snowmelt and surface run off associated with the rising limb of the spring flood induced rapid inputs of DOC likely originating from allochthonous terrestrial organic matter sources. Permafrost distribution (shallow active layer enhancing rapid lateral flow), timing and dynamic of snowmelt inducing variation in the contribution of areas with different stocks of mobilizable C may explain intra-seasonal variability of riverine C loads (Prokushkin et al., 2007). Maximum DOC concentrations were measured a few days (5-7) prior to peak discharge, suggesting that a large pool of DOM could be readily mobilized with the spring thaw in conjunction with a dilution effect occurring at high discharge when the DOM pool start to be depleted (Hornberger et al., 1994; Boyer et al., 1997, 2000; McGuire et al., 2009; Fouché et al., 2017). This phenomenon of mismatch between peak DOC and discharge during spring freshet has also been reported for Yenisei Central Siberian Plateau rivers (Prokushkin et al., 2011), and hysteresis effect inducing DOC concentrations maxima on the rising limb of the hydrograph have been reported for watershed underlain with permafrost (Carey, 2003; Finlay et al., 2006; Guo and Macdonald, 2006). The specific DOM pool corresponds to the snowmelt runoff flushing organic carbon within fresh plant litter and the upper shallow organic-rich layer due to the presence of impermeable frozen ground in permafrost areas (Balcarczyk et al., 2009; O'Donnell et al., 2010; Mann et al., 2012; Pokrovsky et al., 2015).

Post freshet conditions characterized by decreasing DOC concentrations suggest reductions in terrestrial surface run off associated with active layer deepening and interaction with deeper soil horizon including sorption and/or mineralization processes associated with longer residence time that can lower DOC concentrations (Kawahigashi et al., 2004; Frey, 2005; Striegl et al., 2005; Guggenberger et al., 2008). This might be combined with the depletion of the DOC pool stored in topsoil from the antecedent winter (Neff et al., 2006; Spencer et al., 2009a; Striegl et al., 2005).

Prokushkin et al. (2001, 2007, 2011a, 2011b) have investigated DOC dynamic, sources and fluxes in Yenisei river tributaries of the central Siberian plateau. Main tributaries studied are the Nizhnyaya Tunguska (174 300 km², mean annual discharge 51 km³.yr⁻¹) and the Kochechum (96 400 km², 29.9 km³.yr⁻¹) in Tura and the Podkamennaya Tunguska (163 100 km², 30.7 km³.yr⁻¹) in Baykit. They could be considered as representative of the contribution to the Yenisei River of the boreal forest ecosystem of central Siberia with differing permafrost coverage. From an hydrological point of view, these rivers show peak flow occurring in the first week of June (2006-2010) which would be after Yenisei peak flood in 2014 and 2015 (25-27 May) and close to the timing of 2016 (9 June). Winter (October-April) flow of these rivers represents only a very small portion (3-11%) of the annual water export, with small rivers of the region being completely frozen (zero discharge in March). The main water export corresponds to the May-June period accounting for 55-71% of the annual discharge. DOC concentrations were highest during spring with concentration average of 14.5 ± 4.7 mg/L for the Kochechum, 21.3 ± 2.2 mg/L for the Nizhnyaya Tunguska and 20.1 ± 2.2 mg/L for the Podkamennaya Tunguska. The average annual DOC exports from the Kochechum were 0.43 Tg, 1.24 Tg from the Nizhnyaya Tunguska and 0.52 Tg from the Podkamennaya Tunguska. This suggests that the central Siberian Plateau Rivers are important DOC suppliers to the Yenisei River contributing to almost 50 % of global DOC flux of the Yenisei River.

Kawahigashi et al. (2004) have studied small streams (tributaries of the Yenisei river) along a gradient from discontinuous to continuous permafrost. They observed an increase in DOC concentration (from less than 5 mg/L to almost 30 mg/L) with increasing latitude (from 65° to 67°N), i.e. with increasing permafrost coverage (differing depth) suggesting that export of DOM from soils to streams in permafrost regions may be controlled by the active layer thickness.

Tolomeev et al. (2014) have conducted an integrated study of the Carbon Cycle components within the Yenisei basin, from middle to lower reach during the summer 2012. Concerning DOC concentration evolution along the course of the Yenisei river, they observed increase of DOC concentration from the Angara river (58°N) to the confluence with the Kureika river (66°N), followed by a stable concentration before reaching the zone where river and seawater mix characterized by a sharp decrease of DOC concentration. These results suggest that main carbon sources are mostly located within the central part of the Yenisei basin, corresponding in particular to the boreal forest ecosystem.

DOC measurements of 2014, 2015 field campaigns have been used to calibrate a model to reconstruct DOC concentration along the hydrological cycle using High Spatio-Temporal Optical Remote Sensing (Herrault et al., 2016). Similar approach has also been employed for the Kolyma river (Griffin et al., 2011).

Our measurements allowed us to calibrate the relation between fDOM and DOC for the Yenisei River. We obtain significative correlation ($R^2=0.94$, Figure 2.10) making fDOM a relevant, efficient and simple proxy for in situ monitoring of DOC concentration at high temporal resolution.

DOC flux

Our flux estimate, based on 2014-2016 data (4.53 Tg.yr^{-1}), is within the lower range of published data ($4.65\text{-}5.08 \text{ Tg.yr}^{-1}$) (Table 2.1), however our study is the only one based in Igarka which is the gauging station for the lower Yenisei and our estimate includes a year (2016) with overall small discharge compared to average year. The spring flood period is a crucial moment for DOC export with up to 68.8% of annual transfers due to high discharge combined with high DOC concentration. According to the estimates of Prokushkin et al. (2011), the central Siberian plateau rivers (Kochechum, Tembenchi, Nidym, Nizhnyaya Tunguska, Podkamennaya Tunguska), covering $470\,900 \text{ km}^2$ (about 18.5 % of the total Yenisei watershed), potentially contributes to up to 50% of the annual DOC flux of the Yenisei (Table 2.1). The Yenisei river is one of the main contributor of DOC within the Pan-Arctic region just after the Lena river. The pan-Arctic watershed covers $20.5 \times 10^6 \text{ km}^2$ with the six greatest arctic rivers (Yukon, Mackenzie, Kolyma, Lena, Yenisei, Ob') representing about 53% of this area. At the pan-Arctic scale, rivers export annually about 34.042 Tg of DOC (Holmes et al., 2012) of which the Yenisei accounts for 13.3%.

Flux calculation generally derives from DOC/discharge relationship, although DOC flux estimation may not be totally straightforward during snowmelt peak flood because of complex relationships between landcover (wetland impact, influence on specific waterflowpath and available DOC for leaching) and DOC flux (Laudon et al., 2004; Finlay et al., 2006; Laudon et al., 2011; O'Donnell et al., 2016 and references therein).

Net Ecosystem Production (NEP) is the balance between Gross Primary Production (GPP) and ecosystem Respiration (R). River systems link terrestrial landscapes, in particular soils, to aquatic and marine environments, transporting, transforming and storing terrigenous organic carbon which can represent a significant fraction of the global annual terrestrial NEP (Cole et al., 2007; Battin et al., 2008). Quegan et al., (2011) have estimated the net biome productivity (NBP) of central Siberia to $27.5 \pm 7.2 \text{ gC.m}^{-2}\text{.yr}^{-1}$, indicating that the region act as a carbon sink. Comparing this to DOC yields of the Yenisei basin, lateral DOC export would represent about 6.8% of NBP.

Our study and many others in arctic rivers only focused on samples taken from lower reach or river mouth. Thus, Ecological processes taking place along the river to ocean continuum are often neglected (Cole et al., 2007; Battin et al., 2008; Romankevich and Vetrov, 2013; Tolomeev et al., 2014).

Potential climate change influences

The most probable climate change scenario for Siberian Arctic region implies shift of permafrost boundary further north and active layer deepening (Frey and McClelland, 2009; Romanovsky et al., 2010; Anisimov et al., 2013; Pokrovsky et al., 2015; Schuur et al., 2015; Grosse et al., 2016). The change from continuous to discontinuous permafrost may induce decrease in DOC concentrations of the northernmost rivers by a maximum of 2 folds depending on the specific geology and soil characteristics. Active layer thickness increase will involve deeper soil horizons (clay, sand/silts) in water pathways inducing increased sorption of organic compounds on mineral phase (Kaiser et al., 2002; Oosterwoud et al., 2010; Mergelov and Targulian, 2011; Gentsch et al., 2015).

Other modifications that could be induced by climate change and impact DOC cycling in arctic regions include changes in precipitation, seasonal and ice cover, fire regime and vegetation structure (Wrona et al., 2016 and reference therein). Important changes are also predicted for hydrological regime induced by increased overall

precipitation coupled to increased winter baseflow and groundwater feeding (Pokrovsky et al., 2015 and references therein). Higher river discharge could balance the potential reduction in DOC export associated with active layer thickening. Increased permafrost thaw could induce a shift in arctic river systems from surface-water to groundwater dominated systems (Frey and McClelland, 2009) which correspond to the current state during winter and late summer baseflow exporting relatively lower amounts of DOC (Mann et al., 2012).

Climate change also implies modifications in plant production and vegetation structure (Cramer et al., 2001; Boisvenue and Running, 2006) influencing DOC production and quality (Neff and Hooper, 2002; Judd and Kling, 2002; Armstrong et al., 2012; van den Berg et al., 2012; Camino-Serrano et al., 2014).

2.5 CONCLUSION AND PERSPECTIVES

Our results show that the spring flood period of the Yenisei River is crucial for DOC export, contributing up to 70% of total DOC export in less than 2 months. Our high temporal resolution observations allowed us to detail DOC dynamic. We identified that DOC signal is mainly driven by discharge with a huge increase in DOC concentration during the rising limb of the freshet. However, peak in DOC concentration occurs before maximum discharge. This may imply the interplay of a huge DOM pool readily mobilizable to aquatic system during snowmelt period when flushing of the upper organic horizon and plant litter is the dominant flowpath for water. This high DOM input probably undergoes a dilution effect during the peak flood about 5-7 days after the DOC concentration reached its maximum. As highlighted previously, DOC concentration undergoes strong seasonal variations with different areas of the watershed contributing successively. Thus, we can expect that sources and composition of DOM are also changing significantly along the hydrological cycle and that these changes are especially rapid and pronounced during the spring flood events. These hypotheses will be tested in the following chapter through the investigation of DOM quality using optical properties, lignin biomarkers and radiocarbon datation to gain insight into the sources, degradation state and age of the riverine DOM.

Field data collected at key hydrological moment and at relatively high temporal resolution can be valuable inputs for modelers to develop, validate and refine models (Herrault et al., 2016; Fabre et al., 2017). Cross-watershed investigation would facilitate

global interpretations of trends of the integrated DOC signal observed at the river mouth. Sampling campaigns at main tributaries mouth would allow a better evaluation of their respective impact on the global DOM signal of the Yenisei River and permit to decipher between contribution of different watershed components combining temporal and spatial trends observation. In addition, long-term monitoring of basic DOC and water chemistry variables over the seasonal cycle would enable to compare dynamics across drainage basins and serve as basis for reliable assesment of future changes impacts.

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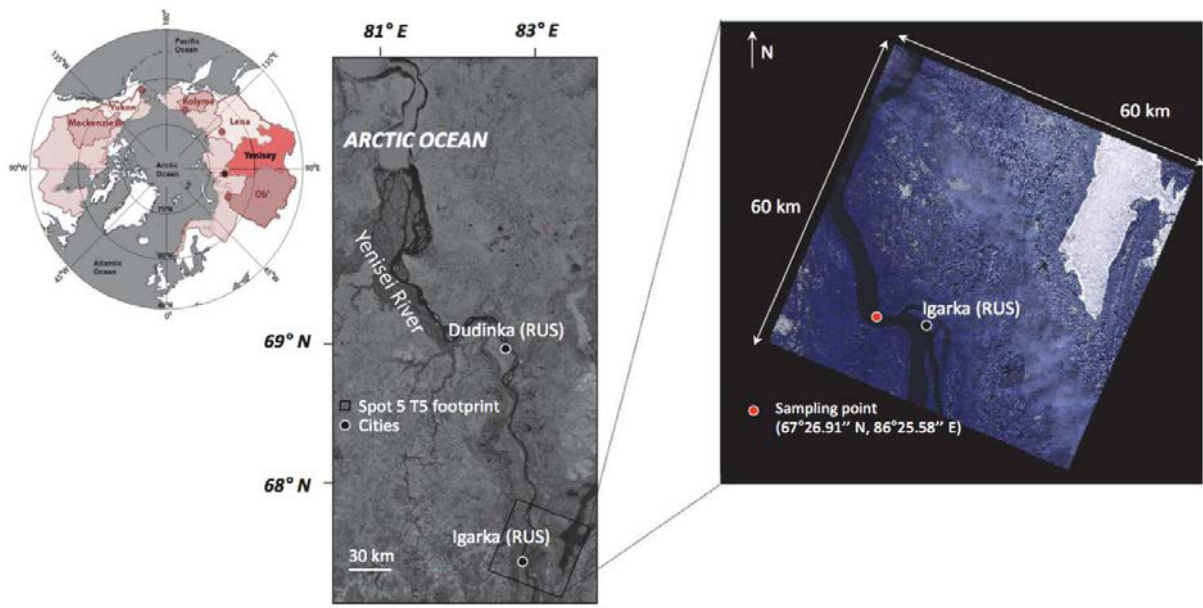


Figure 2. 2 Sampling site localization. (sources: top left Arctic map modified from Amon et al. (2012), Spot5 Take5 from Herrault et al. (2016))

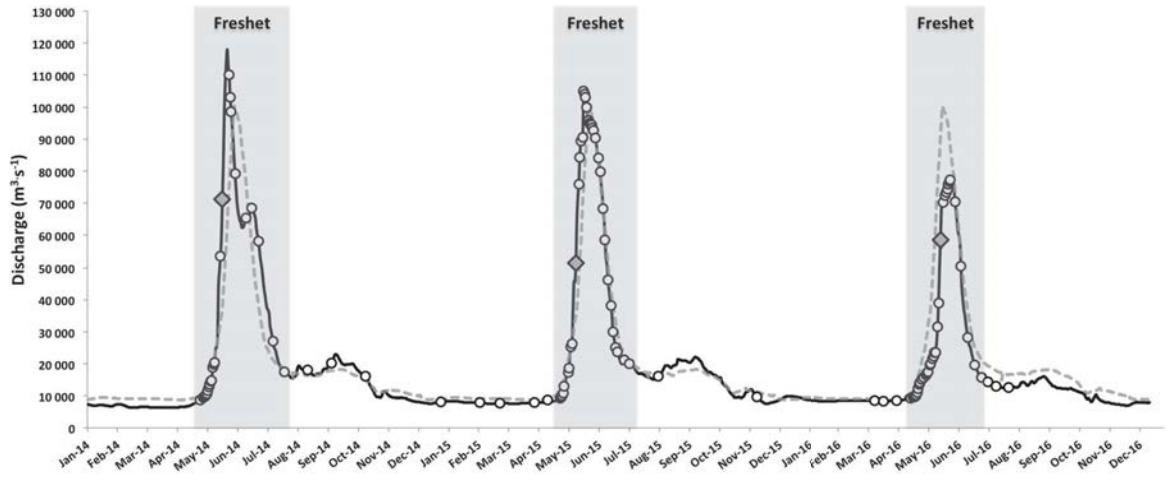


Figure 2. 2 Daily discharge ($m^3.s^{-1}$, Black line, source: Roshydromet), grey rectangles delimitate the freshet period, dashed grey line represents the daily mean discharge (1999-2014, source: Arctic GRO), white dots correspond to each sampling point and grey dimonds indicate icebreak timing.

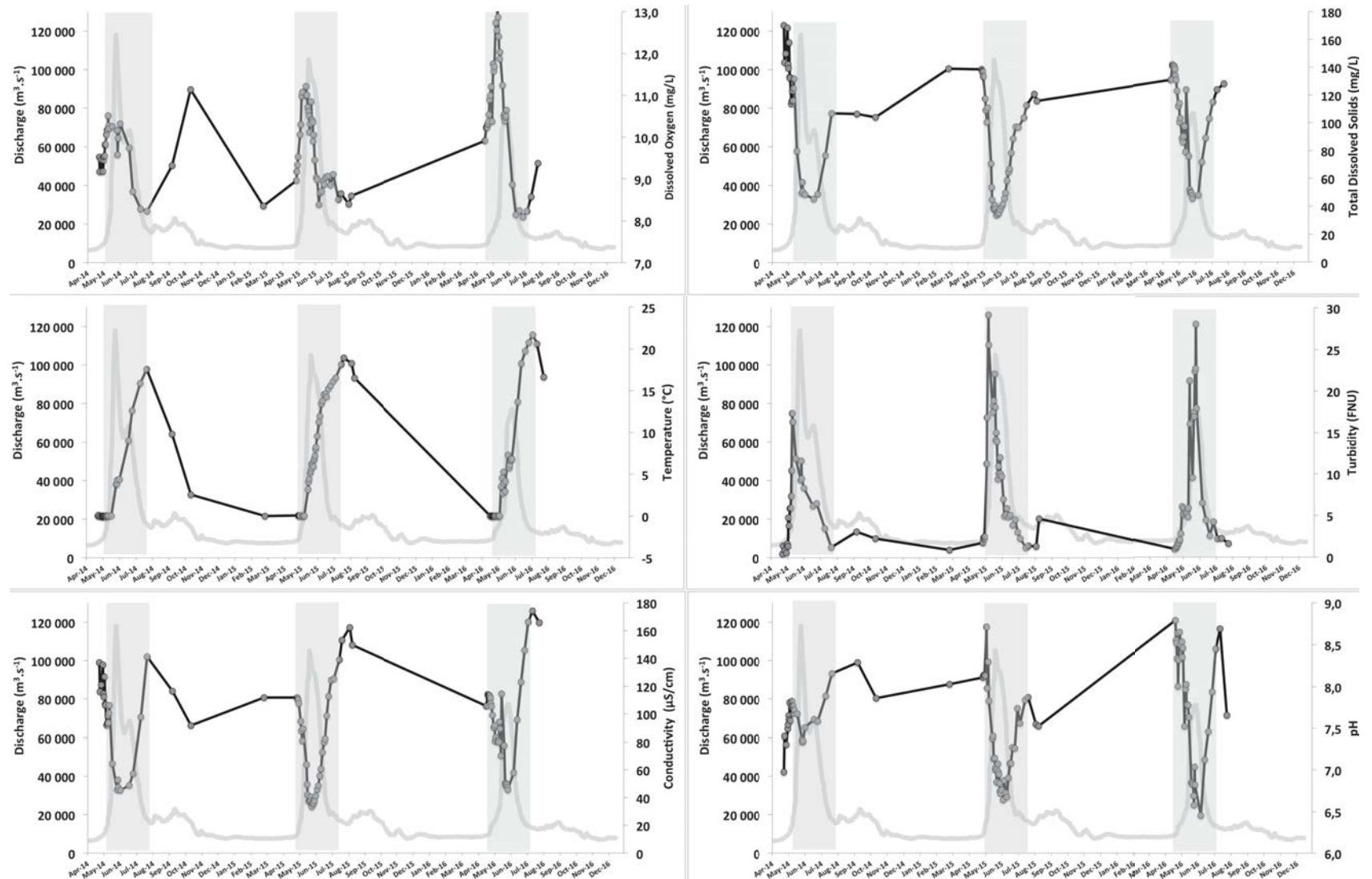


Figure 2. 3 Water physico-chemical variables evolution along with discharge ($\text{m}^3 \cdot \text{s}^{-1}$) measured with multi-parameter probe (EXO-2), grey dots are point measurements, grey line represents daily discharge (source: Roshydromet), grey rectangle delimitate freshet periods. Variables reported are Dissolved oxygen (mg/L), Total dissolved solids (mg/L), Temperature ($^{\circ}\text{C}$), Turbidity (FNU), Conductivity ($\mu\text{S}/\text{cm}$), pH.

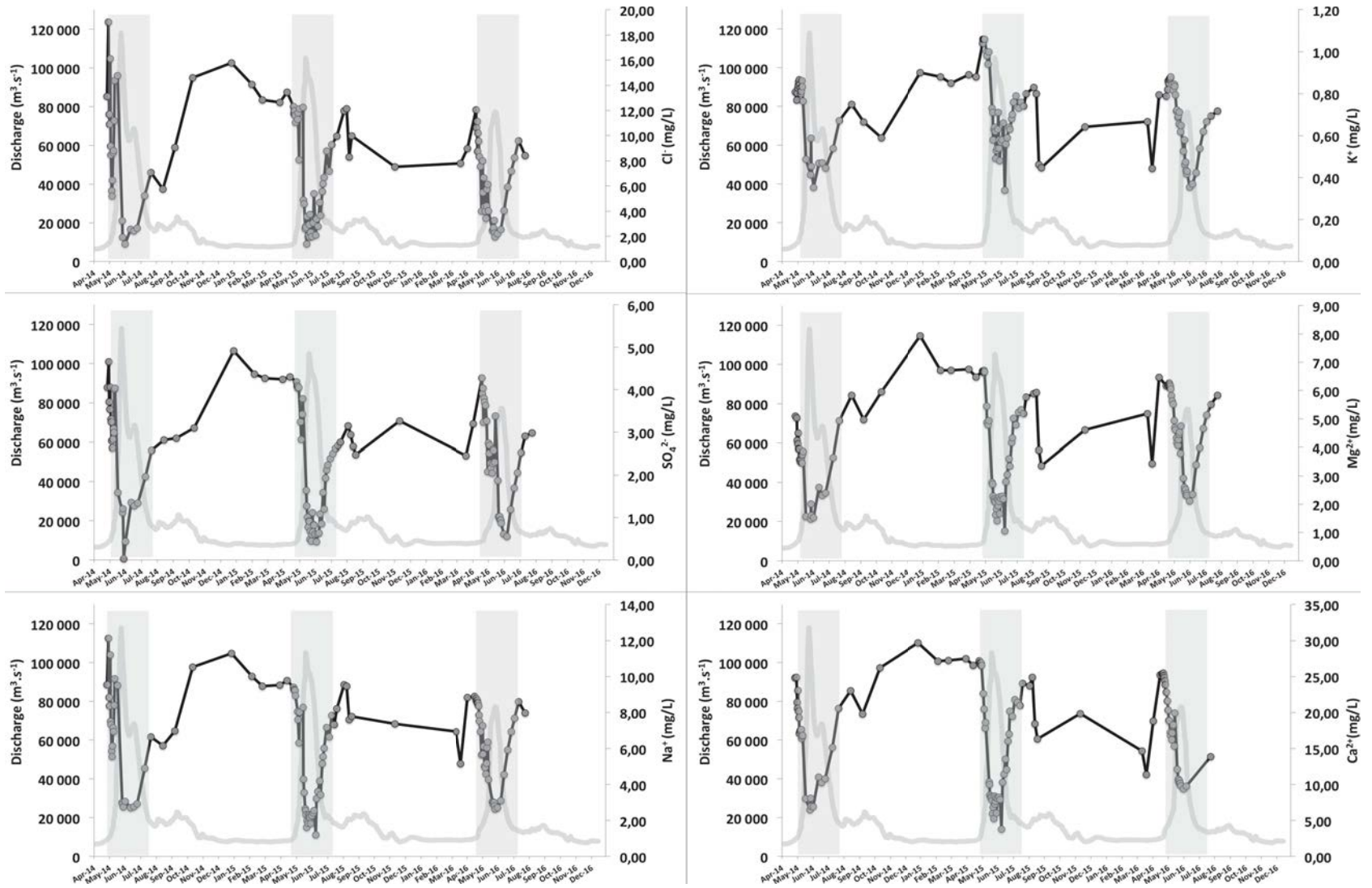


Figure 2. 4 Major ions concentrations (mg/L) along with daily discharge (m³.s⁻¹). Grey dots are point measurements, grey line represents daily discharge (source: Roshydromet), grey rectangle delimitate freshet periods. Ions concentrations reported are Cl⁻, K⁺, SO₄²⁻, Mg²⁺, Na⁺, Ca²⁺.

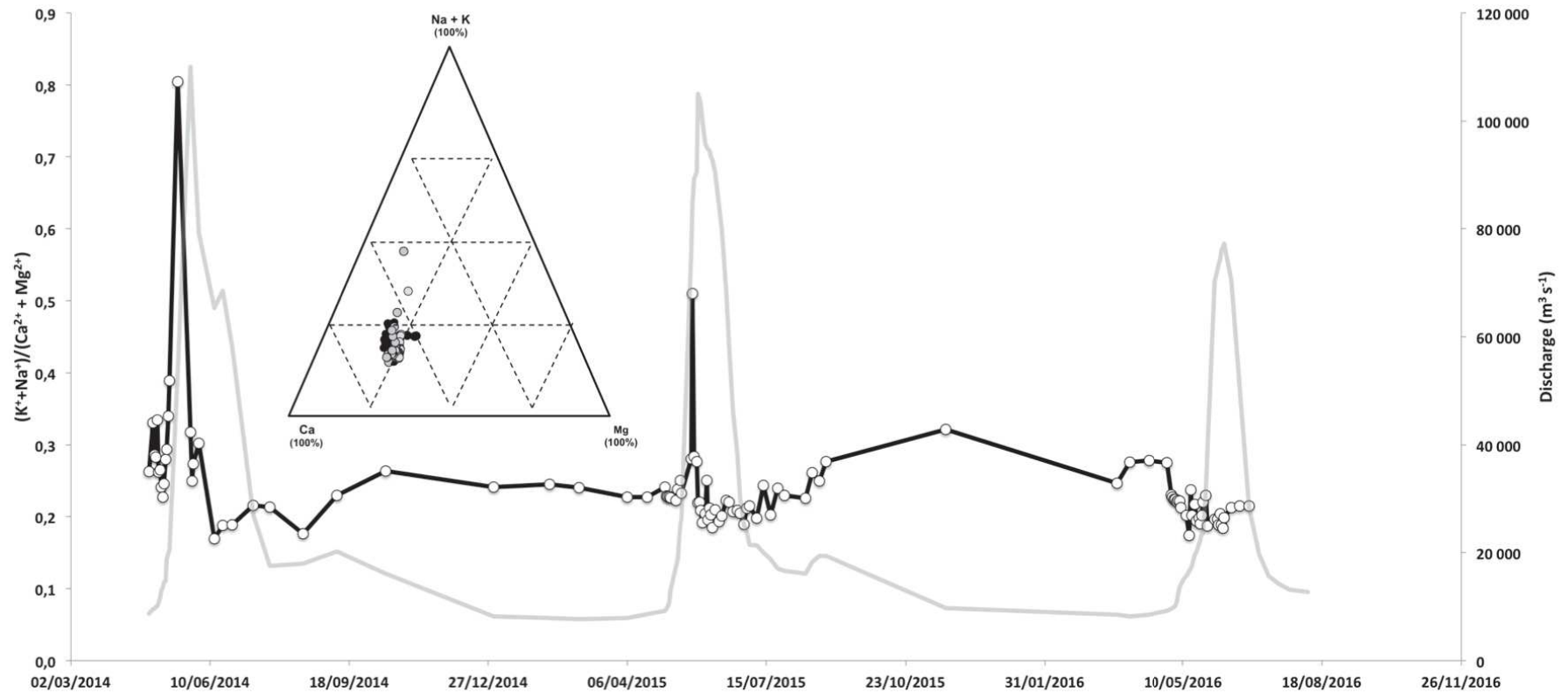


Figure 2. 5 Temporal variation of $(K^{+} + Na^{+}) / (Ca^{2+} + Mg^{2+})$ ratio showing relative contribution of carbonate versus silicate rocks to water ions concentration. Included, Piper diagram showing the water chemical composition, expressed in percentage of total equivalent per liter, (grey dots represent spring flood samples and black dots represent low flow samples).

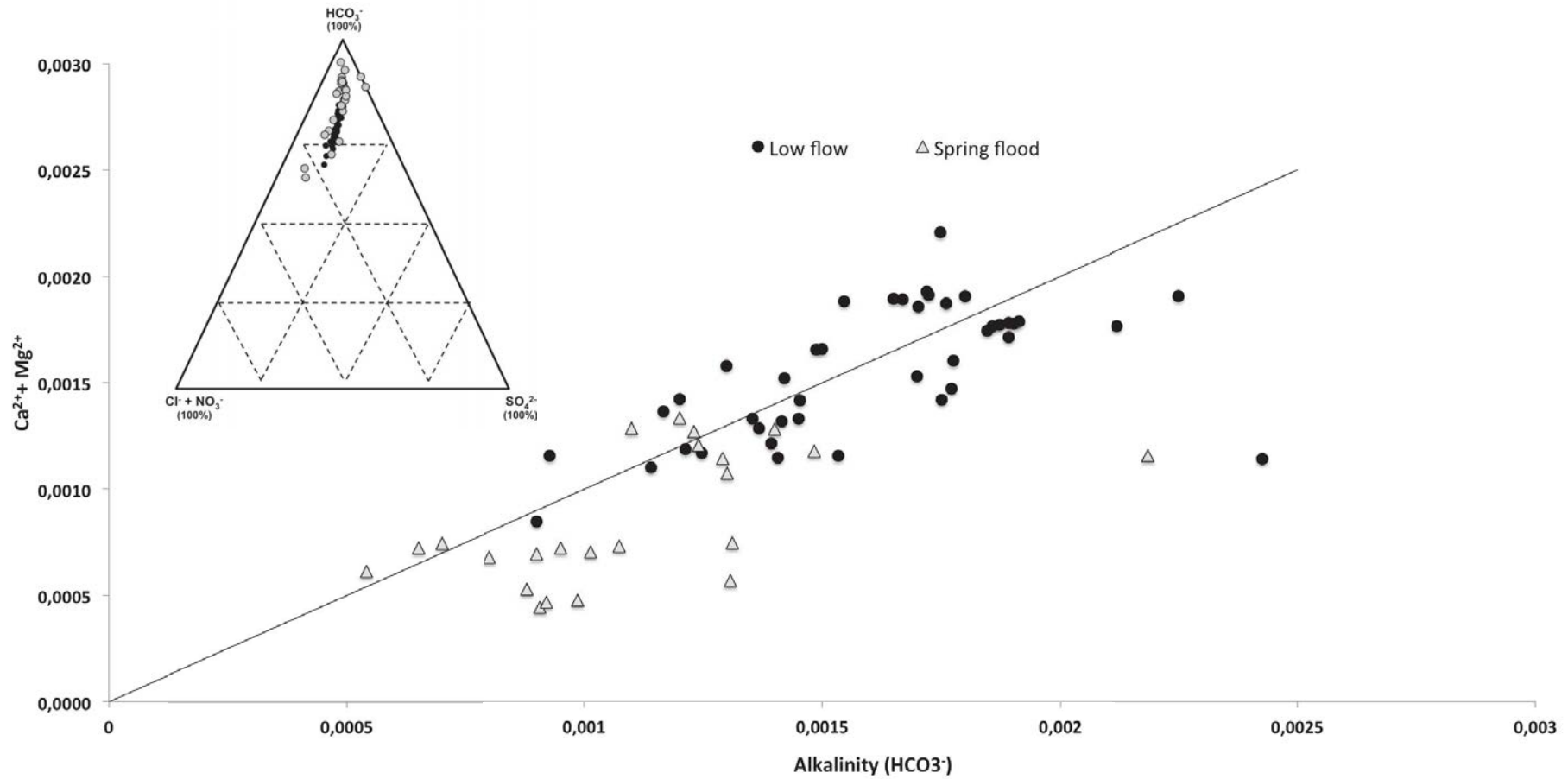


Figure 2. 6 Relationship between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and Alkalinity (HCO_3^-) expressed in equivalent per liter, black thin line represent the equilibrium of carbonates and calcium. Included, Piper diagram showing the water chemical composition (bottom left: Chloride type, bottom right: Sulfate type, top: Bicarbonate type), expressed in percentage of total equivalent per liter, (grey dots represent spring flood samples and black dots represent low flow samples).

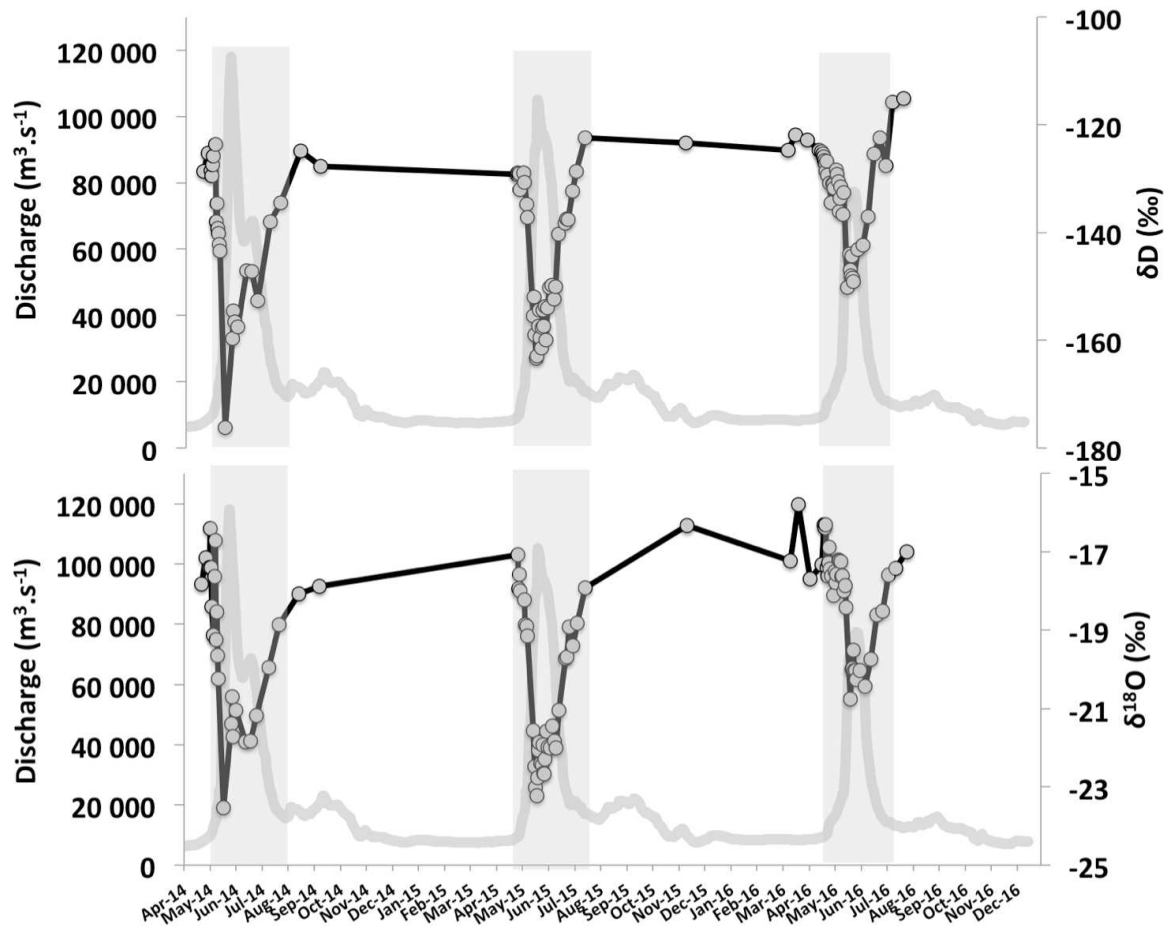


Figure 2. 5 $\Delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰) of Yenisei river waters. Grey dots are point measurements, grey line represents daily discharge ($\text{m}^3\cdot\text{s}^{-1}$, source: Roshydromet), grey rectangle delimitate freshet periods.

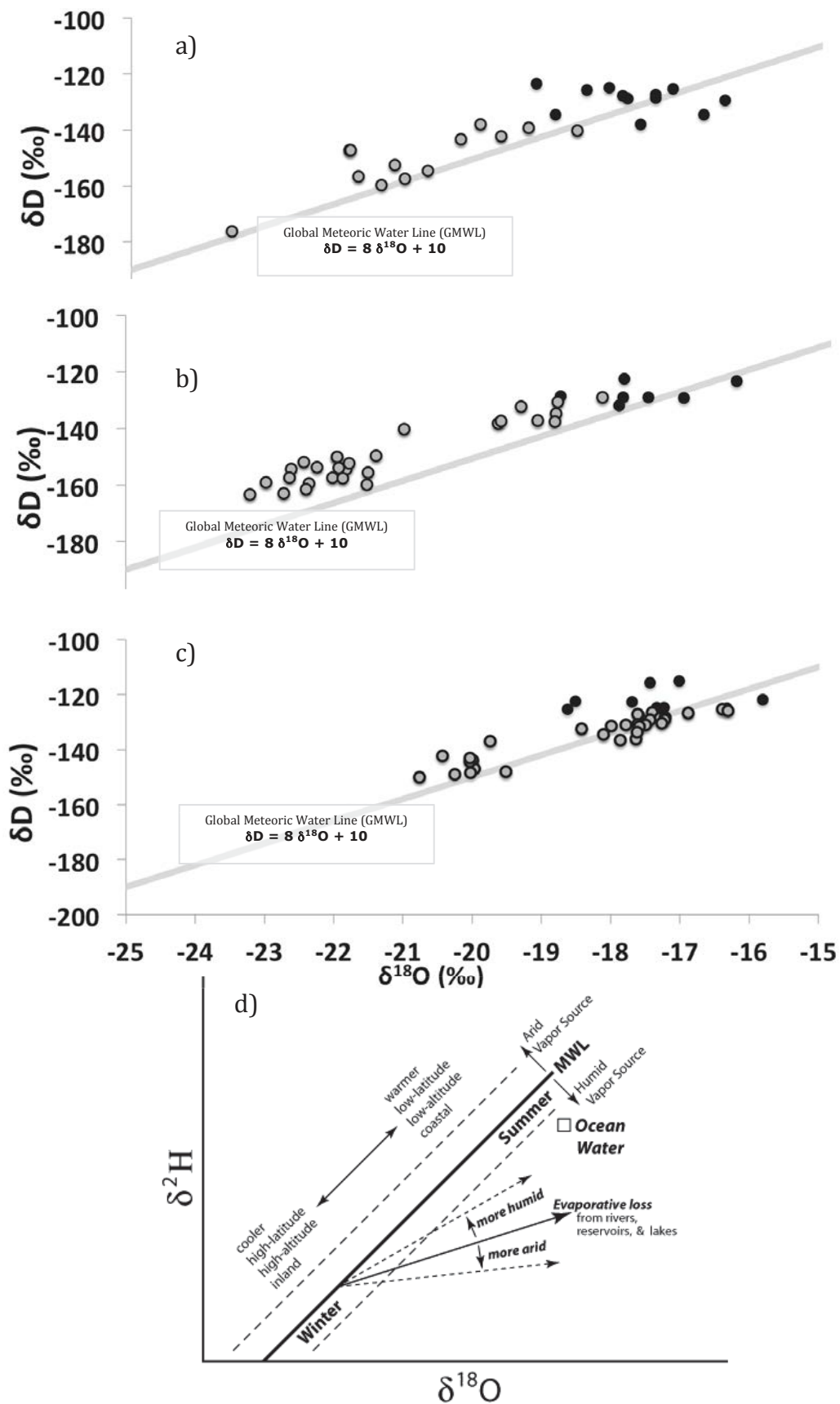


Figure 2. 6 Comparison of $\Delta^{18}O$ and δ^2H (‰) of Yenisei river waters with the Global Meteoric Water Line. a) 2014 samples, b) 2015 samples, c) 2016 samples, d) Summary diagram of hydrologic processes influence on oxygen and hydrogen isotopic composition of water (source : <http://web.sahra.arizona.edu/programs/isotopes/oxygen.html>)

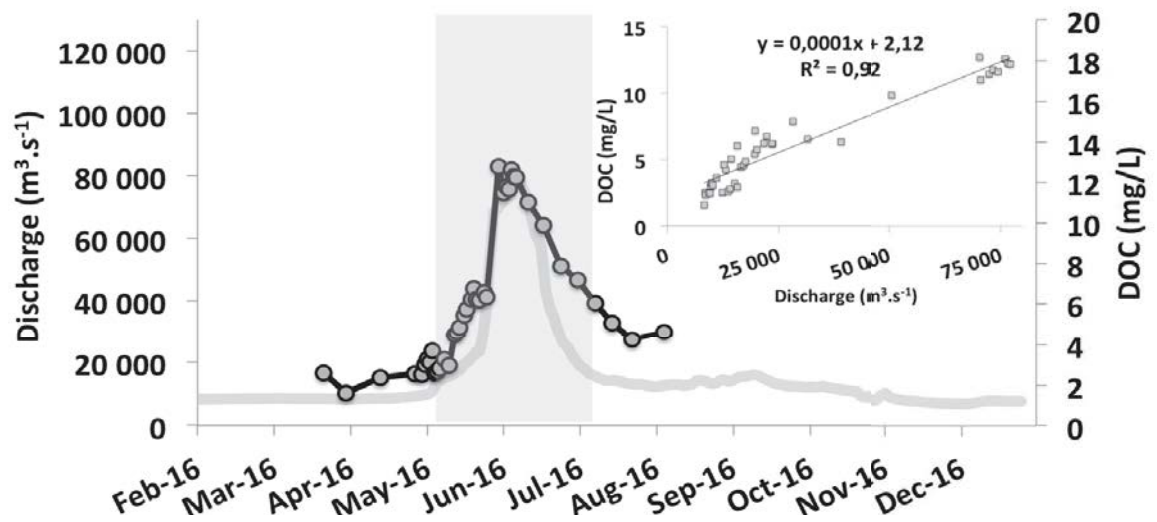
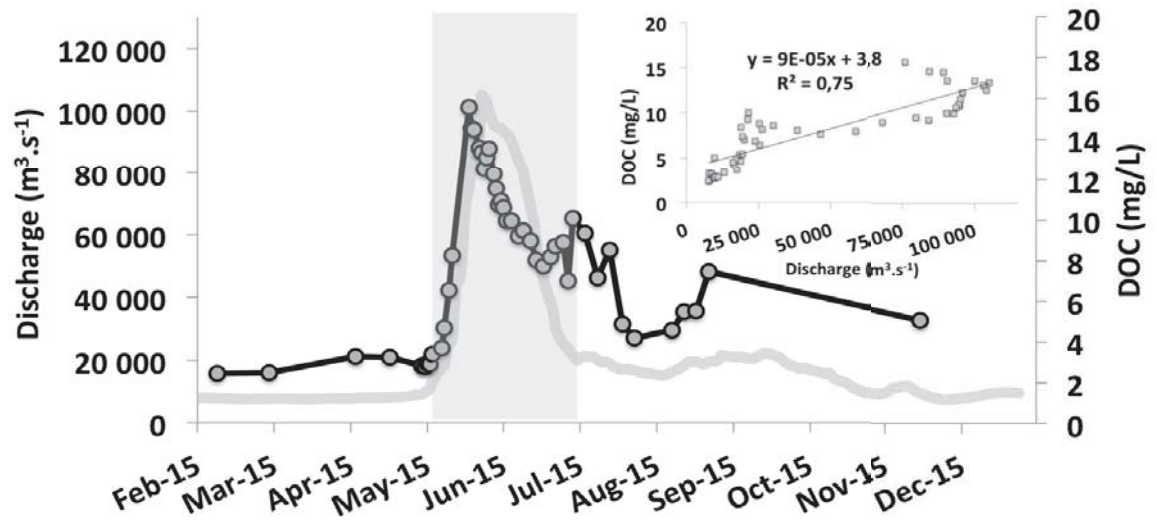
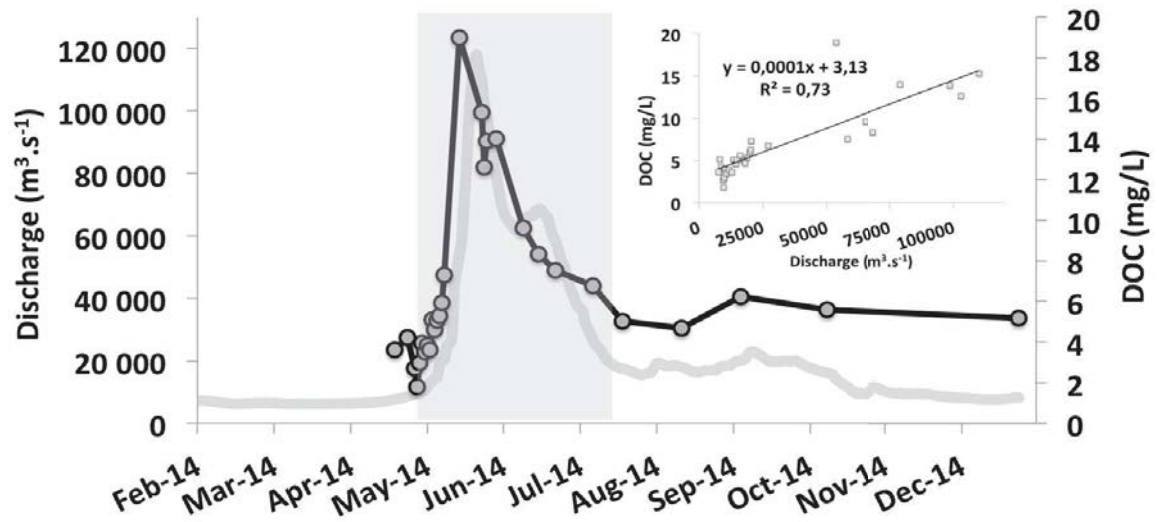


Figure 2. 7 DOC concentrations (mg/L) along with daily discharge. Grey dots are point measurements, grey line represents daily discharge ($\text{m}^3 \cdot \text{s}^{-1}$, source: Roshydromet), grey rectangle delimitate freshet periods. Right side graph shows the relationship between daily discharge and DOC concentration.

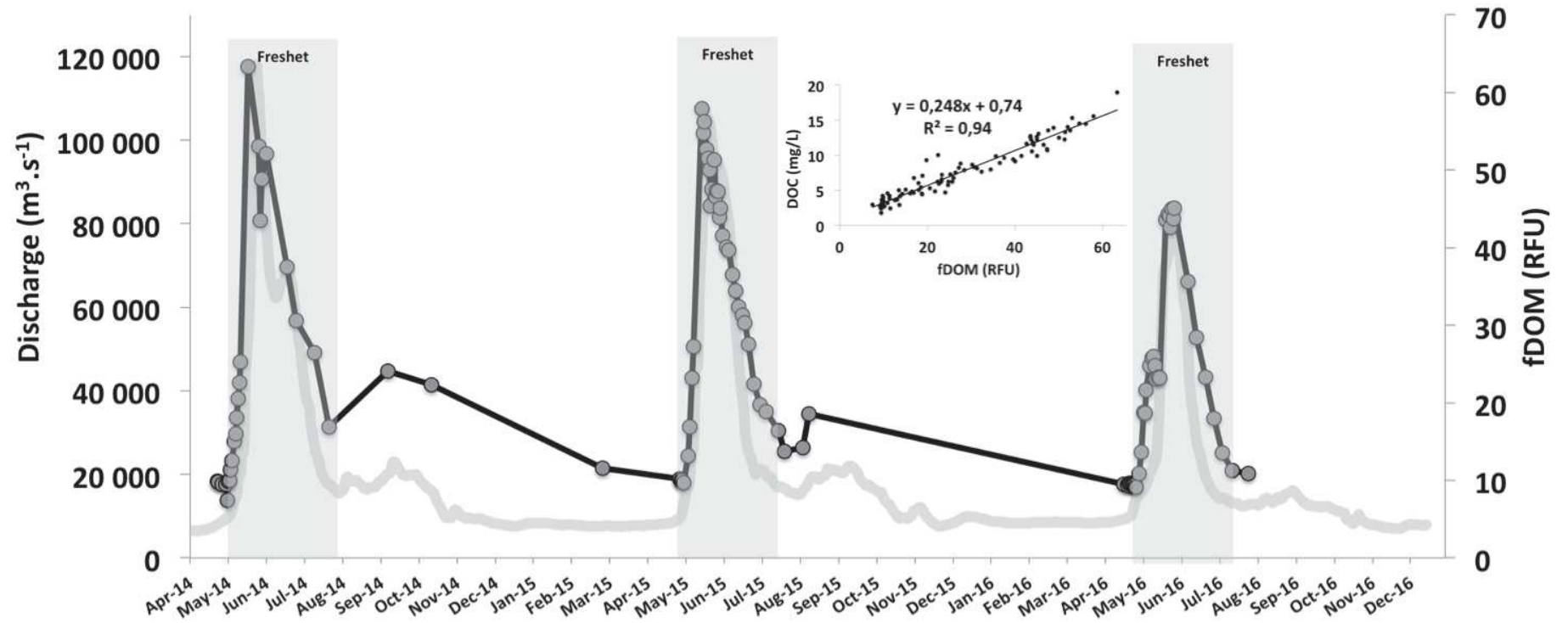


Figure 2. 10 fDOM (RFU) measured in-situ with EXO-2 probe along with daily discharge ($\text{m}^3 \cdot \text{s}^{-1}$, source: Roshydromet), grey rectangle delimitate freshet periods. Top graph represents the relationship between fDOM and DOC concentration.

Table 2. 1 Published estimates of annual flux of DOC for the Yenisei

Reference	Sampling location	Period	DOC Flux (Tg.yr ⁻¹)	Spring flood flux (% total)
Holmes et al. 2012 ¹	Dudinka	(1999)2003-2008	4.65	Average : 63
Amon et al. 2012 ¹	Dudinka	2003-2007	5.08	-
Raymond et al. 2007 ¹	Dudinka	2004-2005	4.69 (2004 : 5.76, 2005 : 3.62)	2004 : 63, 2005 : 58
Lobbés et al. 2000	Delta	1994	4.86	-
Amon and Meon 2004 ²	Delta	-	5.10	-
Herrault et al., 2017 ⁴		2001-2014	4.14 +/- 0.21	-
This study	Igarka	2014-2016	4.53 (2014 : 5.45, 2015 : 4.86, 2016 : 3.27)	2014 : 71, 2015 : 68, 2016 : 67
Prokushkin et al. 2011	Yenisei sub-basins ³	2006-2010	2.32	73

¹PARTNERS data set.

²derived from DOC concentrations from Köhler et al., 2003.

³Kochechum, Tembenchi, Nidym, Nizhnaya Tunguska, Podkamennaya Tunguska (470 900 km²).

⁴Estimate of DOC export predicted with a model derived from MODIS time series (UV and visible absorbance as chromophoric dissolved organic matter proxy) calibrated with field DOC concentration data and in situ optical properties measurements.

CHAPITRE III

DISSOLVED ORGANIC MATTER QUALITY AND ITS DYNAMIC IN THE YENISEI RIVER: COMPOSITION, SOURCES, AGE AND DEGRADATION STATE

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*« Ils m'ont jeté à l'eau,
Comme c'est bien fait, j'n'attendais qu'ça,
Moi, j'ai toujours fait de mon mieux,
Ça les étonne mais je n'coule pas,
Depuis j'regarde passer les berges,
J'n'attendais qu'ça pour tout lâcher,
Une petite brasse pour l'homme moderne
Qui perd un peu pieds,
Ils m'ont jeté à l'eau »*

« Jeté à l'eau », Ma Pauvre Lucette

RÉSUMÉ

Les rivières arctiques transportent des quantités importantes de matières organiques terrigènes vers l'océan Arctique. Le Ienisseï est un des fleuves arctiques contribuant le plus aux transferts de carbone organique dissous vers l'océan. La majeure partie du flux de carbone organique dissous a lieu chaque année durant la crue de printemps (mai-juin). Les outils de caractérisation offrent la possibilité de tracer les sources, l'âge, l'état de dégradation et la composition générale de ce carbone organique extrêmement mobile. De telles informations permettent d'améliorer notre compréhension du cycle des matières organiques dissoutes (MOD) dans les régions arctiques et d'évaluer son potentiel impact sur le fonctionnement de l'océan Arctique et du climat.

Ici, nous présentons des données collectées à haute fréquence temporelle durant des campagnes d'échantillonnage de 2014 à 2016 avec une attention particulière sur la crue de printemps. Un dispositif d'osmose inverse a été utilisé pour isoler et concentrer les MOD. La qualité des MOD a par la suite été déterminée grâce aux biomarqueurs de la lignine, aux propriétés optiques des MOD et à la datation ^{14}C du COD.

Les indicateurs associés aux ratios des phénols de la lignine suggèrent que les MOD dérivent principalement de bois de gymnospermes pendant la crue de printemps et ont une signature plus influencée par le bois d'angiospermes pendant la période de basses eaux. La forêt boréale est donc certainement un des pourvoyeurs principaux de MOD durant la crue de printemps. Les indicateurs de dégradation et de diagenèse suggèrent que durant les périodes de débits maximums, les MOD proviennent de la lixiviation des horizons de surface et des litières végétales alors que la période de basses eaux est caractérisée par des écoulements plus profonds. Les indicateurs de fluorescence montrent une qualité des MOD contrastée entre la période de crue et de basses eaux avec une influence terrestre supérieure pendant la période de crue associée avec un poids moléculaire et une signature humique plus élevés. Les mesures d'absorbance suggèrent une aromaticité plus prononcée au cours de la période de crue. La datation ^{14}C du COD indique des exports de MOD plus jeunes en période de crue contrastant avec des MOD plus âgées en basses eaux.

Mots clé: MOD, rivières arctiques, Yeniseï, Siberia, biomarqueurs de la lignine, Absorbance, Fluorescence, Isotopie du carbone.

ABSTRACT

Arctic Rivers transport vast amounts of terrestrial organic material (TOM) to the Arctic Ocean. The Yenisei River is one of the major contributors. Most of the flux occurs each year during peak river discharge (May-June), known as the spring freshet. Characterization tools offer the opportunity to trace sources, age and degradation state along with insight in the composition of this very mobile carbon pool. Such information can improve our understanding of DOM cycle in arctic regions and its potential impact on the Arctic ocean functioning and climate change feedback.

Here, we present new high resolution data collected from extensive sampling campaign from 2014 to 2016 with a special focus on spring flood periods. Reverse osmosis system was used for DOC isolation and concentration. DOM quality was determined combining characterization techniques, using lignin biomarkers, optical properties and radiocarbon age of DOM.

Lignin phenol ratio indicators suggested that DOM is primarily derived from gymnosperm wood sources during spring freshet and have a higher influence from angiosperm wood during low flows. Thus, boreal forest is likely the main supplier of DOM during the freshet.

Degradation and diagenic indicators suggest that, during high discharge, DOM originates from leaching of surface soil horizon or plant litter whereas base flow period is characterized by deeper waterflow path. Fluorescence indicators suggest contrasting DOM quality between spring freshet and base flow with higher terrestrial influence during flood period associated with higher molecular weight of DOM molecules and humic fingerprint. Absorbance measurements indicate higher aromatic DOM content during peak discharge period. Radiocarbon age of DOM supported the export of younger DOM during high flow against older DOM during base flow.

Keywords: DOM, Arctic River, Yenisei, Siberia, Lignin biomarkers, Absorbance, Fluorescence, Carbon Isotopy

3.1 INTRODUCTION

High northern latitudes encompass a huge organic carbon (OC) reservoir, estimated to 1400-1850 Pg and representing about 50% of global soil OC, with the major part lying in permafrost-affected soils (Tarnocai et al., 2009; Hugelius et al., 2013). Arctic rivers draining these regions transport annually large amount of terrestrial organic matter (TOM). About 5.8 Tg is transferred as particulate organic carbon (POC) (McClelland et al., 2016) and 34-38 Tg as dissolved organic carbon (DOC) (Holmes et al., 2012). Consequently, great arctic rivers play an important role in global OC cycle as an interface between the large permafrost OC pool and the Arctic Ocean. Mobilization and degradation of short term cycling OC (recently produced OC) imparts no change on atmospheric CO₂ concentrations whereas release of ancient OC trapped in frozen soils or peatlands may constitute significant positive feedback to Arctic warming and disturb the current equilibrium between short term and long term C cycling (Schuur et al., 2008; Grosse et al., 2011; Koven et al., 2011; Schuur et al., 2015).

Dissolved organic matter (DOM) found in rivers consists in a complex mixture of compounds originating from various terrestrial or aquatic sources (phytoplankton, vegetation, surface or deep soil horizon, peat) along with microbial products and showing contrasting chemical/physical properties (recalcitrance, age)(Kalbitz et al., 2000). Main factors controlling riverine DOM composition comprise the type of vegetation and soil organic matter (Ward and Cory, 2015), leaching and sorption processes occurring in soil mineral layers (Kawahigashi et al., 2006) and Photo-Bio-degradation processes occurring within the soil-aquatic continuum (Mann et al., 2012; Olefeldt et al., 2013). Accordingly, investigating the source and age of OC carried by arctic rivers can provide relevant knowledge to better understand global and regional scale carbon cycling and transfers under the influence of climate change (Feng et al., 2017). Indeed, as the Arctic warms, the biogeochemical signature of rivers and streams will likely be a relevant indicator of the response of aquatic and associated terrestrial ecosystems to climate change (Holmes et al., 2000; Frey and McClelland, 2009). In addition, great arctic river catchments cover several climatic zones implying differing climate change sensitivity and response from temperate to arctic regions. Subsequently, knowing where the OM derives from (Southern vs Northern part of the watershed) may improve our evaluation of climate change potential impact in these regions.

Arctic rivers undergo pronounced seasonal cycle in terms of water runoff and organic matter concentration. To date, most studies were performed during the ice free period missing a portion of the spring freshet (Dittmar and Kattner, 2003), where most of the annual DOM flux occurs (Dittmar and Kattner, 2003; Finlay et al., 2006; Amon et al., 2012; Mann et al., 2012). This is mainly due to the logistic challenge of fieldwork in these remote areas associated with harsh climate conditions particularly during winter and spring campaigns. In addition to quantitative changes in exported DOC, a growing body of evidence also suggests a large seasonal variability in its quality (composition, age, bio- photo-lability). Various observations have shown marked changes in chemical DOM composition in soil and stream water induced by precipitations, snowmelt and storm events (Frank et al., 2000; Buffam et al., 2001; Dalzell et al., 2005; Hood et al., 2006; Vidon et al., 2008; Sanderman et al., 2009). Significant seasonal change of DOM composition has been documented specifically for Great Arctic rivers (Stedmon et al., 2011; Amon et al., 2012; Walker et al., 2013; Mann et al., 2016) and in particular the Yukon (Guo and Macdonald, 2006; Striegl et al., 2007; Spencer et al., 2008; Cao et al., 2016) and Kolyma (Finlay et al., 2006; Neff et al., 2006; Mann et al., 2012) rivers indicating, as a general trend, shift from recently produced DOM during Spring flood to more aged DOM during base-flow period. Therefore, it is now apparent that examining seasonality is important to understand the fate of Arctic river DOC as this controls its composition, and thus influence its susceptibility to bacterial and photochemical degradation processes during riverine transport and later in the Arctic Ocean.

Concerning solute transport, hydrological connection of a stream to its watershed is of particular importance (Jencso et al., 2009; Laudon et al., 2011; Massicotte and Frenette, 2011; Birkel et al., 2014; Burns et al., 2016). This connectivity changes during seasons, with higher connectivity during freshet (Inclusion of hill slopes, valley bottoms, lowlands) and lower connectivity during winter low flow conditions (in particular disconnection of hill slopes). In the case of a great arctic river, such as the Yenisei, it would imply that during spring flood period, the major part of the watershed is hydrologically connected to the stream network and consequently that the organic matter can originate from the whole area including the boreal forest. In contrast during base flow conditions, a significant part of the watershed is isolated and organic matter are thus restricted to valley bottoms, lowlands and wetlands (Amon et al., 2012). For the Yenisei, the main channel is fed by tributaries draining areas with differing geological

(Kharuk et al., 2003; Kawahigashi et al., 2004; Kawahigashi, 2006; Sulla-Menashe et al., 2011; Roth et al., 2013; Tolomeev et al., 2014), climatic and vegetational influences which can impact DOM signal (Dillon and Molot, 1997; McGlynn and McDonnell, 2003; Eckard et al., 2007; Roth et al., 2014).

We conducted our fieldwork near the city of Igarka relatively close to the rivermouth of the Yenisei. This location allowed us to record an integrated signal of all sources and processes occurring at the whole watershed scale. Previous investigation on DOM degradation in rivers have stressed that stream microorganisms can significantly alter terrestrial DOC, including humic substance and lignin (Frazier et al., 2005; Seitzinger et al., 2005; Battin et al., 2008; Fasching et al., 2014). Thus, DOC in downstream ecosystems potentially represents a legacy of prior metabolic activities. However, during the freshet period, DOM exported might undergo reduce transformation during its transport due to reduced residence time and low water temperature. In a recent paper, Raymond et al., (2015) introduced the pulse-shunt concept. The pulse corresponds to hydrological events, such as spring flood, that mobilize DOM. The shunt corresponds to rapid downstream transport, limiting residence time and exposure to microbial and photochemical reactions. This is induced by increase in stream water velocities associated with high-discharge periods. We focused our sampling effort on the key period of the spring freshet sampled at high temporal frequency combined with additional samples spanning the whole range of hydrological condition across three consecutive years. Here, we report optical properties in combination with lignin biomarkers and radiocarbon age data to give information on DOM sources and degradation state along the hydrological cycle of the Yenisei river. The Yenisei is one of the biggest Arctic rivers in terms of area drained, water supply and OC export to the Arctic ocean (Dittmar and Kattner, 2003; Raymond et al., 2007; Amon et al., 2012; Holmes et al., 2012). In the past decade, few studies have investigated DOM transfers in the Yenisei watershed (Prokushkin et al., 2007; Raymond et al., 2007; Prokushkin et al., 2011; Amon et al., 2012; Holmes et al., 2012; Roth et al., 2013; Tolomeev et al., 2014; Herrault et al., 2016; Mann et al., 2016), however, evaluation of DOM composition and quality along the hydrological cycle is still scarce. Our objectives were to answer the following questions : How does overall composition of DOM change over the annual hydrological cycle ? What are the DOM sources in the

Yenisei River and how do they change seasonally? What is the age of the riverine DOM and how does it change seasonally?

3.2 MATERIAL AND METHOD

3.2.1 Sampling site:

Our sampling site is located close to the river mouth (about 300 km south), at Igarka (67°28'19''N, 86°33'31''E), northern Krasnoyarsk Krai, Russian Federation. This specific location allows us to monitor an integrated signal of most of the watershed without tidal and marine influence on salinity and water chemistry. The watershed area at this point covers 2.44 million km². For more details on the Igarka context and the Yenisei watershed description see chapter 2 section 2.2.1 and 2.2.2 and Figure 2.1.

3.2.2 Sampling, sample preparation and analysis:

We collected water samples daily (except when safety was not guaranteed, in particular during ice flow) during the spring flood and at lower temporal scale during lowflow period to capture the seasonal variability of DOM from the Yenisei watershed. A total of 117 samples have been collected over the 3 years of sampling (2014-2016). For details about sampling times and key hydrological events see chapter 2 section 2.2.3 and figure 2.2.

Water samples for fluorescence and absorbance measurements were filtered immediately after collection in Igarka Geocryology Laboratory through GF/F (0.7µm) glass fiber filters (Whatman, United States) (precombusted for 5h at 450°C) on glasswire filtration system (Sartorius, Germany). Filtered samples were transferred in 30 mL nalgene bottles and stored refrigerated at 4°C in the dark. Fluorescence measurements were made on a Fluoromax-4 (Horiba, Kyoto, Japan), at the Plateforme Eau in the IC2MP, CNRS and Poitiers University laboratory. Excitation wavelength ranges from 230 to 400 nm and emission from 300 to 550 nm with an increment of 5 nm. Measurements were made in 10 mm Quartz tube with 2 mirrors at 20°C. Fluorescence index (FI) was calculated as the ratio of emission intensities at wavelengths 470 and 520 nm observed for excitation at 370 nm (McKnight et al., 2001; Cory and McKnight, 2005; Fellman et al., 2010a). Freshness index ($\beta : \alpha$) was determined as the ratio of emission intensity at 380 nm divided by the maximum intensity observed between 420 and 435 nm at excitation 310 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009). Humification index (HIX) was calculated as the peak area under the emission spectra 435-480 nm

divided by the peak area under 300-345 nm at emission 254 nm (Zsolnay et al., 1999). Fluorescence components were identified using the full dataset (n=115) by Parallel factor analysis (PARAFAC) of Excitation Emission Fluorescence Matrices (EEFMs) using PROGMEEF software (PROTEE Laboratory, Toulon, France) in Matlab.

Absorbance spectra (wavelength 190-900 nm) were acquired on a spectrometer (Uvi Light XT5, Secomam/Aqualabo, Champigny, France) in 10 mm Quartz tube, at the physico chemical analysis platform of EcoLab in Toulouse, France. Specific ultra violet absorbance at 254 nm (SUVA 254, L mg-C⁻¹ m⁻¹) was determined as the Absorption coefficient measured at 254 nm divided by the DOC concentration (Weishaar et al., 2003). Absorbance units were converted to absorption coefficients as:

$$a = 2.303 A/l$$

where a = absorption coefficient (m⁻¹), A = absorbance and l = path length (m). The spectral slopes were calculated for the intervals 275-295 nm and 350-400 nm using linear regression of the log-transformed absorbance coefficient spectra (Helms et al., 2008).

For lignin analysis and radiocarbon datation, large volume of water was pumped from the central part of the river channel, in an integrative way from the first 5 meters of the water column in 20L plastic carboy. Immediately after collection, these large water samples (100L) were filtered and concentrated at the Igarka Geocryology Laboratory (Krasnoyarsk Krai, Russia), using a coupled tangential flow filtration unit (TFF) (Peristaltic pump + Pellicon2 cassette filters ultrafiltration, Millipore corporation, Billerica, U.S.A.) and a reverse osmosis system (RO) (RealSoft PROS/2S, Portable Reverse Osmosis Systems, Atlanta, U.S.A.). The first step of TFF allows concentrating particulate material and obtaining filtrate that can be properly processed by RO. The RO system allows concentrating dissolved material about 10 times to obtain large quantities of material (hundreds of mg) to be able to conduct molecular and isotopic analysis on DOM. RO systems have been employed in several studies for the isolation of DOM reference material (Suwannee River) (Serkiz and Perdue, 1990; Green et al., 2015) and divers DOM concentration/characterization purposes in various aquatic environments (Clair et al., 1991; Sun et al., 1995b; Gjessing et al., 1998; Kitis et al., 2001; Ouellet et al., 2008; Koprivnjak et al., 2009; Mao et al., 2012; Zhang et al., 2014; John R. Helms, 2015). This technique has proven to have one of the best recovery efficiency for DOM (over 90%) (Maurice et al., 2002; Minor et al., 2014). Concentrated water samples were then

frozen for storage and transported to EcoLab facilities in Toulouse, France. Prior to further analysis, samples were freeze-dried (Alpha 1-2 Freeze Dryer, Martin Christ, Osterode, Germany) to obtain a concentrated dissolved material powder easy to store and handle for preparation and further analysis.

To determine OC content and C/N ratios of freeze dried DOM, samples were acidified to remove inorganic carbon. The protocol consists in acid fumigation with concentrated HCl (12M) of the freeze-dried DOM in silver boats in a dessicator. Our protocol followed the description of Komada et al. (2008). C and N quantifications were performed on an elemental analyzer Flash 2000 (ThermoFisher, Waltham, U.S.A.) at the physico-chemical platform of Ecolab, Toulouse, France.

Samples from 2014 field campaign were analyzed for lignin phenols at Texas A&M, department of Marine Science, following Louchouart et al, (2010) protocol. Analyses for 2015 and 2016 samples were performed at the Geosciences, Marine Geochemistry Laboratory at the Alfred Wegener Institute, Bremerhaven, Germany. Sample preparation, prior to GC/MS identification and quantification of individual biomarkers, consisted in Microwave Alkaline CuO oxidation method to extract Lignin-derived phenols (see Goñi and Montgomery, 2000; Winterfeld et al., 2015). The procedure was carried out in Teflon vessels with nitrogen-purged 2N NaOH at 150°C for 1.5 h in a microwave digestion system. Prior to extraction, internal recovery standard (EVI at 44 µL/mL and CnAd at µL/mL) was added. Samples were extracted with ethyl acetate, evaporated under a nitrogen stream and re-dissolved in pyridine. Prior to GC/MS processing, samples were derivatized with *bis*-trimethylsilyl trifluoroacetamide (BSTFA) +1% trimethylchlorosilane (TCMS). GC-MS sample analysis method was similar to Goni et al., (2009), Hatten et al., (2012), Winterfeld et al., (2015). As lignin phenols identification and quantification were made in two distinct labs with globally similar protocols, apart from some specific calibration steps made for measurements at Texas A&M (2014 samples). Potential sources of discrepancies between measurements may originate from the differing sensitivities and set up of the GC/MS used. Such phenomenon mostly affected C phenols quantification (that were the less concentrated of the studied phenols). Therefore we adjusted 2015, 2016 C phenols quantifications, made at AWI, based on a simple linear regression derived from replicate measurements of 2014 samples analyzed at both Texas A&M and AWI.

Radiocarbon dating were performed on freeze-dried dissolved material powder at the Geosciences, Marine Geochemistry Laboratory at AWI on a MICADAS system (Ionplus AG Dietikon, Switzerland)(Synal et al., 2007, Wacker et al., 2010a). Samples were weighted into silver boats to obtain about 1 mg of OC for analysis. In order to remove carbonates, samples were acidified by dropwise addition of HCl (12N), and reaction was made on hot plate. Samples were then combusted on an Elementar Analyzer system, Vario Micro cube (Elementar, Langenselbold, Germany) coupled to an AGE automated graphitization unit (Wacker et al., 2010) prior to ^{14}C analysis as graphite target on the MICADAS system. Due to time restriction, to date, we only have available data for 2014 and 2015 samples.

Dissolved lignin fluxes were estimated using the USGS software LOADEST (Runkel et al., 2004). This software developed by the USGS has been largely used to determine elements loads and fluxes in worldwide rivers including great arctic rivers (Raymon et al., 2007; Holmes et al., 2012). LOADEST allows to reconstruct daily dissolved lignin loads using regression models calibrated with discrete pairs of measured dissolved lignin concentration and daily discharge data and applying it to the complete daily discharge data set. The model selection was based on AIC (Akaike Information Criteria) and a specific model was calibrated for each sampling year (AIC for 2014 = 1.321, 2015=0.473, 2016=0.834). The general form of the selected Adjusted Maximum Likelihood Estimation (AMLE) model was:

$$\ln(\text{Lignin Load}) = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi \text{dtime}) + a_4 \cos(2\pi \text{dtime})$$

with Lignin Load in kg/d ; Q = discharge ($\text{m}^3 \text{s}^{-1}$) ; dtime= decimal time and

$a_0=13.1504$ $a_1=3.2739$ $a_2=-1.1382$ $a_3=0.6063$ $a_4=-1.4383$ in 2014 ;

$a_0= 12.4765$ $a_1=2.2116$ $a_2=-0.4473$ $a_3=-0.1290$ $a_4=-0.4358$ in 2015 ;

$a_0= 12.2673$ $a_1=2.3232$ $a_2=-0.6301$ $a_3=-0.1159$ $a_4= -0.0826$ in 2016.

The Yenisei hydrograph is characterized by two contrasting periods, low flow period and the freshet period. We defined the low flow period as discharge $< 20\,000 \text{ m}^3 \cdot \text{s}^{-1}$ (except for late summer/ early autumn). It lasts from post flood conditions in mid-July to pre flood in late April (about 9 months). Low flows generally oscillated around $8\,000 \text{ m}^3 \cdot \text{s}^{-1}$ in winter, however, the period of late summer/early autumn showed higher discharge likely due to higher precipitation rate in some parts of the watershed

generally inducing response in DOM composition and concentration. It has to be noted that the overall low flow period only accounts for about 50% of the annual water exports and for less than 15% of annual lignin discharge. The spring flood period, commonly lasting from early May to mid-July is characterized by high variations in discharge, generally $> 20\,000\text{ m}^3\cdot\text{s}^{-1}$ and often higher than $100\,000\text{ m}^3\cdot\text{s}^{-1}$ around peak discharge. We will present and discuss the results according to these defined periods.

3.3 RESULTS

Table 3.3 summarises the average values of DOM characterization indicators presented in this section according to hydrological periods (Spring flood/Low flow/Annual) along with average values reported in the literature.

3.3.1 Optical properties:

Absorbance

SUVA₂₅₄ values ranged from 2.1 to 5.8 L mg-DOC⁻¹ m⁻¹ (average=3.98, n=115), with highest values during spring flood (average=4.2, n=56), and lowest values during winter and low summer flow (average=3.8, n=59) (Figure 3.1) (Table 3.3). SUVA₂₅₄ signal showed a specific pattern of pronounced decrease prior and after spring flood. It was particularly visible in 2015 where SUVA₂₅₄ values recorded at these periods were lower than winter average (<3). In 2014, the signal seems to be slightly off set compared to discharge dynamic, with SUVA₂₅₄ peaking after the highest discharge, during a particular rebound of discharge (not observed in 2015 and 2016) in late June whereas it peaked prior to the highest discharge the following years.

a₃₅₀ ranged from 2.7 to 46.8 m⁻¹ (average=19.7, n=115)(Figure 3.2). a₃₅₀ signal was similar across sampling years, with a dynamic close to the discharge, with increasing a₃₅₀ with increasing discharge and peaking 5-7 days before peak discharge. Highest a₃₅₀ values were recorded during freshet period (average=28.7, n=56) and lower values were observed during low flow period (average=9.8, n=59) Slight discharge increase during late summer/early autumn 2014 and 2015 induced response in a₃₅₀ signal with higher values for this period compared to direct post flood and winter period (from 9.1 to 13.8 in 2014 and from 7.6 to 20.4 in 2015). a₃₅₀ correlated with good agreement to general lignin variables, L8 ($L8=8.5a_{350} + 0.13$, $R^2=0.7$, n=104) and S8 ($S8=6.55e^{21.219a_{350}}$, $R^2=0.76$, n=104)(Figure 3.3).

$S_{275-295}$ ranged from 0.009 to 0.08 (average=0.03, n=115)(Figure 3.4). $S_{275-295}$ was correlated to DOC concentration ($DOC = 0.3S_{275-295}^{-0.819}$, $R^2=0.87$, n=115) and discharge ($Q = 334.24S_{275-295}^{-1.193}$, $R^2=0.84$, n=115) (Figure 3.5). The $S_{275-295}$ dynamic was relatively similar on an interannual scale; lowest values were reported during Spring flood (average=0.016, n=56) and highest during winter low flow condition (average=0.05, n=59). $S_{275-295}$ increased just after the end of the flood in mid summer, when discharge is back to baseflow. Discharge rise during late summer/early autumn induced a slight decrease in $S_{275-295}$ signal before a steady rise until stable winter low flow conditions.

Fluorescence indices

FI varied along with discharge, FI decreasing with increasing discharge. The relationship between FI and discharge was strong for low flow and absent at high discharge ($R^2=0.06$) with FI values reaching a plateau (low flow relation $FI = 6 \times 10^{-6}Q + 1.58$, $R^2=0.58$, global average=1.45, n=115) (Figure 3.9). Values ranged from 1.34 to 1.57, with lowest values recorded during spring flood (average=1.4, n=56) and highest during low flow (average=1.49, n=59)(Figure 3.6). Signal evolution was relatively similar between 2015 and 2016 but we recorded slightly higher FI during 2014 spring flood.

HIX followed discharge dynamic with increasing HIX values with increasing discharge. The relationship between HIX and discharge was strong for low flow and absent ($R^2 = 0.03$) for high flow (low flow relation $HIX = 2 \times 10^{-4}Q + 1.52$, $R^2=0.55$, global average=6.50, n=115)(Figure 3.9). HIX was also highly correlated to DOC dynamic ($HIX = 0.65DOC + 1.9$, $R^2=0.81$, n=115). Values ranged from 2.23 to 14.50, with highest values observed during spring flood period (average=8.6, n=56), lowest during low flow a (average=4.5, n=59)(Figure 3.7). Trends across the sampling years were similar.

Freshness index varied along with discharge, freshness index values decreasing with increasing discharge. The relationship with discharge was strong at low flow and weak at high discharge ($R^2=0.25$)(Low flow relation Freshness index= $2.6933Q^{-0.163}$, $R^2=0.87$, global average= 0.52, n=115) (Figure 3.9). Values ranged from 0.41 to 0.66, with lowest values reported for spring flood period (average= 0.45, n=56) and highest values during winter low flow and pre flood period (average= 0.59, n=59) (Figure 3.8). Global signal trend was similar across the three sampling years.

PARAFAC

Three fluorescent components were identified by the PARAFAC model (corcondia=60.7). Component 1 has an excitation maximum at 360 nm and an emission maximum at 480. Component 2 has an excitation maximum at 320 nm and an emission maximum at 415 nm. Component 3 has an excitation maximum at 240 nm and an emission maximum at 430 nm (Figure 3.10).

The fluorescence intensity of components 1 and 2 increased with discharge whereas component 3 fluorescence was more stable and decreased with increasing discharge (Figure 3.11). For components 1 and 2, elevated values were recorded during spring flood and lower values during winter base flow conditions. It can be noted that fluorescence intensity for these components responded positively to discharge increase in late summer/early autumn (2014-2015). Component 3 showed lowest fluorescence intensity during spring flood and relatively stable values from post flood to winter base flow conditions. All components peaked (including Cp3 before plummeting) during rising limb. Relative contribution to total fluorescence of components 1 and 2 was predominant (Cp1>Cp2) during spring flood periods of the 3 sampling years and component 3 was largely predominant during winter base flow condition and also during post flood conditions (end of recession 2015-2016) (Figure 3.12).

Component 1 and 2 were significantly correlated to discharge (logarithmic regression, $R^2=0.81$ and 0.71 respectively) whereas Component 3 showed no relation to discharge (linear regression, $R^2=0.0045$). Component 1 and 2 were significantly correlated to DOC concentration (linear regression, $R^2=0.80$ and 0.72 respectively) whereas Component 3 showed no relation to DOC (linear regression, $R^2=0.002$). Component 1 and 2 showed linear relationship of differing strength to lignin biomarkers (highest for L8, S8 and P/V) whereas component 3 showed absolutely no relationship with none of the lignin biomarkers (Table 3.1).

3.3.2 Lignin parameters

Similar to optical properties of DOM, dissolved lignin concentration (S8, $\mu\text{g/L}$) displayed large variations between baseflow and peak flow, ranging from 1.38 to 506.68 (Figure 3.13). Lignin concentrations were maximal during spring flood (average=135.84, $n=54$) and lowest during low flow (average=18.94, $n=53$). Lignin concentration peaked at 506.68, 236.06, and 267.57 in 2014, 2015 and 2016 respectively, about 5–7

days prior to peak discharge in 2014 and 2015 and 1 day before peak discharge in 2016 (global average = 77.94, n=107) .

Carbon normalized lignin yields (L8, mg/100 mg OC) showed similar trend than S8 (ranging from 0.05 to 2.67), with maximum reached during spring flood of 2.67, 1.76, 2.18 for 2014, 2015 and 2016 respectively (global average= 0.86, n=107) (Figure 3.14). Average high flow L8 was 1.25 (n=54) and average low flow L8 was 0.46 (n=53). Correlation (linear regression) between S8 and DOC ($R^2=0.84$, Figure 3. 15c) and Discharge ($R^2=0.63$, Figure Figure 15d) was higher than for L8 ($R^2=0.58$ for DOC and 0.5 for Discharge) (Figure 3. 15 a-b).

Average annual lignin flux was 53.7 Gg (2014-2016); annual flux was 70.0 Gg in 2014, 54.1 Gg in 2015 and 37.0 Gg in 2016. Freshet (May-June) flux represented on average 85.7% of the annual flux (46.1 Gg) with 89.2% (62.4 Gg) in 2014, 81.9% (44.3 Gg) in 2015 and 85.9% (37.8 Gg) in 2016 (Table 3.2).

Ratios of $(Ad/Al)_v$ evolved similarly to lignin concentrations (ranging from 0.65 to 2.17, global average= 1.20, n=107) along the hydrological cycles, highest values were reached during high flow (average=1.41, n=54; peaked at 2.17, 1.98, 1.64 for 2014, 2015 and 2016 respectively), and base flow showed lowest values (average= 1.00, n= 53). $(Ad/Al)_s$ followed $(Ad/Al)_v$ trend (Figure 3.16 a-b and Figure 3. 20).

pCd/Fd ratio (ranging from 0.39 to 1.75) shifted from lowest values during spring flood (average=0.57, n=54) to higher values during base flow (average=0.86, n=53) (Figure 3.16 c).

PON/P ratios (ranging from 0.2 to 0.4) decreased during spring flood (high flow average=0.27, n=54) and progressively increased from post flood conditions in late summer to winter base flow and then decrease again slowly until pre-flood period (April) (low flow average=0.30, n=53)(Figure 3. 16 d)(global average=0.28, n-107).

$P/(V+S)$ values (ranging from 0.16 to 0.64) dropped from high values during low flow period (average=0.40, n=53) to low values during spring flood (average=0.22, n=54). The winter base flow period (February/April) showed slightly lower values than during autumn/late summer (Figure 3. 16 e and Figure 3. 19).

$3,5Bd/V$ ratio showed similar trend to $P/(V+S)$ (ranging from 0.12 to 0.62, global average=0,29, n=107)). Lowest values were recorded during spring flood (average=0.23, n=54). Highest values were reached during late summer and autumn and intermediate

values were reported during winter base flow conditions (average=0.35, n=53) (Figure 3.16 f and Figure 3.19).

S/V ratios and C/V showed similar behavior with decreasing values during spring flood period (S/V average=0.34, n=54; C/V average=0.07, n=54). Low flow period displayed higher values (S/V average= 0.43, n=53; C/V average=0.10, n=53). Maximum ratios for both S/V and C/V were reported for the beginning of the rising limb and the end of recession each year (Figure 3.17 a-b). Property property plot shows that Yenisei DOM plots close to gymnosperm wood end-member with closer values during spring flood (Figure 3.18).

P/V ratios (ranging from 0.2 to 0.96, global average= 0.44, n=107) decrease significantly during spring flood period (average=0.31, n=54), increased during recession to reach highest level during the early winter season and then decreased slightly until the pre-flood period (average= 0.58, n=53) (Figure 3.17 c).

3.3.3 ^{14}C -DOC and C/N

Measured $\Delta^{14}\text{C}$ -DOC displays a global modern signature, ranging from -48.3 to 79.5‰. DOC was younger (modern) around peak flood and older (around 350 yr BP) during winter base flow. Values reported for late summer/early autumn 2014 were intermediate (Figure 3.21).

The C/N ratio of DOC ranged from 7.5 to 51.7 with lowest values measured during low flow conditions (average=3.9, n=54), highest values measured during spring flood (average=33.2, n=55), average was 25.9 (n=109).

3.4 DISCUSSION

3.4.1 Low flow period:

Low flow DOM optical signal was characterized by decreasing SUVA_{254} values (Figure 3.1) indicating less aromatic compounds (Weishaar et al., 2003). Higher $S_{(275-295)}$ values (Figure 3.4) suggested low molecular weight DOM predominance. $S_{(275-295)}$ has been shown to be inversely correlated to average molecular weight of DOM (Helms et al., 2008) with lower values indicative of high molecular weight fraction of chromophoric dissolved organic matter (CDOM) associated with terrestrial DOM sources and higher values linked to the presence of low molecular weight CDOM fractions derived from more degraded and/or autochthonous sources (Helms et al., 2008; Stedmon et al., 2011; Fichot and Benner, 2012). These results can be related to deeper soil water flowpath

and groundwater supply. This is well shown by the spectral slope signal which is intermediate during the late summer and early autumn when the active layer depth is maximal implying water percolation along the soil profile and the highest values of spectral slope during late winter when the supply of water is mostly assured by groundwater. They are also supported by the fact that Cryosol within Siberian permafrost contain higher proportion of fluvic acids (low molecular weight) and less aromatic content than surface organic horizons flushed during freshet (Kimble, 2004). Export of low molecular weight and more degraded OM during base flow is linked to longer hydrologic residence times due to the deep soil and groundwater flowpath that allow for enhanced sorption processes (Kalbitz et al., 2005; Kawahigashi et al., 2006) and increased microbial processing (McKnight and Aitken, 1998; Striegl et al., 2005; Chen et al., 2010; Williams et al., 2010). These results confirm the observations made in chapter 2, where water isotopy and ions concentration and ratios suggested dominant ground water flowpath.

Deeper flowpath and higher degradation state were also confirmed by specific lignin phenols ratios. 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5Bd/V) ratio can serve as proxy for degradation, pedogenesis and contribution of deeper mineral soil horizons as 3,5-Bd, likely deriving from tannins and flavonoids in cells of degraded plant tissues, is formed during humification in soils (Gordon and Goñi, 2003; Hedges et al., 1988; Hedges and Prahl, 1993; Louchouart et al., 1999; Teisserenc et al., 2010; Tesi et al., 2014).

Thus, 3,5Bd concentration should increase from fresh organic horizons to more degraded OM from deeper mineral horizons (where 3,5Bd tends to accumulate as it is highly resistant to degradation) whereas Vanillyl phenols are more susceptible to degradation (Dickens et al., 2007). Therefore, higher 3,5Bd/V values indicate more degraded terrigenous organic matter. This degradation proxy has been suggested as more reliable than Ad/Al ratios as it is not affected by leaching/absorption processes between carbon pools (Salvadó et al., 2016). We recorded the highest 3,5Bd/V (Figure 3.16 f) during the late summer/early autumn period when discharge re-increased slightly ($>20\,000\text{ m}^3\cdot\text{s}^{-1}$) and active layer was deepest, confirming deep soil inputs of DOM. Winter values leveled off at an intermediate value indicating the shift to predominance of groundwater supply. High values of 3,5Bd/V during wintertime have been previously reported for arctic rivers (Amon et al., 2012).

$P/(V+S)$ is an indicator of degradation of terrigenous OM. This specific biomarker is related to the brown-rot degradation pathway of lignin which leads to demethylation of methoxylated V and S groups whereas P groups are not affected (Dittmar and Lara, 2001). Thus ratio increases with higher state of degradation. Higher $P/(V+S)$ ratios (Figure 3. 16 e) reported during low flow period also indicate more degraded DOM export (confirming 3,5Bd/V interpretation). We recorded slightly lower values during the second part of low flow period (January-April) when soils are totally re-frozen, compared to earlier in the season (August-December).

Acid to Aldehyde ratio of vanillyl and syringyl phenols ($(Ad/Al)_v$ and $(Ad/Al)_s$) are often presented as indicators of relative degradation of plant derived DOM as aldehydes degrade faster than corresponding phenol group acids, thus, high ratio indicates more degraded material (Goñi and Hedges, 1992; Hedges and Prahl, 1993). However, this indicator must be taken with caution as sorption processes have been shown to induce lower ratios, as lignin-derived acidic phenols appear to be selectively sorbed in mineral soils (Kaiser et al., 2004; Hernes et al., 2007). Thus a signal of “degraded” DOM (high Ad/Al) might be transformed into “fresh” DOM signal (low Ad/Al), because of intense sorption processes. Therefore, lower Ad/Al ratios observed during low flow period, that are in contradiction with 3,5Bd/V and $P/(V+S)$ values, likely reflect increased sorption processes during percolation through mineral horizons. It has been shown through stable isotope investigation that sorption and desorption processes becomes more important in late summer, fall and winter as larger fraction of river water comes from groundwater (Gibson and Prowse, 2002).

Ratio of p-coumaric to ferulic acids (pCd/Fd) can provide information on diagenetic state (preferential degradation of ferulic acid), leaching and sorption/desorption processes (Sanger et al., 1997; Houel et al., 2006). Elevated pCd/Fd ratios have also been observed in leaves, needles, sphagnum mosses and wetland and tundra soils (Ugolini et al., 1981; Williams et al., 1998), indicating that specific sources may also influence observed dynamic of pCd/Fd ratios. Here, pCd/Fd seems to confirm the more degraded state of DOM during wintertime with higher values of the ratio during low flow (Figure 3. 16 c). However, in our case this indicator should be handle with care. The phenols used are present at very low concentrations, often close to detection limits. Thus, they potentially induce uncertainties and artefacts in the variation of this ratio.

Lignin phenols are produced by vascular plants. Consequently they are relevant tracers of terrestrial DOM inputs to aquatic systems. Drop in S8 (Figure 3. 13) implies a reduction in lignin phenol contribution to the total DOM pool indicating less terrestrial inputs during the low flow period. Typically, DOM in subsurface and deep soils displays lower lignin content than upper soils (Kaiser et al., 2004).

Specific lignin phenols ratios can help to characterize terrestrial sources of DOM in rivers (Hedges and Mann, 1979; Amon et al., 2012; Mann et al., 2016). Syringyl to Vanillyl (S/V) ratio indicate vegetation contribution with low ratio indicating gymnosperm inputs and high ratio angiosperm inputs whereas Cinnamyl to Vanillyl (C/V) ratio allow to distinguish between woody lignin and other lignin sources such as herbaceous plants, leaves or needles as non-woody tissues produce much more cinnamyl phenols (Hedges and Mann, 1979). Base flow period displayed higher ratios of S/V (Figure 3.17 a) and 3.18) and C/V (Figure 3.17 b) and 3.18) suggesting either increased contribution from angiosperm (woody and non-woody) (Hedges and Mann, 1979) from southern part of the watershed or tundra regions; or contribution from subsurface soils as Yenisei soil studies have shown an increase of S/V and C/V ratios in DOM from subsurface soils (Amon et al., 2012 and references therein).

As Amon et al. (2012) we measured globally elevated P/V (0.2 to 0.96) (Figure 3. 17 c) and Pn/P values (0.2 to 0.4) (Figure 3. 16 d), with overall higher ratios during base flow. This specific lignin phenols groups (p-hydroxybenzenes) have been detected at high levels in different sphagnum species as well as in peat soils (Williams et al., 1998), which are especially enriched in Pn (up to 60% of total P phenols). Therefore, elevated P/V and Pn/P values indicate important contribution from sphagnum and peat derived DOM to aquatic systems during base flow conditions (Amon et al., 2012; Dubinenkov et al., 2015).

Fluorescence indicators also reflect lower terrestrial inputs during low flow period. Fluorescence index allow to decipher between general DOM sources, i.e. either: microbial/autochthonous (high FI ,1.8, derived from extracellular release and leachate from bacteria and algae) or terrestrially derived (low FI ,1.2, terrestrial plant and soil organic matter) (Fellman et al., 2010). Therefore, higher FI recorded during winter indicate higher proportion of microbially derived compounds and potential contribution of algae. HIX reflect the humification degree of DOM (Zsolnay et al., 1999;

Ohno, 2002). Thus, low HIX values of the low flow period suggest less humic compounds in DOM and consequently lower direct inputs from soils.

According to spectral characteristics, correlation with variables linked with terrestrial processes and timing of concentrations peaks (table 3.1 and Figures 3.11, 3.12), we associated the PARAFAC component 1 (Cp1 : ex 360/em 480) and 2 (Cp2 : ex320/em415) (Figure 3. 10) to highly aromatic compounds, UVC humic-like compounds derived from fresh plant source (terrestrial sources in particular forested environment) and high molecular weight compounds. These components were similar to the Peak C identified by Coble et al., (1990, 1998), the component α identified by Parlanti et al., (2000) and the Component 1 of Cory and McKnight, (2005) . Cp1 and Cp2 fluorescence intensities were in particular correlated with discharge and DOC concentration (table 3.1) suggesting allochthonous sources, such as inputs from upper organic horizons and litter layer, associated with surface run off processes. Based on spectral characteristics, we related the PARAFAC component 3 (Cp3 : ex240/em430) (Figure 3. 10) to low molecular weight, fluvic-like, UVA humic-like compounds and classical Peak A (ex260/em426) (Korak et al., 2014). This component was similar to the C3 observed by Stedmon and Markager, (2005), the BERC1 identified by Walker et al., (2009), the C1 component of Mann et al., (2012) and other PARAFAC components reported in the literature (Coble, 1996; Parlanti et al., 2000). The link with low molecular weight was confirmed by significant relationship between Component 3 relative contribution to fluorescence and $S_{275-295}$, showing low molecular DOM (High values of $S_{275-295}$) for high proportion of Component 3. Moreover, the overall lack of relationship between this component and DOC concentration, discharge and terrestrial biomarkers (lignin phenols ratios) (table 3.1), suggest that it is a potential proxy for processes such as DOM microbial degradation or autochthonous DOM production (probably alga-derived), which are not directly linked to terrestrial processes (Walker et al., 2013). According to previous PARAFAC studies and our results, PARAFAC components are not specific of a single terrestrial DOM source, but rather, various sources may contribute to each component in varying proportions (Walker et al., 2013). We recorded an increase in intensity and relative contribution of the PARAFAC component 3 (associated to low molecular weight compounds, microbial and autochthonous DOM production) during low flow period (Figure 3.11, 3.12). It was particularly predominant during the under-ice samples of the pre-flood period and

peaked during the launch of the rising limb, prior to ice-break. Such phenomenon has been observed in the Kolyma where high protein-like fluorescence intensity and microbial fingerprint, low aromatic and low molecular weight DOM compounds have been shown to characterize base flow of late winter period, prior to ice break and spring flood (Mann et al., 2012). Protein like fluorescence predominance has been linked to increased supply of DOM from ice melt during this period (Lafrenière and Sharp, 2004; Hood et al., 2009; Fellman et al., 2010b). The PARAFAC component 3 dominance also increased steadily during summer, potentially indicating rising of relative contribution of autochthonous DOM while water temperature increased (Stedmon et al., 2003; Stedmon and Markager, 2005).

C/N ratios may allow to distinguish specific DOM sources, alga-derived DOM with C/N around 14 (Amon and Meon, 2004), soil-derived DOM with C/N between 14-25 (Kaiser et al., 2004b; Kawahigashi et al., 2006), vascular plant sources with C/N about 54 (Amon and Meon, 2004). During low flow period C/N ratios tend to lowest values (prior to the launch of the rising limb of the spring flood, around 10), indicating dominance of autochthonous contribution (potentially alga and phytoplankton)(Amon and Meon, 2004). However low C/N ratio can also potentially indicate soil derived DOM due to slight overlapping of end-member values (Amon et al., 2012).

¹⁴C-DOC provides an estimation of DOC age. As expected and previously reported in the Kolyma river in eastern Siberia (Neff et al., 2006), our ¹⁴C-DOC measurements suggest older DOM inputs during low flow period (Figure 3. 21) illustrating a shift to deeper soil flowpath along with active layer deepening during summer.

During low flow conditions, water percolates through deeper soil horizons as the active layer thaw until refreezing during wintertime when the main water supply is provided by groundwater. This has been linked to the introduction of older DOM, containing less aromatic and lignin phenol compounds, lower C/N ratios and higher proportion of hydrophilic acids relative to hydrophobic acids (Neff et al., 2006; Spencer et al., 2008; O'Donnell et al., 2010; Amon et al., 2012). Our results confirmed most of those previously observed phenomena.

3.4.2 Spring flood period:

During the snowmelt driven spring flood, large area of the soils are still frozen, limiting connection with deep mineral soil horizon and inducing flushing effect of

soluble material from organic horizon and litter of the watershed (Boyer et al., 2000; Rember and Trefry, 2004; Finlay et al., 2006; Ågren et al., 2010). Permafrost watersheds (31% of permafrost extent in the Yenisei watershed), tend to have limited exchange of DOM with deep soil layers and greater coniferous cover which produces higher aromatic carbon with low decomposition rates (Balcarczyk et al., 2009). Hydrological events have been shown to export DOM that tends to have higher degree of aromaticity and humic content (Hood et al., 2006; Vidon et al., 2008; Fellman et al., 2009). The spring flood period in arctic rivers has been characterized by high terrestrial inputs of DOM, illustrated by high lignin yields, and predominance of young, boreal-vegetation- derived leachates (Amon et al., 2012).

High SUVA values (Figure 3.1) measured during the spring flood events of the Yenisei river, indicate export of DOM with high aromatic content (Weishaar et al., 2003), low FI implies (Figure 3.6) higher terrestrial contribution (Cory and McKnight, 2005; Fellman et al., 2010) Higher HIX (Figure 3.7) during peak discharge indicates increased Humic content (Zsolnay et al., 1999) with predominant PARAFAC components during this period associated with humic-like compounds (Figure 3. 11, 3.12). Low $S_{(275-295)}$ (Figure 3.4) were reported during spring flood period of the Yenisei, therefore DOM exported comprise high molecular weight compounds likely originating from organic rich surface horizons. Shift toward humic-like enriched DOM during storm events associated with high surface water runoff have been previously reported (Inamdar et al., 2011; Jaffé et al., 2012; Singh et al., 2013; Jaffé et al., 2014).

Low $P/(V+S)$ and $3,5Bd/V$ during peak flow (Figures 3.16 e) f), 3. 19) suggest freshly leached DOM from upper organic soil horizons. Amon et al. (2012) remarked that low values for this ratios were observed in particular for the watersheds with the most permafrost (Yenisei, Lena and Kolyma).

For fresh plant material, typical Ad/Al ratios are around 0.1-0.2 (Hedges et al., 1988). However, here, Ad/Al ratios observed (Figures 3. 16 a) b), 3.20) do not suggest “fresh” DOM as expected according to the previous lignin phenol ratios and top soil and fresh plant litter flushing processes occurring during the spring freshet. The high Ad/Al ratios measured during the spring flood period likely reflect reither enhanced leaching processes than actual « degraded » DOM. Leaching of DOM have been shown to induce higher Ad/Al ratios (Hernes et al., 2007). In addition, Moingt et al., (2016) discussed the fact that in landscapes having mixed vegetation cover, a high contribution of woody

gymnosperm to the lignin pool (which is likely the case for significant areas of the Yenisei watershed) could induce higher $(Ad/Al)_v$ ratios without actual higher state of OM degradation. Such high values of Ad/Al during peak flow have been observed in almost all the Great Arctic rivers (Amon et al., 2012).

Elevated concentrations of lignin phenols during spring freshet suggest vascular plants and fresh litter as dominant DOM sources to river (Raymond et al., 2007; Amon et al., 2012). Elevated lignin export during hydrological event has been associated to enhanced leaching of surface vegetation and organic-rich upper soil layers and the shunt of lower soil profiles (which have higher affinity for DOM sorption) in combination with short residence time (Hernes et al., 2008; Raymond et al., 2016).

Dissolved lignin fluxes estimates for the Yenisei river are scarce in the literature. Our estimate of annual export was similar to the one of Amon et al. (2012) which is much higher than the one derived from CDOM (Lignin₃₅₀) developed by Mann et al. (2016) (Table 3.2). We observed a strong interannual variation with a difference of almost 33 Gg between 2014 and 2016 annual fluxes (likely due to lower discharge in 2016) and the predominance of the spring freshet in dissolved lignin export accounting for an average of 85.7% of the total lignin flux (Table 3.2). At the Arctic scale the Yenisei is one of the most important dissolved lignin carrier, accounting for 28% of the dissolved lignin flux delivered by the six largest arctic rivers (based on Amon et al. (2012) estimate (192 Gg/yr) of dissolved lignin flux for the Arctic GRO, see Table 3.2).

Decreasing ratios of S/V (Figure 3.17 a and 3.18) and C/V (Figure 3.17 b and 3.18) indicate increased contribution of gymnosperm wood suggesting DOM inputs from the Boreal forest during the freshet (Neff et al., 2006; Raymond et al., 2007; Spencer et al., 2008; Amon et al., 2012; Walker et al., 2013b; Dubinenkov et al., 2015). Peak flow values of ratios are low but still higher than pure gymnosperm wood source reference, suggesting the interplay of additional terrestrial plant sources. Field surveys indicate that moss biomass may represent a significant additional source (with higher S/V values due to low V yields in moss, (Amon et al. 2012)), it may even largely overcome shrub biomass in northern taiga and larch dominated woodlands (Prokushkin et al., 2006). However, angiosperm are abundant in tundra regions as well as in alpine regions of the southern mountainous part of the watershed and likely contribute in some extent to riverine DOM. Moss contribution is also consistent with P_n -yields during high flow conditions as moss produce high proportion of P_n phenols (Williams et al., 1998). A

mixture of only gymnosperm and angiosperm wood and leaves would not be able to explain observed P/V (Figure 3. 17 c) and Pn/P (Figure 3. 16 d) values (Amon et al., 2012).

High C/N ratios recorded during peak flow confirm the predominance of terrestrial plant derived DOM inputs (Holmes et al., 2012). Based on reported C/N during peak flow of arctic rivers, Amon et al. (2012) estimated that vascular plants and litter flushed by surface run-off made up to 70% of the DOM and that the remaining 30% consisted in a combination of algae and soil derived DOM (difficult to distinguish based on C/N). However previous studies on elemental and isotopic DOM composition in the Yenisei suggest minimal algal-derived DOM (6-16%) during this period (Amon and Meon, 2004; Holmes et al., 2012).

Recently produced DOM inputs are confirmed by modern ^{14}C -DOC age reported for the peak flow period. Such observations have also been reported for other arctic river freshets (Benner et al., 2004; Neff et al., 2006; Raymond et al., 2007; Sanderman et al., 2009; Raymond et al., 2016; Feng et al., 2017). This specific information provided by radiocarbon dating gives insight into DOM source and can help to trace permafrost inputs evolution. However, when sampling close to river mouth, recording an integrated signal of the whole watershed, riverine OC is made up of complex mixtures of compounds with potentially differing sources and ages. Indeed, DOC may contain both ancient permafrost derived and modern OC inducing a mixed bulk ^{14}C signal that can be difficult to interpret in terms of dynamics of permafrost OC inputs (Feng et al., 2017). Moreover, it has been shown that permafrost derived DOC could be readily degraded upon release lowering its old signature which is then mixed up with modern DOC that is much more abundant in the river (Butman et al., 2012; Mann et al., 2015; Spencer et al., 2015). Identify changes in permafrost contribution to the radiocarbon age of arctic river DOM would also need long time series measurements to be able to highlight trends in the evolution of the signal.

3.5 CONCLUSION AND PERSPECTIVES

DOM Characterization tools including lignin biomarkers, DOM optical properties (Fluorescence and Absorbance) and DOC radiocarbon dating were successfully employed to describe DOM dynamic, composition, sources and degradation state at an unprecedented temporal resolution capturing a Great Arctic river Spring flood period and its whole hydrological cycle.

General trends, between peak flood and low flow, with contrasting lignin yields, vegetation biomarkers and degradation indicators in combination with DOM age and optical properties suggest significant changes in the relative contribution of different DOM sources and strong variations in the degrees of DOM processing (Photo/bio-degradation either in terrestrial environment or during transport). Most of the indicators confirmed expected high temporal variability of DOM signal driven by hydrological changes, with most of the exports occurring during spring flood (>80% of lignin flux in May-June). This specific period is one of the most important components of OC fluxes in Arctic rivers but also likely a climate-sensitive element. Main trends comprise export of young, freshly leached DOM from terrestrial vegetation and litter during freshet and shift to older more degraded and microbially processed DOM during baseflow. According to vegetation lignin biomarkers (S/V and C/V ratios), main vegetation source during freshet was gymnosperm wood, implying that the boreal forest is the main contributor to riverine DOM. P phenols yields also suggest moss understories as the most likely complementary DOM source during freshet period that could explain the discrepancy from pure gymnosperm source signal with the probable contribution of southern part of the basin that have angiosperm land cover (but can explain alone the P yields). The few data point reported for base flow period suggest more variable signal than expected with significant differences between early cold season (September-December) and late winter season/pre-flood period (January-April) likely driven by changing flow path and degradation rate during the refreezing of the active-layer and the freezing of river waters.

The comprehension of the fate of terrestrial carbon is important to understand its role in the Arctic Ocean ecosystem but also to be able to evaluate the consequences of climate change perturbations. Future studies will need to investigate the sensitivity of particular Arctic DOM pools (in particular permafrost-derived) thus the use of compound-specific analysis (for instance radiocarbon analysis) will be a valuable tool to

overcome the influence of mixed OC sources for studies investigating watershed integrating DOM signals.

Interesting supplementary study would be to put in relation DOC and POC quality. Further investigation of this specific phase could give insight in exportation/mobilization mechanisms (are they similar between phases?) and provide additional information on the global OC cycle as approximately 30% of the total lignin flux delivered by the Yenisei River is delivered in the particulate phase.

Additional investigation could aim to document rapid changes occurring during the spring flood, where DOM signal can drastically change on a daily scale. Efforts could be given in refining our temporal resolution of monitoring as continuous measurements at the local scale have proven to be capable to detect changes that punctual sampling missed. In this perspectives, the use of monitoring proxies will be necessary. Most of the current one are based on optical techniques that are reliable, unable for almost continuous measurements, relatively unexpensive and easy to set up. The potential to increase temporal and spatial coverage of DOM measurements across Arctic river systems would be particularly valuable for the evaluation of climate change impact in these sensitive regions allowing for more accurate estimate of amount, quality and timing of terrigenous DOC exports.

Complementary developments would consist in drawing links between DOM quality signal recorded at the watershed outlet and watershed characteristics and processes occurring in specific regions such as snowmelt and vegetation growth dynamic. This investigations would mobilize remote sensing data and geographical information tools to monitor ecological processes and map variables influencing organic matter cycling (snowcover, precipitation, soil carbon content, permafrost extent, biomass, land cover, fire history, soil temperature, topography etc.) at the scale of a great Arctic river watershed.

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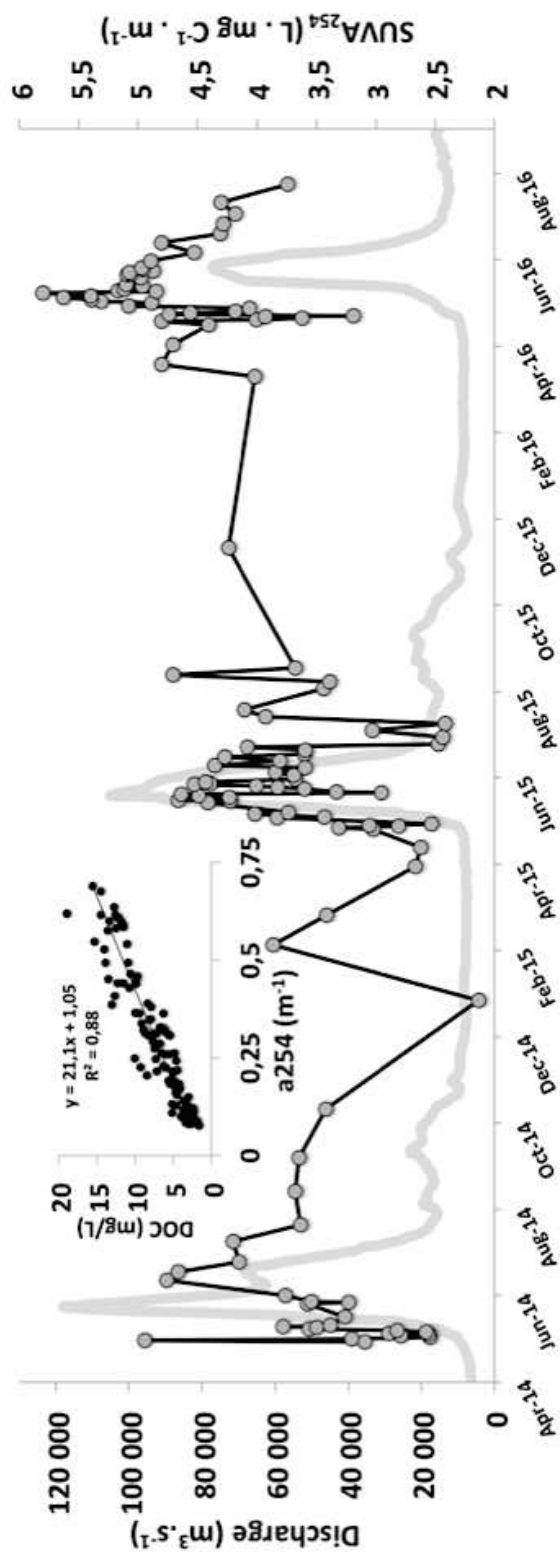


Figure 3. 1 Specific Ultra Violet Absorbance at 254 nm (SUVA₂₅₄, L. mg C⁻¹. m⁻¹) along with discharge (m³ s⁻¹, source: Roshydromet). Top graphic shows linear relationship between DOC (mg/L) and a₂₅₄ (m⁻¹)

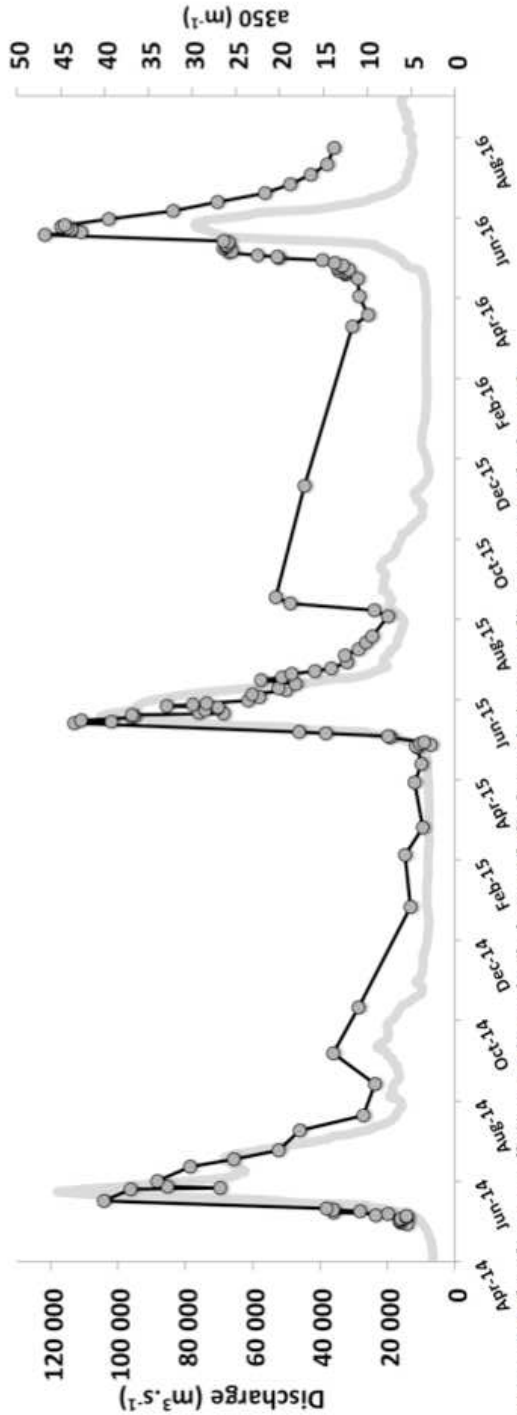


Figure 3. 2 Absorbance coefficient at 350 nm (m^{-1}) along with discharge ($m^3 s^{-1}$, grey line, source: Roshydromet).

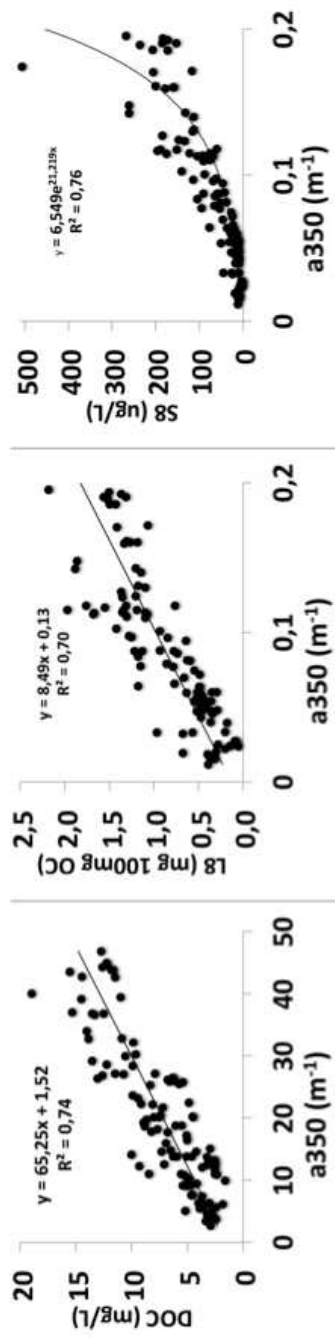


Figure 3. 3 Relationships between a350 (m^{-1}), DOC (mg/L), L8 (mg.100mg OC), S8 (ug/L).

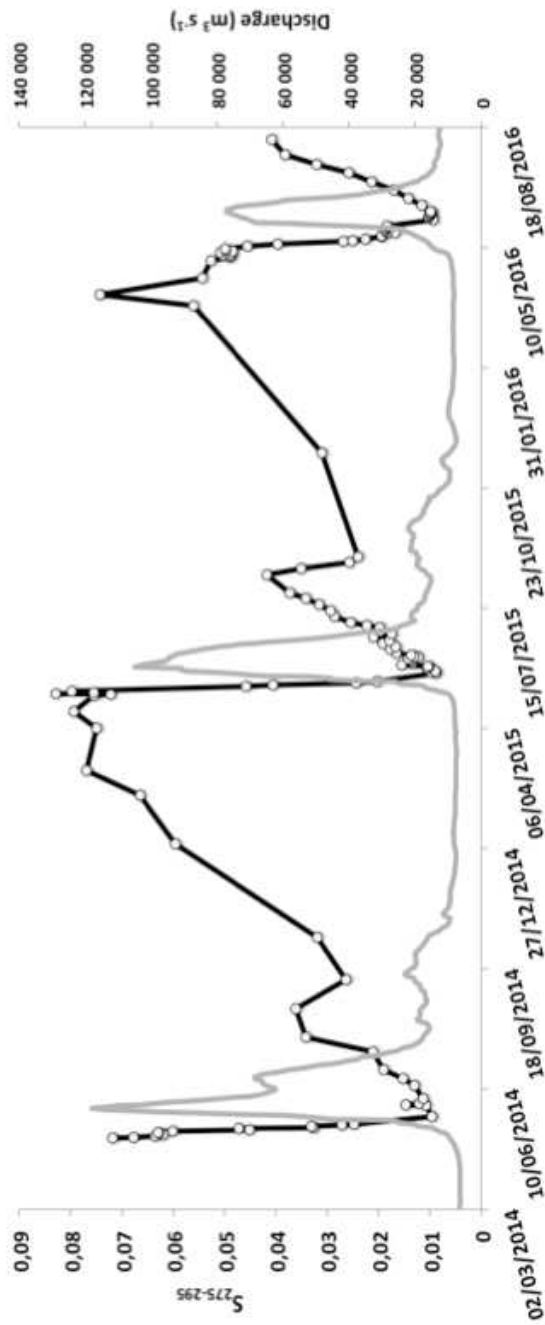


Figure 3. 4 Evolution of Spectral slope 275-295 ($S_{275-295}$) along with discharge ($m^3 s^{-1}$, grey line, source: Roshydromet).

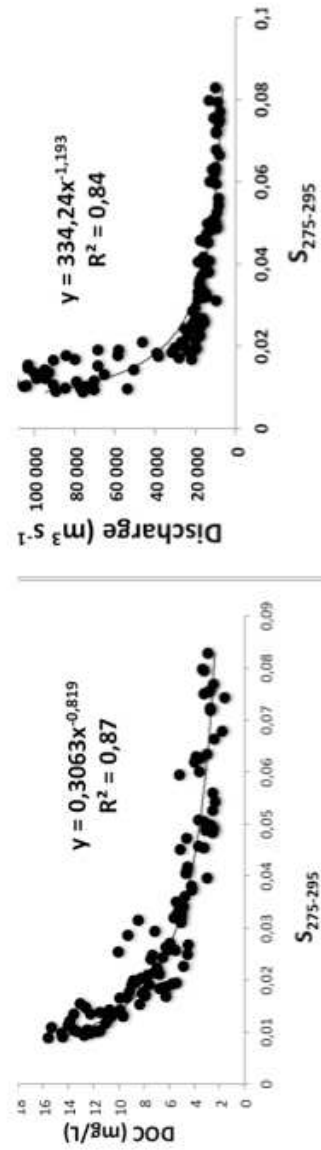


Figure 3. 5 Relationships between $S_{275-295}$ and DOC (mg/L) and discharge ($m^3 s^{-1}$, source: Roshydromet).

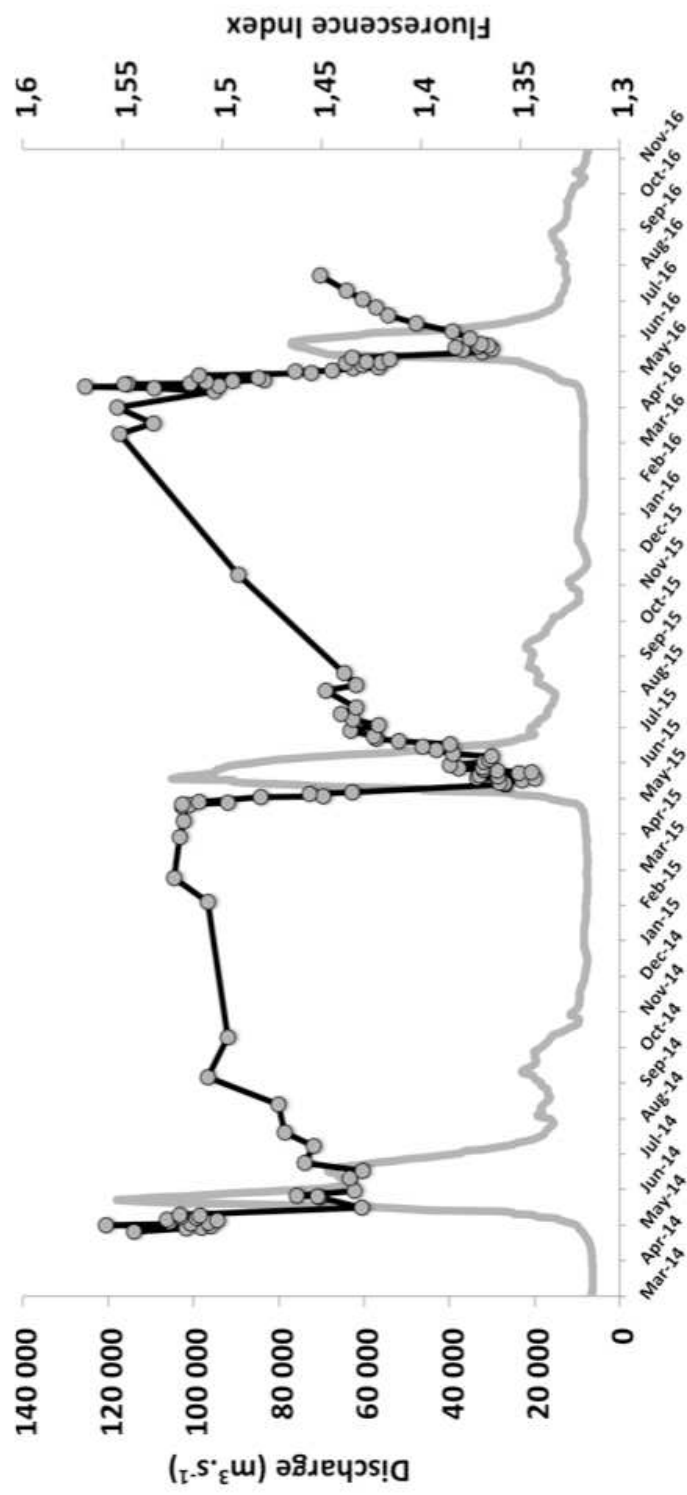


Figure 3. 6 Fluorescence index evolution along with discharge (m³ s⁻¹, grey line, source: Roshydromet).

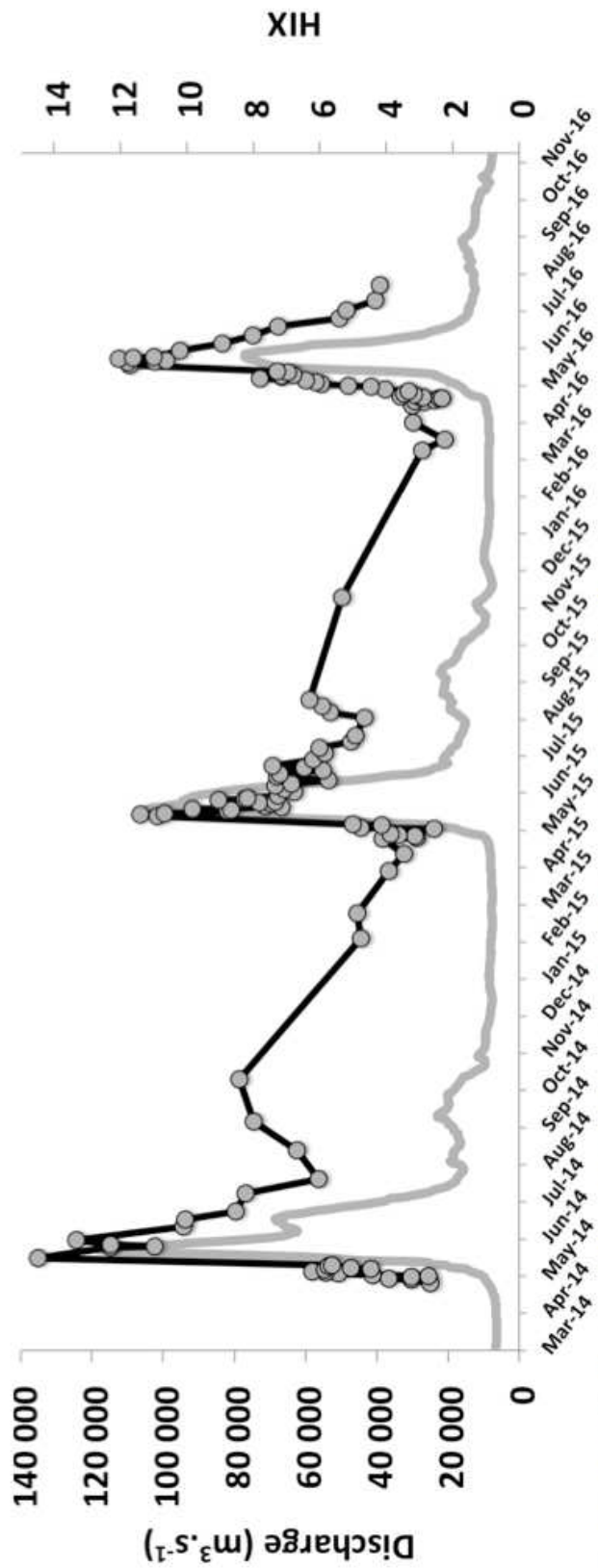


Figure 3. 7 Humification index (HIX) evolution along with discharge (m³ s⁻¹, grey line, source: Roshydromet).

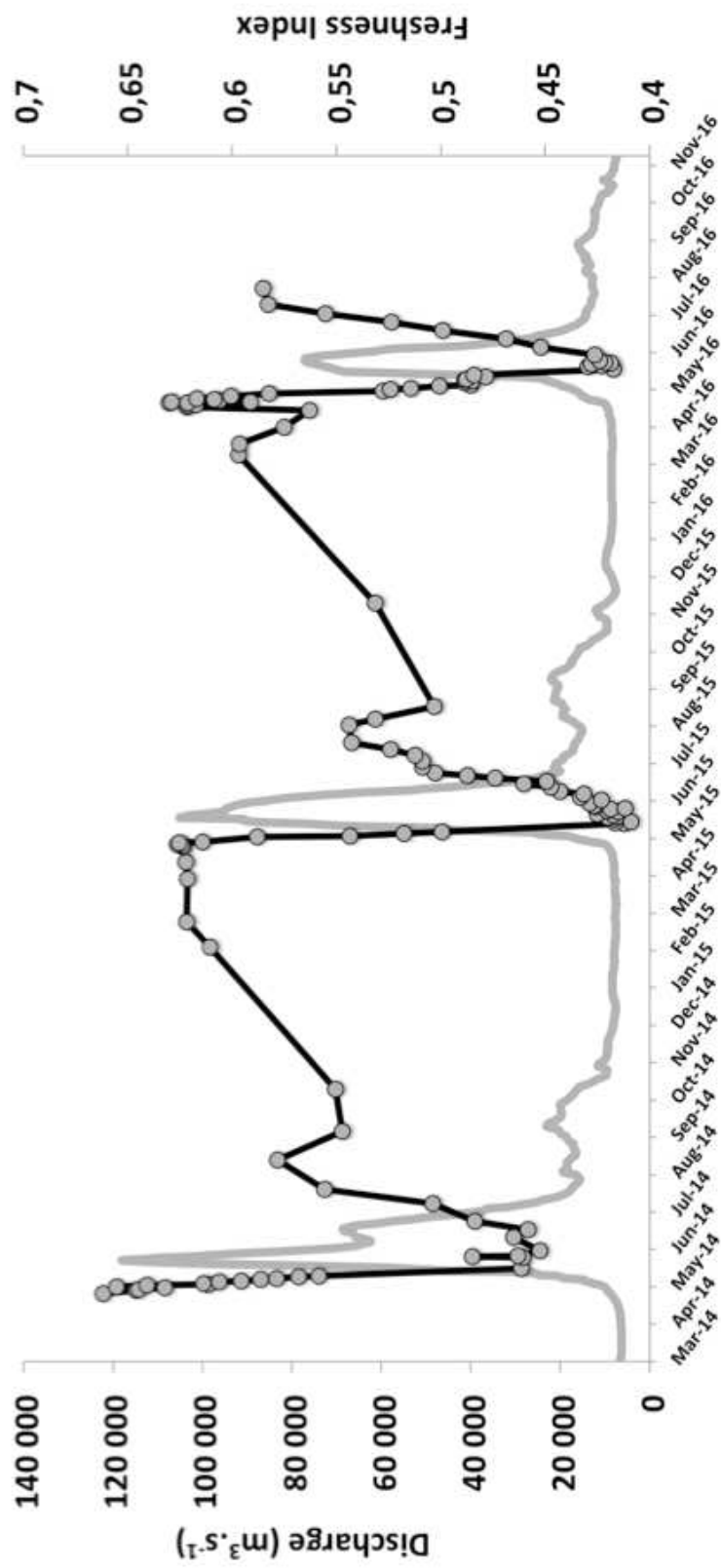


Figure 3.8 Freshness index ($\beta:\alpha$) evolution along with discharge ($\text{m}^3 \text{s}^{-1}$, grey line, source: Roshydromet).

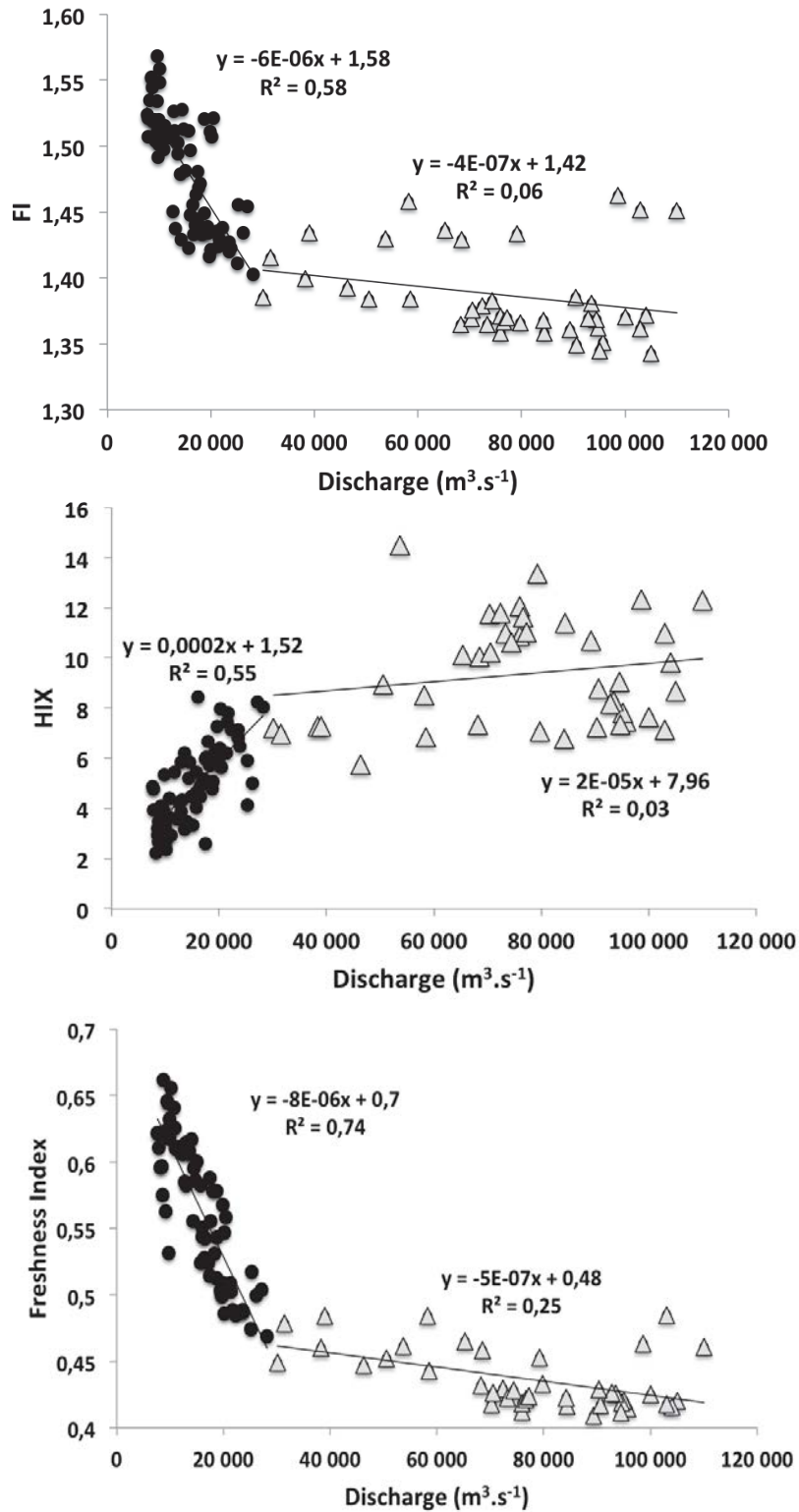


Figure 3. 22 Relationships between fluorescence indices (FI, HIX, Freshness index) and discharge (m³ s⁻¹, source: Roshydromet), black dots correspond to low flow samples, grey triangles correspond to high flow samples.

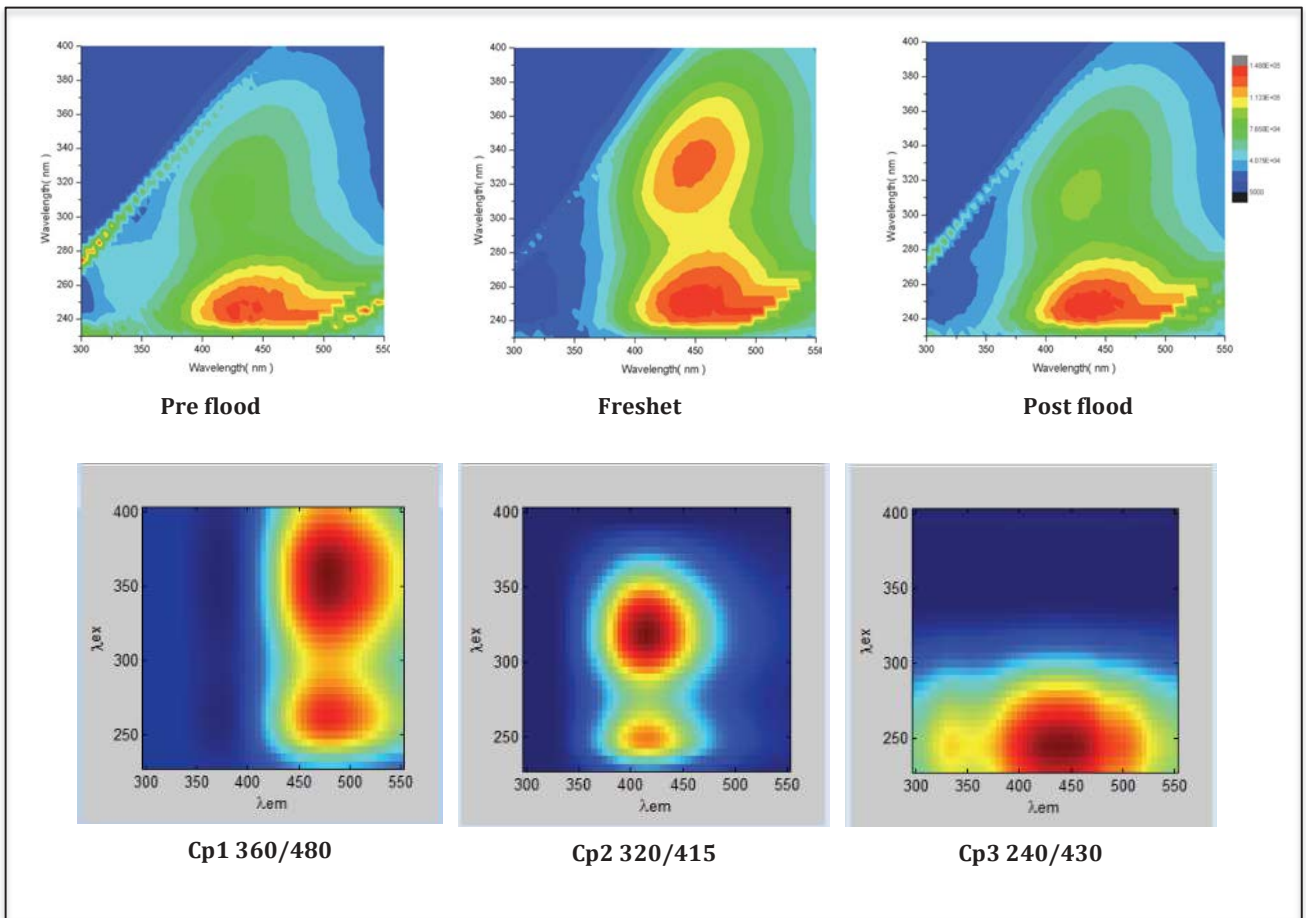


Figure 3. 23 Top pictures show the evolution of excitation/emission matrices between hydrological stages, pre flood (02/05/2014), Freshet (27/05/2014), Post flood (23/07/2014). Bottom pictures represent fluorescence components identified by PARAFAC (corcondia 60.7), along with excitation/emission maxima.

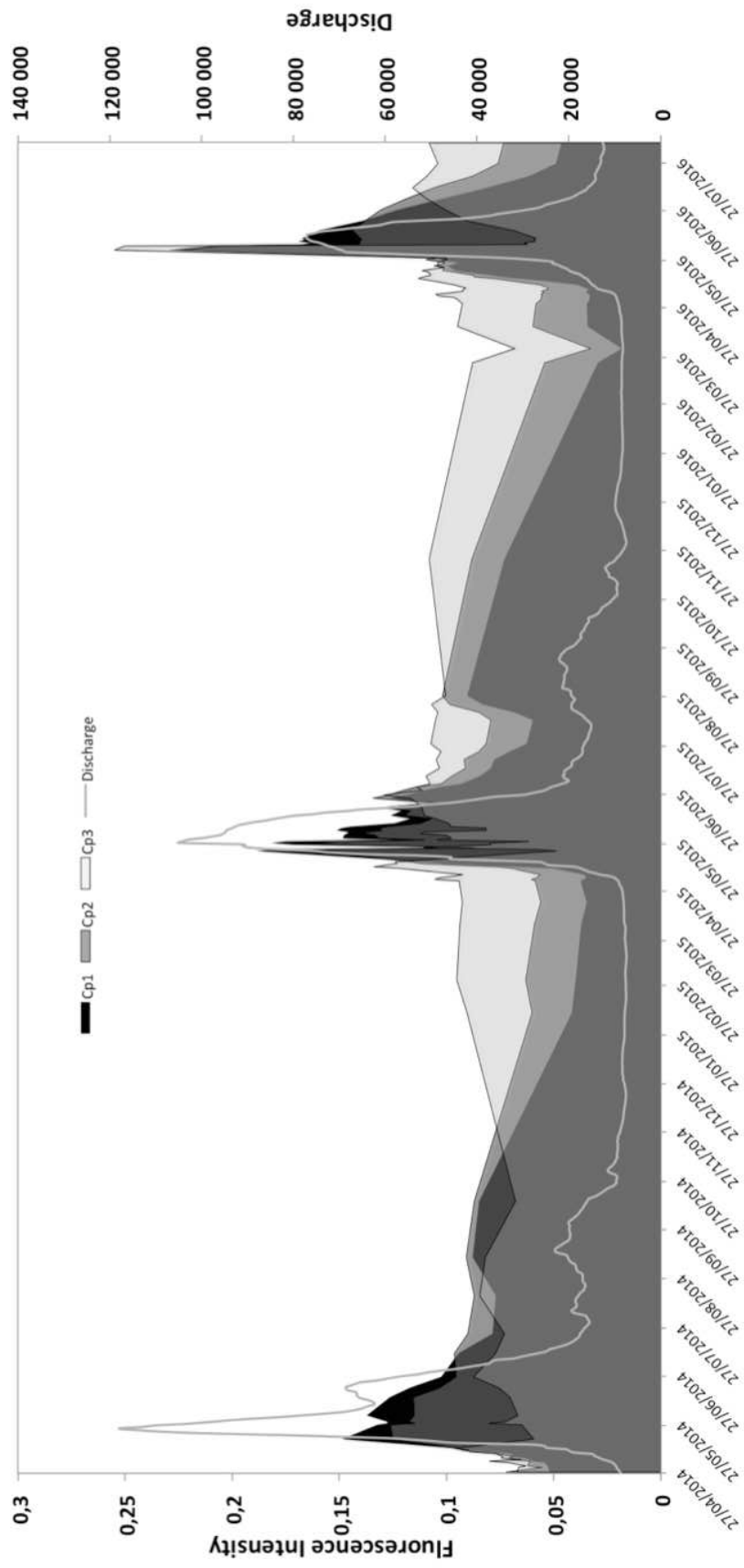


Figure 3. 11 Evolution of fluorescence intensity of each PARAFAC component. Light grey line shows discharge ($\text{m}^3 \text{s}^{-1}$, source: Roshydromet).

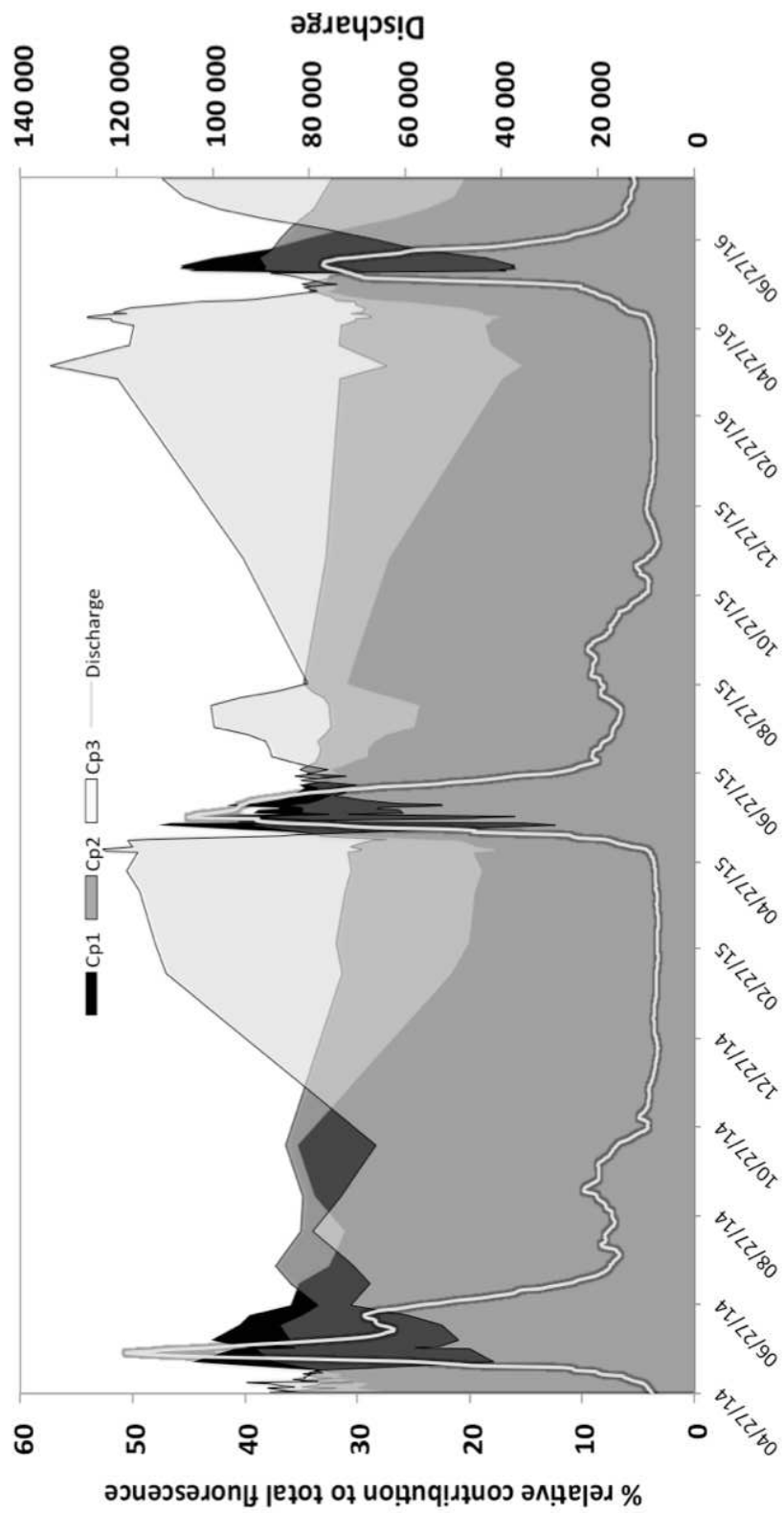


Figure 3. 12 Evolution of relative contribution (%) to total fluorescence of each PARAFAC component. Light grey line shows discharge ($\text{m}^3 \text{s}^{-1}$, source: Roshydromet).

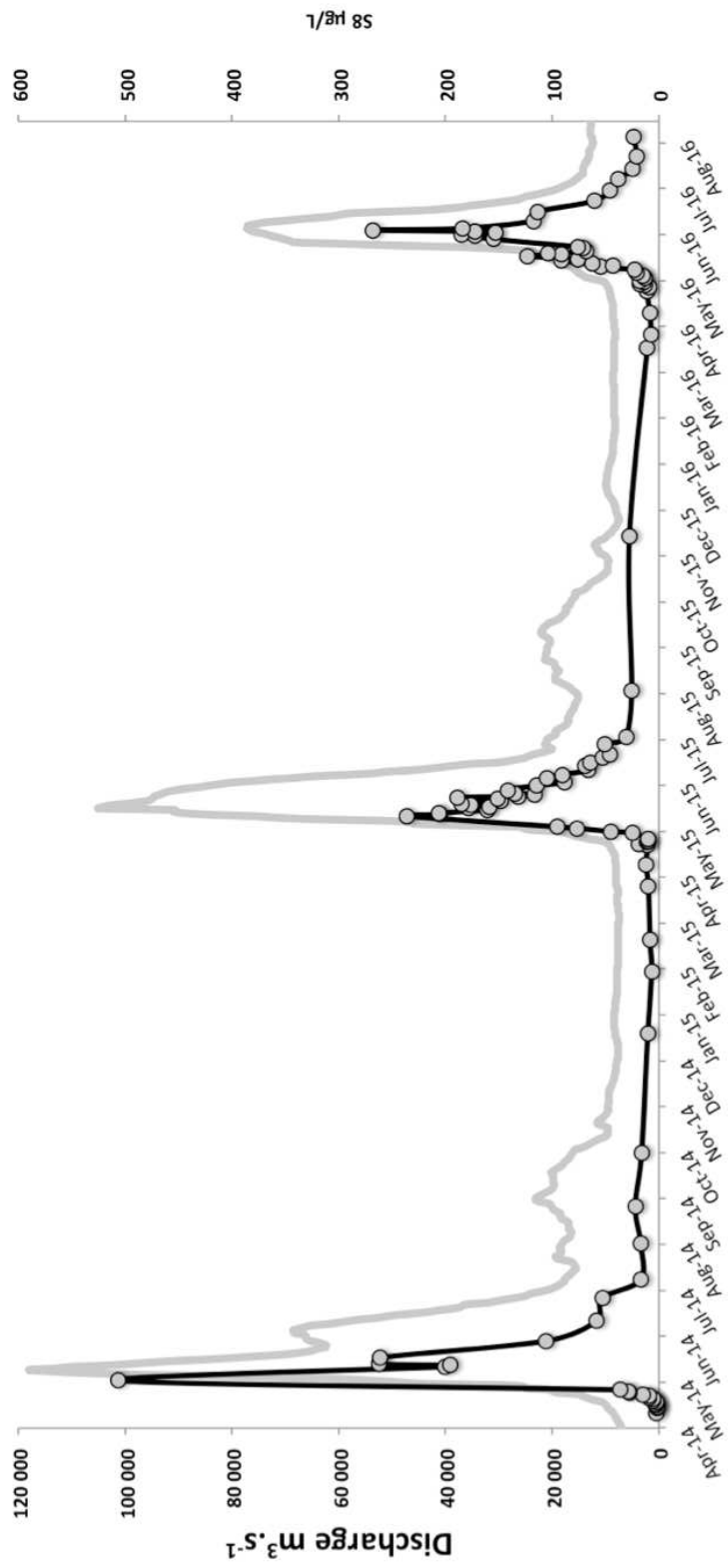


Figure 3. 13 Evolution of Sigma8 (S8, ug/L) along with discharge (m³ s⁻¹, grey line, source: Roshydromet).

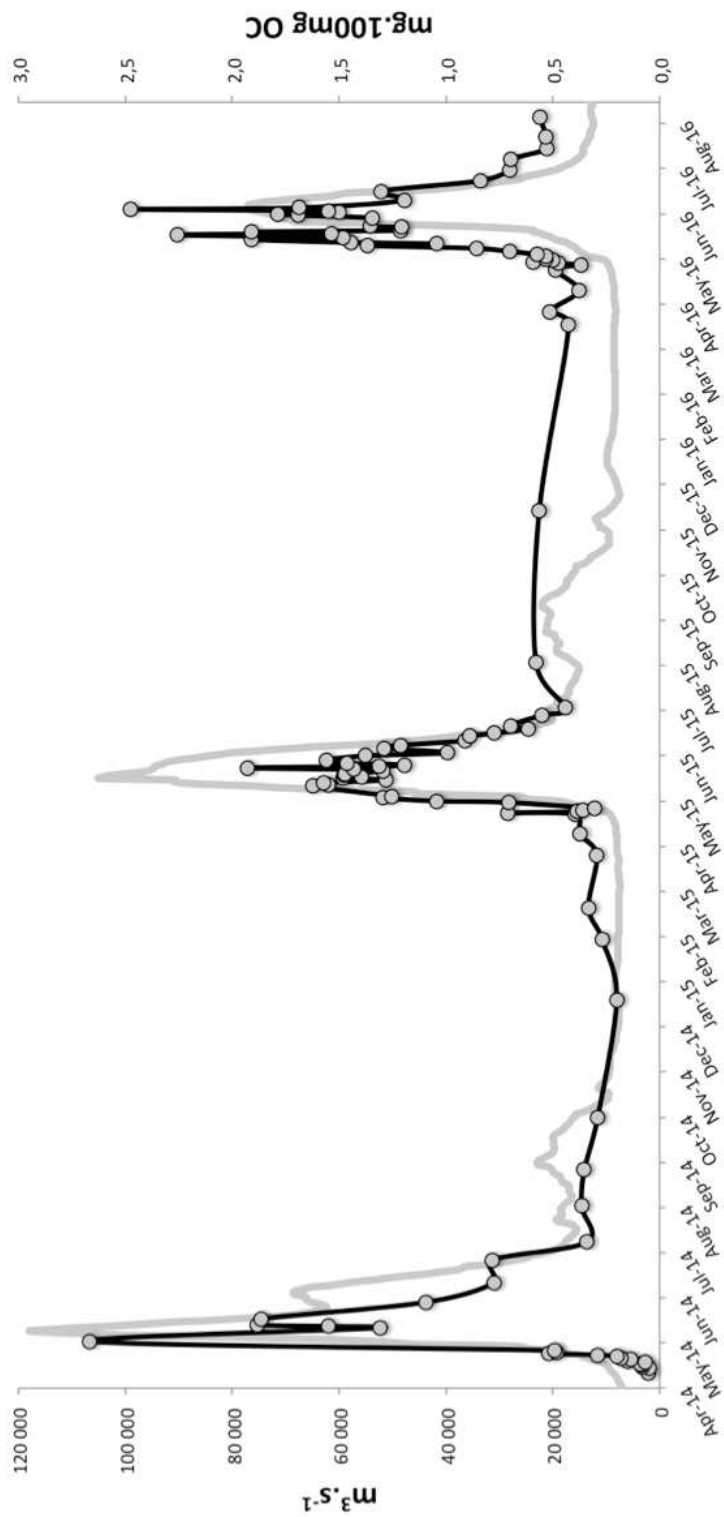


Figure 3. 14 Evolution of Lambda 8 (L8, $mg \cdot 100mg \text{ OC}$, sum of 8 phenols ($C_{1,2,3}$)) along with discharge ($m^3 \cdot s^{-1}$, grey line, source: Roshydromet).

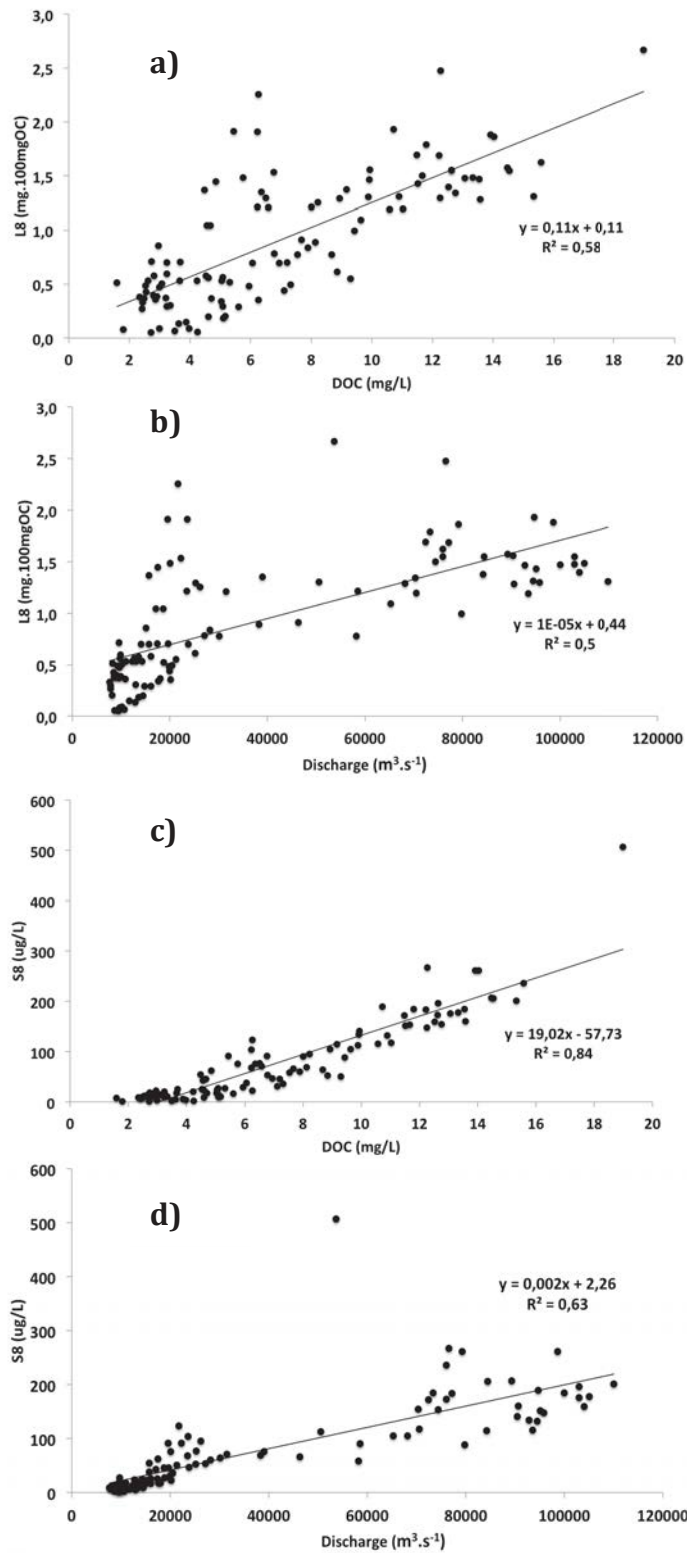


Figure 3. 24 Relationships between Lignin and DOC concentration (mg/L) and Discharge ($m^3.s^{-1}$). a) L8 (mg.100mg OC) vs DOC b) L8 vs Discharge , c) S8($\mu g/L$) vs DOC , d) S8 vs Discharge.

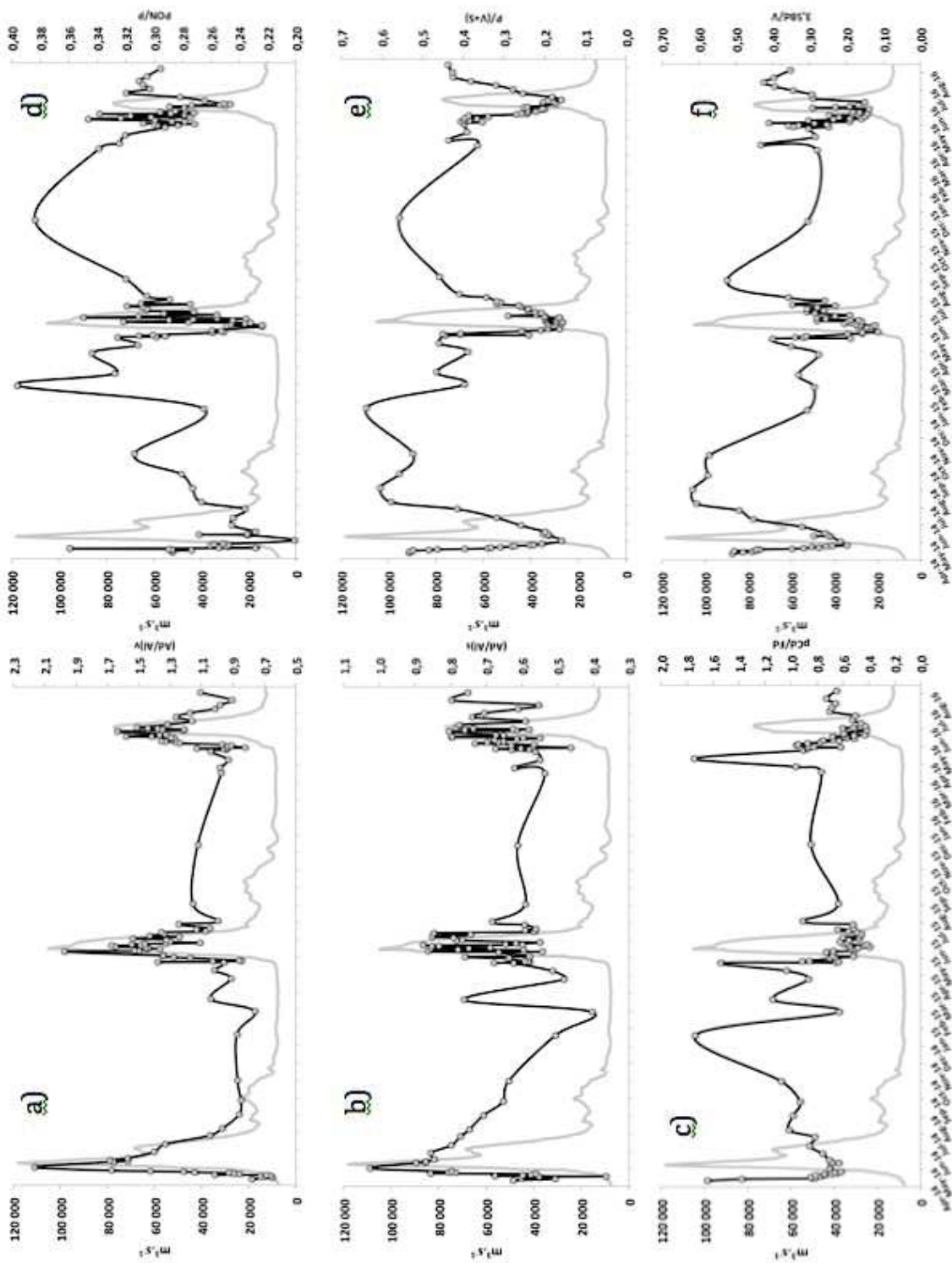


Figure 3. 16 Temporal evolution of degradation state and diagenetic lignin phenol ratio indicators along with discharge (grey line, source Roshydromet, m^3s^{-1}). a) $(Ad/Al)_\alpha$ b) $(Ad/Al)_\beta$ c) pCd/Fd d) PON/P e) $P/(V+S)$ f) $3.5Bd/V$

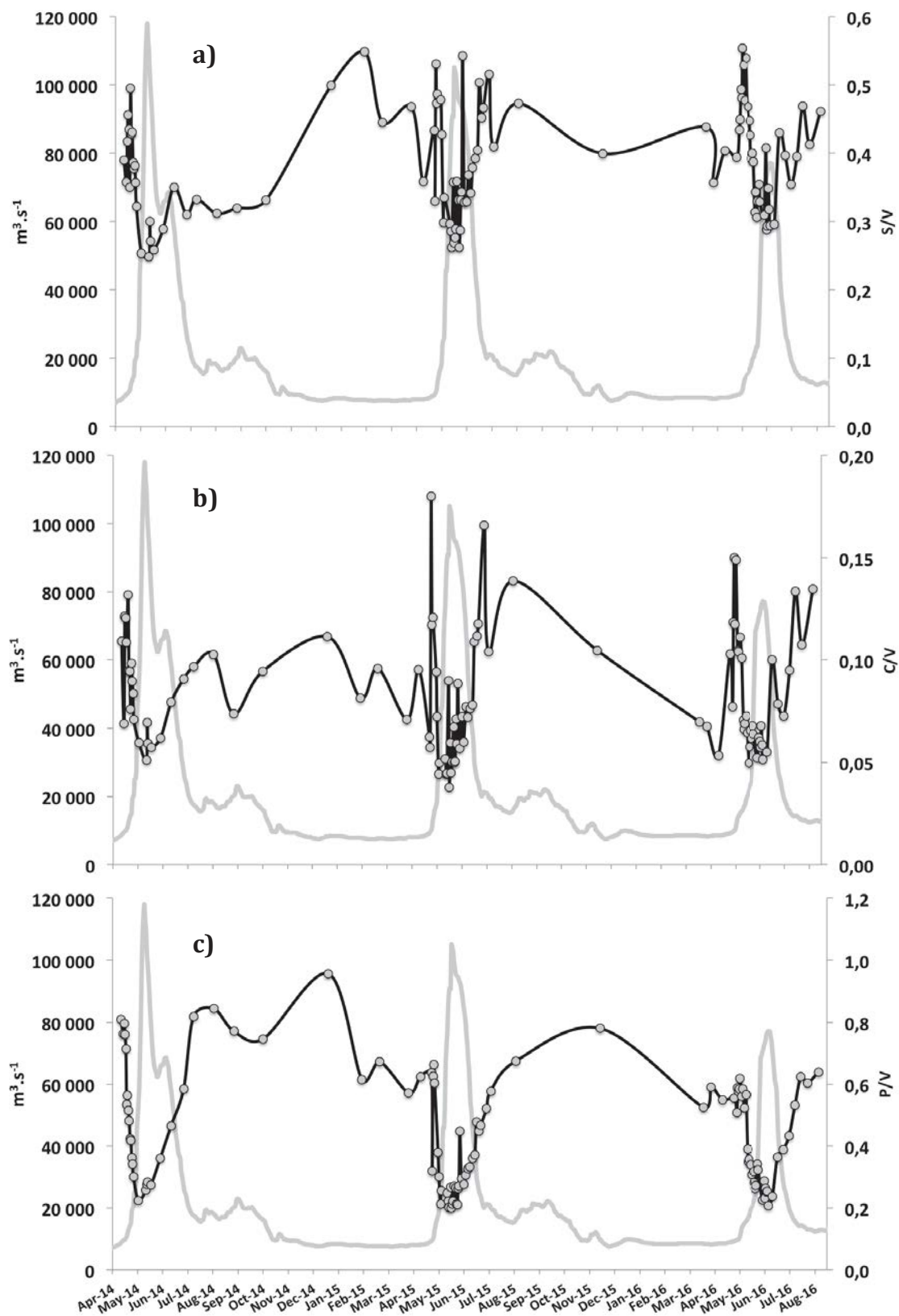


Figure 3. 25 Temporal evolution of vegetation source lignin phenol ratio indicators along with discharge (grey line, source: Roshydromet, $m^3 \cdot s^{-1}$), a) S/V b) C/V c) P/V

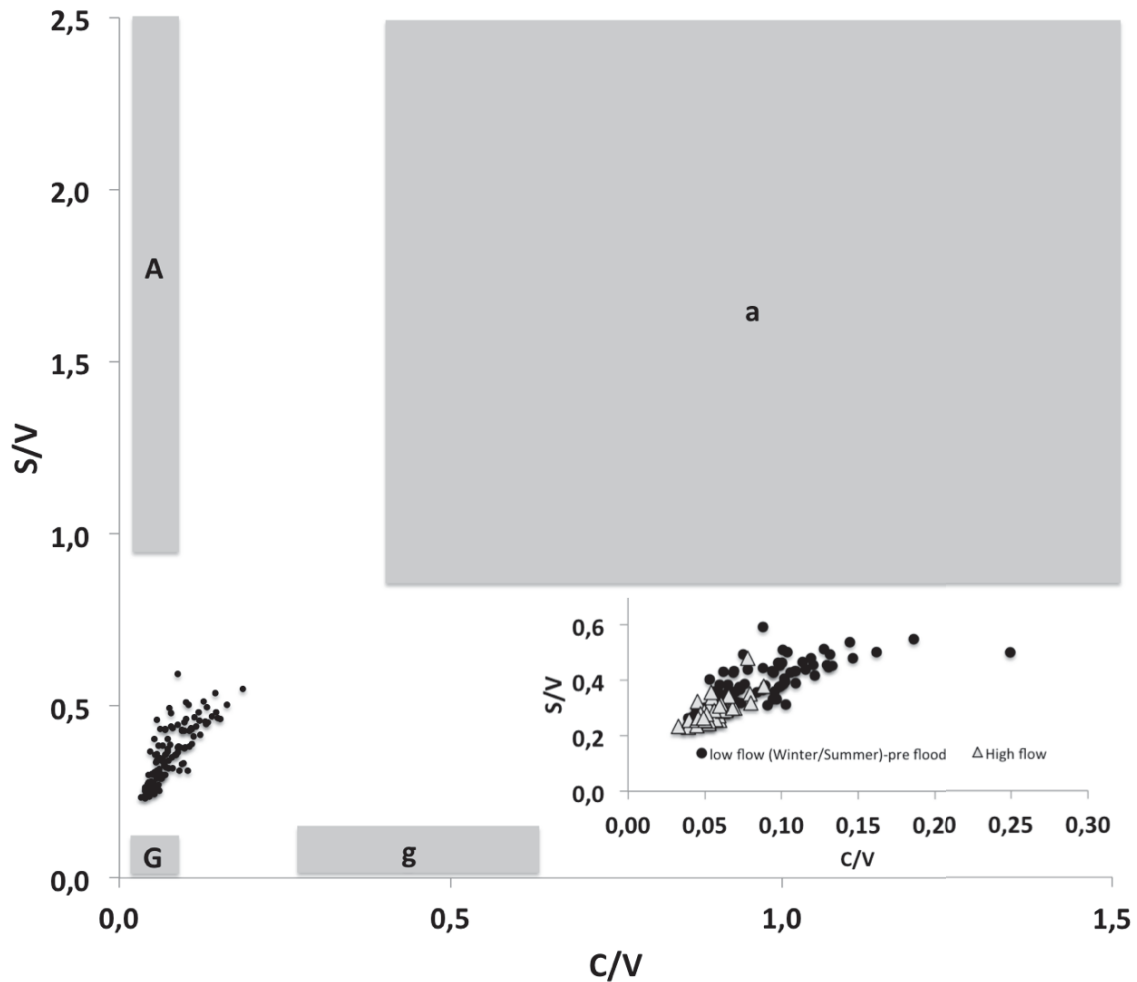


Figure 3. 26 Property-property plots of lignin phenols ratios to trace vegetation sources C/V vs S/V, grey areas delimitate pure vegetation source end members (Hedges and Mann, 1979), G=gymnosperm wood, g=gymnosperm needles, A= angiosperm wood, a=angiosperm leaves and grass. Inner graphic is a zoom on the data points with a separation between hydrological stages, grey triangles correspond to high flood samples and black dots to low flow period, (All samples from 2014 to 2016).

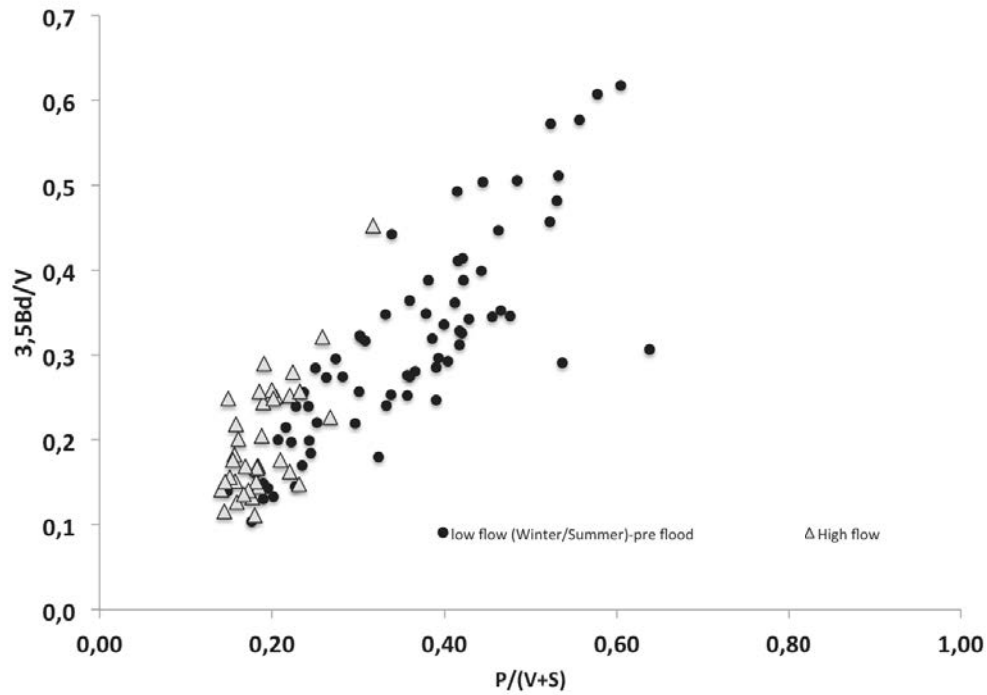


Figure 3. 27 Property-property plot of $P/(V+S)$ vs $3,5Bd/V$ tracing deep soil contribution and DOM degradation state (All samples from 2014 to 2016).

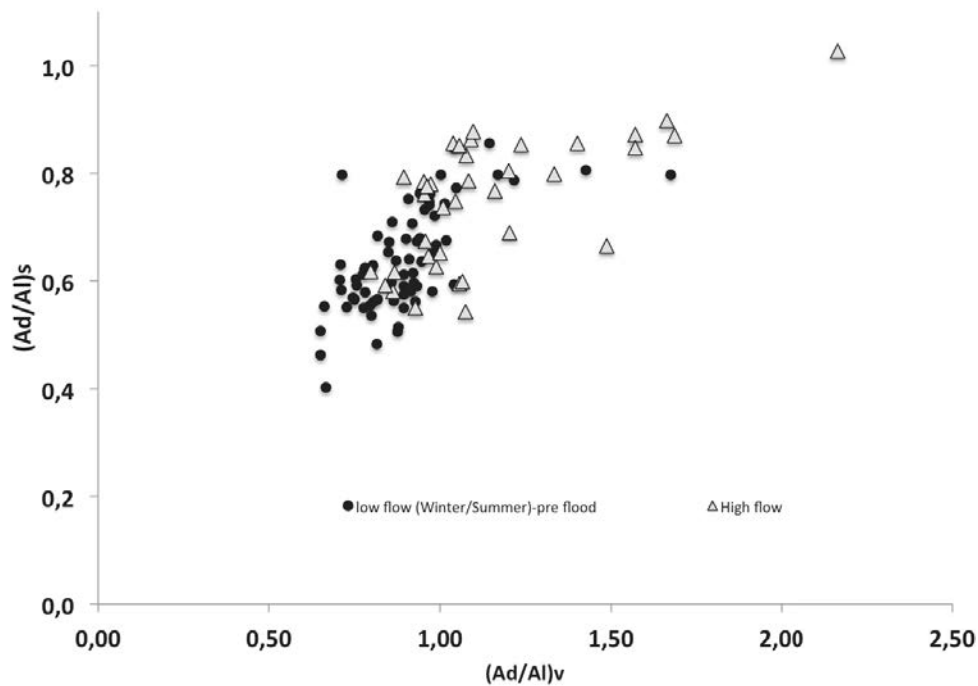


Figure 3. 28 Property property plot of $(Ad/Al)v$ vs $(Ad/Al)s$ tracing degradation state and leaching processes (All samples from 2014 to 2016).

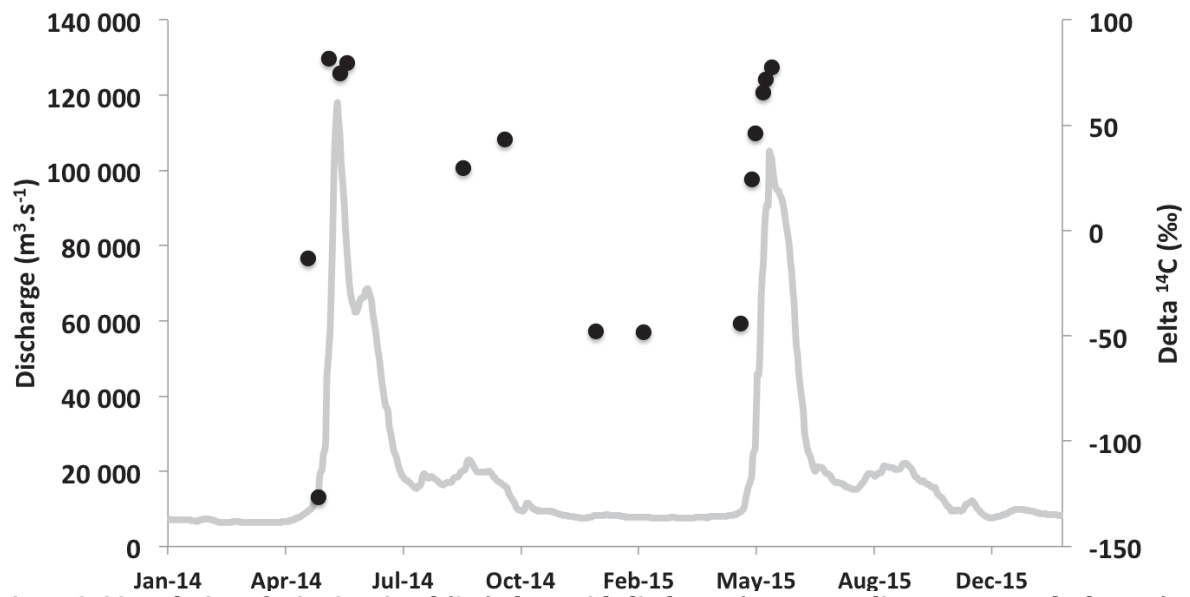


Figure 3. 29 Evolution of ¹⁴C-DOM signal (‰) along with discharge (m³ s⁻¹, grey line, source: Roshydromet) for years 2014 and 2015.

Table 3. 1 Correlation between characterization variables and fluorescence intensity of PARAFAC component (type of correlation, lin=linear, log=logarithmic, pow=power, poly=polynomial)

Component	Discharge (m ³ s ⁻¹)	DOC (mg/L)	L8 (mg,100mg OC)	S8 (ug/L)	3,5Bd/V	(Ad/Ad)v	P/V	C/V	S/V	S ₂₇₅₋₂₉₅	FI	Freshness index	HIX
Cp1	0.81 (log)	0.80 (lin)	0.70 (lin)	0.68 (pow)	0.30 (poly)	0.50 (lin)	0.65 (poly)	0.36 (poly)	0.4 (pow)	0.86 (pow)	0.80 (lin)	0.71 (lin)	0.75 (lin)
Cp2	0.71 (log)	0.72 (lin)	0.58 (lin)	0.71 (pow)	0.28 (poly)	0.45 (lin)	0.58 (poly)	0.31 (poly)	0.35 (pow)	0.85 (pow)	0.72 (lin)	0.71 (lin)	0.67 (lin)
Cp3	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.71* (log)	<0.005	<0.005	<0.005

* correlation with relative contribution to total fluorescence

Table 3. 2 Published estimates of dissolved lignin flux in the Yenisei river

Reference	Annual dissolved lignin flux (Gg/yr)	Freshet ¹ dissolved lignin flux (Gg/period) (percent of total flux) (%)	Sampling years
Amon et al. 2012	54.3	--(78)	2003-2007
Mann et al. 2016 ²	22.3 +/- 2.3	--	(1999) 2009-2010
This study	53.7 +/- 16.5	46.1 +/- 15.4 (85.7 +/- 3.7)	2014-2016
Arctic watershed estimates	Amon et al. 2012	Arctic Great Rivers ³	192
	Man et al. 2016	Arctic Great Rivers ³ (Pan-Arctic)	98.4 (185.3)

¹ May-June

²CDOM-derived lignin (Lignin₃₅₀) modeled since 1999

³Kolyma, Lena, Yenisei, Ob, Mackenzie, Yukon

Table 3. 3 Synthesis of DOM characterization indicators, average and standard deviation by hydrological period and literature data for the Yenisei river close to the river mouth (from Igarka and above for the literature synthesis)

Period	SUVA ₂₅₄	a350	S ₂₇₅₋₂₉₅	FI	HIX	Freshness Index	Cp1 ³	Cp2 ³	Cp3 ³
Spring freshet ¹ (n=56)	4.22 +/- 0.74	28.69 +/- 9.79	0.016 +/- 0.0056	1.40 +/- 0.04	8.61 +/- 2.30	0.45 +/- 0.035	0.13 +/- 0.03	0.12 +/- 0.03	0.10 +/- 0.04
Low flow period ² (n=59)	3.75 +/- 0.83	11.08 +/- 5.47	0.048 +/- 0.018	1.49 +/- 0.04	4.49 +/- 1.44	0.59 +/- 0.044	0.06 +/- 0.02	0.07 +/- 0.02	0.09 +/- 0.02
Annual average (n=115)	3.98 +/- 0.82	19.66 +/- 11.82	0.032 +/- 0.021	1.45 +/- 0.06	6.50 +/- 2.81	0.52 +/- 0.077	0.09 +/- 0.05	0.10 +/- 0.03	0.10 +/- 0.03
Literature synthesis	Spring 3.9 d	high flow	high flow	high flow					
	Summer 2.8 +/- 0.2 ^d	25.97 +/- 1.02 ^d	0.013 +/- 0.0004 ^d	1.30 +/- 0.04 ^d					
	Winter 2.6 +/- 0.2 ^d	Low flow	Low flow	Low flow					
				1.39 +/- 0.03 ^d					
Period	S8 (ug/L)	L8 (mg/100mg OC)	(Ad/Al) _v	(Ad/Al) _s	pCd/Fd	PON/P	P(V+S)	3.5Bd/V	S/V
Spring freshet ¹ (n=54)	135.84 +/- 80.22	1.25 +/- 0.42	1.41 +/- 0.22	0.73 +/- 0.12	0.57 +/- 0.11	0.27 +/- 0.03	0.22 +/- 0.06	0.23 +/- 0.08	0.34 +/- 0.07
Low flow period ² (n=53)	18.94 +/- 16.84	0.46 +/- 0.31	1.00 +/- 0.19	0.62 +/- 0.10	0.86 +/- 0.30	0.30 +/- 0.03	0.40 +/- 0.10	0.35 +/- 0.12	0.43 +/- 0.06
Annual average (n=107)	77.94 +/- 82.49	0.86 +/- 0.54	1.20 +/- 0.29	0.67 +/- 0.12	0.71 +/- 0.27	0.28 +/- 0.04	0.31 +/- 0.12	0.29 +/- 0.11	0.38 +/- 0.08
Literature synthesis	108.45 +/- 86.17 ^c	1.03 +/- 0.77 ^c	1.03 +/- 0.97 ^c	0.72 +/- 0.69 ^c					0.31 +/- 0.31 ^c
	high flow	high flow	high flow	high flow					high flow
	Low flow	Low flow	Low flow	Low flow					0.28 +/- 0.017 ^d
	67.83 +/- 9.03 ^d	0.71 +/- 0.10 ^d	1.32 +/- 0.13 ^d	0.85 +/- 0.07 ^d					Low flow
	15.45 +/- 4.60 ^d	0.32 +/- 0.01 ^d	0.92 +/- 0.11 ^d	0.84 +/- 0.06 ^d					0.36 +/- 0.014 ^d
C/V	P/V	S(mg/100mg OC)	C(mg/100mg OC)	V(mg/100mg OC)	P(mg/100mg OC)	Period	14C ‰	Period	C/N
0.07 +/- 0.02	0.31 +/- 0.09	0.29 +/- 0.08	0.06 +/- 0.02	0.90 +/- 0.33	0.25 +/- 0.07	Spring freshet ¹ (n=8)	65.8 +/- 18.4	Spring freshet ¹ (n=55) Low flow	33.2 +/- 8.7
0.10 +/- 0.03	0.58 +/- 0.15	0.13 +/- 0.09	0.03 +/- 0.02	0.30 +/- 0.21	0.15 +/- 0.08	Low flow period ² (n=7)	-30.3 +/- 55.9	period ² (n=54) Annual average (n=109)	3.86 +/- 10.7
0.08 +/- 0.03	0.44 +/- 0.19	0.21 +/- 0.12	0.04 +/- 0.02	0.60 +/- 0.41	0.20 +/- 0.09	Annual average (n=15)	21.0 +/- 63.0		25.9 +/- 12.2
0.07 +/- 0.08 ^c	high flow						high flow		Yenisei Delta
0.073 +/- 0.066 ^d	Low flow					Literature synthesis	108.8 +/- 14.3 ^e	Literature synthesis	69.1 ^a (summer) Yenisei estuary
0.165 +/- 0.021 ^d	Low flow						Low flow		43.8 +/- 4.5 ^b (summer)

¹ defined as the period when discharge > 20 000 m³s⁻¹ ² defined as the period when discharge < 20 000 m³s⁻¹ ³ Fluorescence intensity

^a Lobbes et al., 2000
^b Amon and Meon, 2004
^c Amon et al., 2012
^d Mann et al., 2016
^e Raymond et al., 2007

CONCLUSION GÉNÉRALE

Les campagnes d'échantillonnages menées entre 2014 et 2016 ont permis de collecter des échantillons représentatifs des différents moments clés du cycle hydrologique du Ienisei. Durant les trois années de prélèvement, près de 117 échantillons ont été collectés, chacun correspondant à une date différente. La majeure partie des échantillons a été collectée durant la période de crue de printemps qui présente la plus grande variabilité au niveau des changements de débit et de flux de matière. Des points de prélèvements ont également été réalisés en fin d'été, en automne et durant l'hiver à une fréquence moins élevée, afin d'avoir un aperçu de ces périodes qui contrastent fortement avec la crue de printemps. Les outils de caractérisation des MOD incluant les biomarqueurs de la lignine, les propriétés optiques des MOD et la datation ^{14}C du COD ont été appliqués avec succès afin de décrire la dynamique, la composition, les sources et l'état de dégradation des MOD transportées par le Ienisei.

La première partie de cette thèse a permis la création d'une base de données recensant les mesures de la qualité des MOD dans les rivières du globe. Nous avons pu dresser un inventaire des méthodes appliquées, identifier les besoins d'amélioration et de développement, estimer la couverture géographique des campagnes d'échantillonnages pour la caractérisation des MOD, et mettre en évidence la variabilité des données relevées selon un gradient de latitude. Une standardisation des méthodes de caractérisation permettant des comparaisons entre études à l'échelle globale est nécessaire, en particulier concernant les méthodes basées sur les études de fluorescence par PARAFAC et les études de bio-labilité. Les efforts d'échantillonnage des dernières années ont permis d'étendre la couverture spatiale mais à l'échelle globale elle reste limitée et polarisée sur des zones privilégiées. La représentativité temporelle des campagnes d'échantillonnage nécessite également des améliorations pour couvrir l'ensemble du cycle hydrologique et l'inclusion des événements extrêmes (crues, tempêtes, sécheresses, pollutions ponctuelles etc...) qui sont particulièrement importants dans les bilans globaux. Le développement de capteurs *in situ* est donc spécialement nécessaire afin de faciliter l'acquisition de données à haute fréquence permettant de capturer les dynamiques les plus éphémères et reposera sur la recherche, le développement et la validation de proxies fiables de la qualité des MOD.

Dans la deuxième partie de cette thèse nous avons étudié la dynamique du carbone dissous dans le Ienisei au cours de trois cycles hydrologiques consécutifs. Nous avons suivi les concentrations en COD et en avons déduit des estimations des flux transitant par le fleuve. Nous avons également rapporté les teneurs en éléments majeurs dans les eaux du Ienisei ainsi que les principales variables physico-chimiques afin de donner un aperçu de l'environnement dans lequel les MOD sont exportées. Nos résultats viennent confirmer le rôle crucial de la crue de printemps dans les export de COD par le Ienisei, cette courte période (mai-juin) contribuant jusqu'à plus de 70% des exports annuels. Le suivi à haute fréquence a permis de décrire de façon détaillée les variations du COD au cours de la crue de printemps. Le signal du COD semble principalement contrôlé par le débit avec une importante augmentation des concentrations observée durant la montée de crue. Cependant, le pic de concentration en COD a été atteint 5 à 7 jours avant le débit maximal. Ce phénomène suggère la mobilisation d'un réservoir important de MOD facilement accessible vers les espaces aquatiques au moment de la fonte des neiges et du lessivage des horizons supérieurs et des litières. Cet apport conséquent de MOD est probablement accompagné d'un effet de dilution lié à la forte augmentation du débit.

La troisième partie de la thèse s'est intéressée à l'évolution de la qualité des MOD au cours de la crue de printemps du Ienisei. La plupart des indicateurs utilisés ont confirmé la forte variabilité temporelle du signal des MOD principalement contrôlé par les changements hydrologiques annuels. La plupart des contributions terrigènes ont lieu pendant la crue de printemps (>80% du flux de lignine). Cette période spécifique est l'un des plus importants composants des flux de carbone organique dans les rivières arctiques mais est aussi très certainement un élément sensible aux changements climatiques. Les principales tendances observées comprennent l'export de MOD jeunes, fraîchement lixiviées de la végétation terrestre et des litières végétales pendant la crue de printemps dominée par les écoulements de surface et un basculement vers des exports de MOD plus anciennes et plus dégradées durant la période de débit de base où les flux d'eau sont majoritairement souterrains. D'après les biomarqueurs de végétations dérivés de la lignine (S/V, C/V ratios), la principale source des MOD pendant la période de crue provient du bois de gymnosperme, suggérant ainsi la forêt boréale comme principale contributeur aux MOD du fleuve arctique. Les taux de *p*-hydroxyl phénols (P) relevés indiquent également que les couverts de mousses sont

potentiellement une source complémentaire de MOD durant la crue de printemps. Cette source additionnelle est la seule pouvant expliquer le décalage du signal de végétation source global des MOD par rapport à une source pure de gymnosperme. En effet, la contribution probable des forêts d'angiosperme du sud du bassin versant du Ienisseï pourrait expliquer la différence par rapport à une source pure de bois de gymnosperme mais pas la présence importante de *p*-hydroxyl phénols. Les quelques données collectées durant les périodes de débit de base, suggèrent, concernant la qualité des MOD, un signal plus variable qu'attendu avec des différences marquées entre le début de la saison froide (septembre-décembre) et la fin de l'hiver et la période précédant la crue de printemps (janvier-avril). Ces différences sont probablement en lien avec les changements d'écoulement des eaux et de taux de dégradation des MOD pendant la période de regel de la couche active et d'englacement des eaux du fleuve. Finalement, lorsque l'on étudie les MOD à l'exutoire d'un bassin versant, surtout dans le cas d'une zone de drainage aussi vaste et hétérogène que celle du Ienisseï, le signal des MOD en terme de quantité et de qualité représente un signal intégré qui retranscrit l'interaction de multiples facteurs incluant le climat, la topographie, l'hydrologie, la végétation, la géologie, l'étendue et l'état du pergélisol, la pédologie et qui peuvent être extrêmement complexes à différencier les uns des autres. Le devenir du COD et ses diverses implications environnementales soulignent la nécessité de développer des études interdisciplinaires incluant des approches physico-chimiques, biologiques et écologiques à différentes échelles et en faisant le lien entre les différents compartiments, terrestre, aquatique continental et océanique. Des études menées en parallèle dans des sous bassins stratégiques du Ienisseï pourraient faciliter les interprétations des tendances observées à l'exutoire et mieux évaluer les processus associés en cours localement. Le développement des techniques d'analyse sur des composés spécifiques, par exemple la datation ^{14}C spécifique de la lignine, des lipides ou des sucres peut également permettre une meilleure différenciation des sources et des processus influençant les MOD de rivière.