INVESTIGATING THE CHEMICAL COMPOSITION AND BIOAVAILABILITY OF

ARCTIC RIVER DISSOLVED ORGANIC MATTER (DOM) USING BIOMARKERS

A Thesis

by

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ABSTRACT

Arctic rivers are the dominant pathways for the transport of terrestrial dissolved organic matter (DOM) to the Arctic Ocean, but knowledge of lability, sources, and transformations of organic carbon and nitrogen in Arctic river watersheds is extremely limited. This study uses chemical analyses of enantiomeric amino acids and carbohydrates as biomarkers to investigate the chemical composition and bioavailability of DOM in five major Arctic watersheds. Carbohydrate-based indicators are sensitive to polysaccharide components derived from all plant sources; hydroxyproline and D-amino acids serve as indicators of plant and bacterial nitrogen, respectively. The results show the bioavailability of DOM in Arctic rivers is strongly correlated with seasonal discharge, vegetation topography, and water residence time. Pulses of bioavailable DOM were observed in the Siberian Rivers during the spring freshet, whereas the Mackenzie River exhibited extensively degraded DOM throughout all stages of the hydrograph. Freshet samples showed elevated input of plant-derived dissolved organic nitrogen. Bacterial organic matter comprised a significant fraction of riverine DOM (20-40%). These results demonstrate the importance of bacteria in regulating DOM composition and reactivity in Arctic rivers.

DEDICATION

To my parents, whose unending support has always pushed me forward.

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NOMENCLATURE

DOM	Dissolved organic matter
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
THAA	Total hydrolysable amino acids
THNS	Total hydrolysable neutral sugars

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1. INTRODUCTION

1.1 Scientific Merit

Arctic rivers deliver large amount of particulate and dissolved organic matter (~42 Tg OC) to the shallow Arctic shelves (Dittmar and Kattner, 2003, Rachold et al., 2004, McClelland et al., 2012, Goñi et al., 2013). Arctic watersheds store 30-50% of global soil organic carbon within shallow permafrost and almost 10% of global biomass in the form of vegetation (Gorham, 1991, Tarnocai et al., 2009). As global temperatures rise, permafrost thaws and water discharge increases, potentially mobilizing reservoirs of ancient and fresh organic matter. However, there is much debate about the extent of the influence of climate on the carbon cycle in the Arctic. Some studies suggest increasing flow paths, residence times, soil interactions, microbial activity, and respiration rates will cause a net reduction of dissolved organic carbon (DOC) export from these watersheds (Moore et al., 1998, Striegl et al., 2005, Alling et al., 2010). Others predict the rate of terrestrial dissolved organic matter (DOM) and DOC export is increasing and will continue to accelerate dramatically over the next century as a result of increased release from permafrost, primarily due to greater water yield caused by a warming climate (Frey and Smith, 2005, Gordeev and Kravchishina, 2009, Kicklighter et al., 2013). This study, which seeks to elucidate the transport and transformations of terrestrial DOM within Arctic watersheds, will contribute novel insights on riverine processes in the Arctic as well as improve our ability to predict the effects of climatic shifts on the fate of terrestrial DOM.

An existing database provided by the Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments (PARTNERS) network and the Arctic Great Rivers Observatory (Arctic-GRO) was integrated into this study to further current knowledge about the composition, bioavailability, and sources of Arctic DOM and understanding Arctic shelf dynamics of carbon and nitrogen cycling.

1.2 Arctic Climate and Ecosystem

The Arctic region, separated into High and Low Arctic, integrates a diverse spectrum of vegetation and soil regimes with complex hydrological and topographic

characteristics dependent on each unique watershed (Amon et al., 2012, Serreze and Barry, 2014). The High Arctic—the region above the tree line—is characterized by an extreme form of tundra, known as polar desert, whereas the Low Arctic transitions from taiga into shrub land and boreal forests in lower latitudes (Serreze and Barry, 2014).

Vegetation across the Arctic region transitions from taiga dominated by coniferous evergreen trees (gymnosperms) in the southern regions, to treeless tundra composed of lichens, mosses, and angiosperm vegetation in the north (Amon et al., 2012, Serreze and Barry, 2014). Subarctic vegetation, located south of the tree line, encompasses spruce, fir, larch, birch, and mountain ash trees, whereas tundra above the tree line gradually shifts northward from spruce, dwarf birch, willow, herbs, and shrubby vegetation to moss, lichens, sedges, rush, and cottongrass (Hannemann and McGinley, 2010).   Over the last two decades, tundra cover has decreased by almost 18% due to warming global temperatures, decreasing the moss and lichen coverage in favor of shrubs (White et al., 2007, Epstein et al., 2015).

Discontinuous and continuous permafrost is widespread above 50-60˚ N, restricting soil drainage that leads to extensive peatlands, especially in the Ob watershed (McGuire et al., 2009, McGuire et al., 2010). The upper layer (30-100cm) of the permafrost, known as the active layer, freezes and thaws seasonally, particularly in the Low Arctic (Hannemann and McGinley, 2010, Serreze and Barry, 2014). Peatlands are formed by extensive wetlands that sequester massive amounts of carbon as dead organic matter is degraded (Hannemann and McGinley, 2010).

Arctic watersheds store 30-50% of global soil organic carbon within shallow permafrost and between 10% and 20% of global biomass in the form of vegetation (Gorham, 1991, Tarnocai et al., 2009, McGuire et al., 2010). Arctic rivers deliver vast amounts of DOM to the Arctic Ocean coastal margins, which could affect ocean primary production, carbon remineralization, and carbon burial (Hedges et al., 1997, Gattuso et al., 1998, Holmes et al., 2013). Terrestrial DOC loading is correlated with many environmental factors but changes over the last few decades have been primarily attributed to climate-induced increases in runoff (Kicklighter et al., 2013).

The Arctic region has experienced disproportionate sensitivity to climate change over the last several decades (Serreze et al., 2000, IPCC and Change, 2007), leading to a growing concern for the potential mobilization of DOM from thawing permafrost (McGuire et al., 2009). Surface coverage of permafrost is estimated to decrease in area by over 10×10^6 km^2 by 2100, which could result in the release of organic matter that has not been previously exposed to decomposition (McGuire et al., 2010). As permafrost thaws and ice melts, river discharge in the Arctic watersheds increases, potentially transporting newly introduced organic matter into the Arctic system (McGuire et al., 2009, McGuire et al., 2010, Vonk and Gustafsson, 2013).

1.3 Arctic River Watersheds

Arctic Rivers integrate a variety of parameters that are indicative of major climatic shifts. For example, increased river discharge over the past few decades corresponds to increased surface air temperature and changing climatic patterns, such as the North Atlantic Oscillation (NAO) (Peterson et al., 2002).

The greatest contribution of riverine discharge to the Arctic Ocean can be attributed to six major rivers: Mackenzie, Yukon, Kolyma, Lena, Ob, and Yenisey (Peterson et al., 2002, Alling et al., 2010, Amon et al., 2012). These watersheds cover over 65% of the total Arctic Ocean catchment area (Dümenil Gates et al., 2000, Holmes et al., 2013). Together, the Lena, Ob, Yenisey, and Mackenzie contribute to almost 70% of the total discharge volume (Serreze and Barry, 2014). These watersheds have been established as primary pathways of DOM storage and transportation, particularly DOC and dissolved inorganic carbon (DIC) from the watersheds to the Arctic Ocean (Amon, 2004, Benner et al., 2005, Striegl et al., 2005, Finlay et al., 2006, Raymond et al., 2007, Amon et al., 2012, Holmes et al., 2012, Anderson and Amon, 2014). Arctic permafrost soils store over twice as much carbon as the atmosphere (Mann et al., 2014, Ward and Cory, 2015), approximately 88% of which is perennially frozen (Tarnocai et al., 2009).

The largest Arctic rivers, based on discharge and watershed area, are mostly located on the Eurasian continent, within Siberia. The Mackenzie is the only river in this study located in the North American Arctic, in northwestern Canada. This river originates in

the Great Slave Lake and extends into the Beaufort Sea, flowing mostly through the Mackenzie Lowlands, a valley 400km wide mostly covered in swamps, bogs, and lakes (Mackenzie River, 2016). Along the western side of the river, the Mackenzie Mountains rise up to 1800m in elevation, limiting the tree line to 900m (Mackenzie River, 2016). The eastern banks are bordered by hills with elevations up to 300m. Vegetation in the northern part of the watershed mostly consist of treeless grasslands and tundra dominated by legumes, carices, and mosses, whereas white and black spruce are abundant in the south (Timoney et al., 1993, Amon et al., 2012). The Mackenzie is the fourth largest Arctic river in terms of discharge, delivering approximately 1.4 Tg C of DOC annually to the Beaufort Sea (Raymond et al., 2007, Holmes et al., 2012).

The Kolyma, the easternmost Siberian river, is the smallest of the major rivers but is the world's largest river watershed that is almost entirely underlain by perennial permafrost (Holmes et al., 2012, Mann et al., 2012) (Table 1). Located in northeastern Siberia, the Kolyma stretches 2091km (Table 1) from the Kolyma Mountains to the East Siberia Sea. The Kolyma discharges the least volume of the studied rivers (Table 1) and only transports between 0.42-0.82 TgC of DOC per year (Rachold et al., 2004, Holmes et al., 2012). Approximately half of the watershed is covered by larch forests, while shrublands and wetlands comprise the rest (Table 1) (Wagner, 1997, Amon et al., 2012).

The Yenisey is the longest of the Arctic rivers and has the greatest discharge (Table 1). This river originates in the Sayan Mountains and exports 4.69 TgC per year to the Kara Sea (Raymond et al., 2007, Holmes et al., 2012). Approximately a third of the watershed is covered in continuous permafrost and ~67% is dominated by forest (Table 1) (Holmes et al., 2012). Slope and elevation vary across the watershed but slope becomes notably steeper closer to the river's source (Amon et al., 2012). The vegetation gradient encompasses tundra, dominated by dwarf birch, sedges, and mosses, in the north, and taiga, including larch, spruce, birch, and pine, in the south. At the southernmost region of the watershed, toward the headstream, scots pine and dark conifers thrive (Amon et al., 2012).

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The Lena is the second largest Arctic river, stretching 4387 km and supplying the Laptev Sea with 5.6-5.8 TgC of DOC per year (Raymond et al., 2007, Holmes et al., 2012). Surrounded by the Biakal Mountains, Verkhoyansk Ridge, and the Central Siberian uplands, this watershed is mostly covered with continuous permafrost (~77%), limiting vegetation to larch forests in the northern region and pine and birch in the south. Forests dominate this watershed (~72%) and shrublands make up the rest (~13%) (Table 1).

Table 1 Geographical Characteristics of Major Arctic River Watersheds. MAAT = mean annual air temperature, BL = broad leaf, NL = needle leaf. Data compiled from Holmes et al. (2002), Holmes et al. (2012) and Amon et al. (2012).

River and Watershed Characteristics	Kolyma	Lena	Ob	Yenisey	Mackenzie
Discharge (km^3 yr^{-1})	111	581	427	636	298
Length (km)	2091	4387	3977	4803	3679
Catchment (10^6 km^2)	0.65	2.46	2.99	2.54	1.78
MAAT (°C)	-10.1	-6.5	1.4	-1.0	0.7
Mean Slope (m km^{-1})	2.16	1.83	1.28	1.94	2.23
Continuous Permafrost (%)	99	77	1	31	13
Deciduous BL Forest (%)	0.4	1.1	10.2	3.4	1.4
Deciduous NL Forest (%)	49.1	58.8	1.5	32.7	0
Evergreen NL Forest (%)	0.2	7.4	14.9	20.6	23.7
Mixed Forest (%)	0.2	4.9	12.0	10.3	9.0
Total Forest (%)	49.9	72.1	38.6	67.3	34.4
Shrubland (%)	32.1	12.5	2.6	9.0	10.5
Grassland (%)	0.1	0.8	15.9	7.2	30.0
Cropland (%)	0	0.6	22.9	6.2	2.4
Wetlands (%)	3.8	3.3	8.5	2.6	0.1

The Ob, the third largest river in terms of discharge, has the most temperate climate of the watersheds and encompasses the larges peat bog in the world (30% of Ob drainage basin) (Gorham, 1991, Amon et al., 2012) (Table 1). The milder climate conditions allow more variable vegetation, including pine and birch dominating in the forests, and sphagnum mosses being most abundant in the peatlands (Wagner, 1997, Zhulidov and Brannen, 1997, Gordeev et al., 2004). The Ob river delivers 15% of the total freshwater discharge into the Arctic Ocean per year and accounts for 3.05-4.2 TgC of annual DOC discharge (Raymond et al., 2007, Amon et al., 2012, Holmes et al., 2012).

1.4 Biomarker Approach

Hedges and Prahl (1993) defined biomarkers as "organic molecules which can be structurally related to a specific biological source." These molecules are diverse and abundant, making them useful in tracing specific information. Biomarkers come with a set of advantages and disadvantages: their specificity allows for finer resolution of source contribution, they provide additional environmental or diagenetic information, and are more sensitive than bulk measurements because they can be quantified against analytical backgrounds of zero. However, information on distribution of molecules is often scattered or incomplete because biomarkers are most often found as trace molecules, and a minor change in structure can render the biomarker useless (Hedges and Prahl, 1993).

Carbon-normalized yields of amino acids and neutral sugars serve as molecular indicators for the bioavailability of organic matter because they are preferentially used during decomposition (Cowie and Hedges, 1994). High yields of carbon-normalized total hydrolysable amino acids (THAA) and neutral sugars (THNS) dominate living biomass and bioavailable DOM (Cowie and Hedges, 1994, Biddanda and Benner, 1997, Benner and Kaiser, 2003). These biochemicals are therefore good indicators of organic matter ''freshness'' and diagenetic state because these compounds are preferentially utilized during the biodegradation of DOM (Cowie and Hedges, 1994, Keil et al., 2000, Amon et al., 2001, Amon and Benner, 2003, Benner, 2003, Benner and Kaiser, 2003).

Decreasing neutral sugars indicate a decrease in the bioavailability of bulk DOM (Cowie and Hedges, 1994, Bianchi and Canuel, 2011). Relative distributions of neutral sugars provide additional information on the diagenetic state of organic matter. Glucose and galactose are typically more abundant in fresh DOM. As DOM becomes more degraded, glucose (Glc), fucose (Fuc), and rhamnose (Rha) increase relatively, while galactose (Gal), mannose (Man), and arabinose (Ara) decrease (Amon and Benner, 2003). Thus, carbon-normalized yields of THNS have been utilized extensively as indicators of DOM diagenesis, with higher yields characterizing fresh material (Cowie and Hedges, 1994, Skoog and Benner, 1997, Amon et al., 2001, Davis et al., 2009).

THAA are major constituents of fresh DOM and are readily utilized by microbes, therefore acting as useful indicators of diagenetic state (Benner, 2003, Yamashita and Tanoue, 2003, Davis et al., 2009). Additionally, D-enantiomers of aspartic acid, glutamic acid, serine, and alanine have been established as important tracers of bacterial DOM due to their unique abundance in bacterial macromolecules (Dittmar et al., 2001, Kawasaki and Benner, 2006, Kaiser and Benner, 2008).

In this study, we measured THAA and THNS concentrations to investigate the composition, bioavailability, and sources of DOM in five major Arctic Rivers. We used D-enantiomers of aspartic acid (Asx), glutamic acid (Glx), serine (Ser), and alanine (Ala) accumulated during microbial processing of DOM, as tracers of bacterially-derived DOM (Dittmar et al., 2001, Kaiser and Benner, 2005, Kaiser and Benner, 2008). Additionally, hydroxyproline (Hyp), a secondary amino acid closely associated with plant proteins, will be used as a tracer of plant nitrogen, as plants are its only significant source in soils (Philben and Benner, 2013).

1.5 Dissolved Organic Matter

1.5.1 Sources

Detailed information on dissolved organic matter (DOM) sources and composition in Arctic rivers is limited. Available data is mostly based on measurements of lignin and hydroxyl-benzene biomarkers, which track the phenolic constituents of terrestrial plants and optical parameters. Lignin and hydroxy-benzene signatures suggest

that DOM in Arctic rivers is largely derived from water-soluble components of freshly leached plant material during the freshet (Amon et al., 2012). Optical measurements demonstrate that a substantial fraction of Arctic river DOM during low flow conditions stems from mosses and peat bogs with older radiocarbon signatures, suggesting drainage from deeper soil profiles (Neff et al., 2006, Spencer et al., 2008, Holmes et al., 2013).

Amon et al. (2012) found that DOM sources vary seasonally; DOM originating from angiosperm and gymnosperm fresh litter is abundant during spring, while peat- and moss-derived DOM dominates in fall and winter. Acid/aldehyde ratios of lignin phenols vanillyls and syringyls (Ad/Al_v, Ad/Al_s, respectively) and total dissolved lignin phenol (TDLP) concentrations increase during times of peak discharge (spring freshet) as fresh organic litter originating from vascular plant sources is produced (Amon et al., 2012).

Between autumn and spring, most terrestrial precipitation is stored as snow; as this snow melts during late spring and early summer, there is a rapid, large increase in the discharge of water through the rivers known as the freshet period (Amon et al., 2012, Serreze and Barry, 2014). The freshet period across Arctic rivers is characterized by pulses of DOM and DOC flux parallel to increased water flow (Holmes et al., 2008, Amon et al., 2012). A large fraction of spring freshet DOM is composed of freshly leached, highly labile material that reaches the rivers after interacting with frozen, organic-rich soils for a short period of time, explaining the little decomposition and high bioavailability during this period (Holmes et al., 2008, Mann et al., 2012, Wickland et al., 2012).

1.5.2 Composition (DOC, DON)

Biogeochemical composition and concentrations of DOM in Arctic rivers varied greatly across seasons, with a distinct spike during the spring freshet period (Amon et al., 2012). This study focuses on two main components of DOM: dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) throughout the year.

The Arctic Ocean basin and the rivers that drain to it contain the highest concentrations of DOC in surface waters relative to the global average and

approximately 60% of the total organic carbon in rivers exists as DOC (Hope et al., 1994, Freeman et al., 2001, Benner, 2003, Benner et al., 2005). Amon (2004) estimated DOC concentrations in Arctic Rivers to be highest (greater than 1000uM) during the late spring and early summer (freshet period) and begin decreasing in early fall, reaching concentrations as low as 300 μM L^{-1} by winter. The large contribution of terrigenous DOM from Arctic rivers is responsible for the elevated concentrations of DOC in Arctic surface waters (Benner et al., 2005).

DOC age is greatly dependent on seasonal variation. As temperatures rise, flow paths in the soil deepen and hydrological connectivity increases, allowing for previously undisturbed ancient carbon reserves to be released. During the snowmelt and into summer, DOC seems to be only a few decades old and becomes older as the seasons progress (Neff et al., 2006, Raymond et al., 2007). Most Arctic river DOC studied so far has shown modern radiocarbon signatures, but there is a trend of increasing age from spring to summer as the active layer deepens (Neff et al., 2006, Raymond et al., 2007). Some studies suggest that DOC at the mouths of Arctic rivers is much younger than in temperate rivers despite the large reserves of ancient carbon stored in Arctic soils (Raymond and Bauer, 2001, Benner et al., 2004).

DON in Arctic rivers serves as a significant nutrient source for near-shore primary production along coastal shelves (Holmes et al., 2012, Tank et al., 2012) but information on DON sources and compositions in Arctic rivers is extremely limited. Nitrogen demand in river ecosystems strongly depends on bacterial remineralization (Brookshire et al., 2005). Amino acids are important components of DON (Stepanauskas et al., 2000) and appear to be major constituents of bioavailable DOM in Arctic rivers (Brookshire et al., 2005, Wickland et al., 2012). Amino acids are among some of the most rapidly consumed forms of DOM and thus provide key labile end members useful in tracing DON (Brookshire et al., 2005). Some reports have estimated a substantial fraction of DON in aquatic environments is contributed by bacteria (Stepanauskas et al., 2000, Kaiser and Benner, 2008, Tremblay and Benner, 2009). Dissolved amino acids are important components of DON in boreal streams and amino

acid yields have been established as good predictors of DON bioavailability in these systems (Stepanauskas et al., 2000, Wickland et al., 2012).

Kaiser and Benner (2008) estimated that bacteria contribute approximately half of DON in marine environments, establishing the importance of microbial processing in regulating marine productivity and ocean biogeochemical cycles. This study will investigate the extent of bacterial contribution to DON in comparison to plant-derived nitrogen in Arctic rivers at different discharge regimes.

High contributions of bacterial DON during seasons with low flow conditions and in watersheds with longer water residence times, e.g. the Mackenzie River (Yi et al., 2012) are expected because DOM in these rivers will have likely undergone greater decomposition than fresh DOM released during the freshet. Significant transformation of DON already occurs in headwater streams (Brookshire et al., 2005), and it is possible that biomarkers provide conservative estimates of bacterial contributions as DOM molecular structures are altered by extensive diagenesis.

The Arctic holds a significant portion of global biomass as vegetation. Plant-derived nitrogen constitutes a major part of DON (and thus DOM). Hyp has been successfully applied as a useful tracer of plant-derived nitrogen in boreal forest soils and peatlands because Hyp-rich glycoproteins in the cell walls of plants are its only major source in soils (Philben and Benner, 2013). Together, Hyp and D-amino acids provide a powerful suite of biomarkers to determine sources, bioavailability, and reactivity of DON reservoirs in Arctic watersheds.

1.5.3 Lability and Bioavailability

The bioavailability and lability of DOC also seem to be related to season, which determines composition and thus DOC susceptibility to degradation processes (Holmes et al., 2012, Mann et al., 2012, Jørgensen et al., 2015). Recent studies have shown that the chemical composition of DOM is directly related to its lability, or its susceptibility to microbial degradation (Ward and Cory, 2015). DOM in Arctic rivers released during the low flow regime is derived from mosses and peat bogs (Amon et al., 2012), where decomposition rates are lower relative to other anoxic wetland soils and sediment

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primarily due to low soil temperatures, low pH, organic matter quality, and the low availability of nutrients (Moore and Basiliko, 2006). During the freshet period, an increase in DOC and DOM concentrations corresponds to increased freshwater discharge (Mann et al., 2012), with DOM originating from freshly produced, undecomposed vascular plant litter (Amon et al., 2012). Some studies have suggested that leaching and sorption could cause a false degraded biochemical signature of riverine DOM as these processes have skewed these signatures in the past (Aufdenkampe et al., 2001, Hernes et al., 2007). A large fraction of the annual DOC transported across the entire Arctic appears to be labile; consequently, understanding the fate of terrestrial carbon within the Arctic watersheds will further current understanding of coastal and marine processes along the Arctic Ocean shelves and future effects of climate change (Holmes et al., 2012, Mann et al., 2012).

Determination of degradation state of DOM is based on structural changes in biomolecules and changes in relative abundance as the material is processed. Amino acids have been successfully used as indicators of diagenetic state in DOM, where relative abundance of glycine, serine, and threonine increases with increasing degradation, while nonpolar amino acids decrease (Dauwe and Middelburg, 1998). Total hydrolysable amino acids (THAA) are an important component of the labile fraction of riverine DOM (Ittekkot and Zhang, 1989, Spitzy and Ittekkot, 1991, Bianchi and Canuel, 2011) and are therefore useful indicators of DOM decomposition.

Riverine DOM exported into the ocean is susceptible to rapid biodegradation and photochemical alterations (Mopper et al., 1991, Opsahl and Benner, 1997, Kaiser and Guggenberger, 2000). Kaiser and Guggenberger (2000) found that labile DOM derived from polysaccharide sources exhibits weaker sorption in soils than lignin-derived DOM, resulting in refractory lignin DOM accumulation.

Until recently, available Arctic river samples were collected during the summer months and the low flow period resulting in idea that DOM is highly refractory in both the rivers and the Arctic Ocean, with little influence on biogeochemical cycles, especially on the coastal shelf region (Lara et al., 1998, Dittmar and Kattner, 2003,

Köhler et al., 2003, Amon, 2004, McGuire et al., 2009). However, DOM removal appears to have a great dependence on nutrient availability and soil temperature (Davidson and Janssens, 2006, Wickland et al., 2012). Low nutrient levels may limit DOC consumption in rivers during the spring freshet, resulting in a pulse of activity once the riverine DOC enters the coastal ocean, where nutrient levels are higher (Alling et al., 2010). Following the freshet period, as soils thaw and the active layers deepen during summer, hydrologic flow paths interact less with surface soils enriched in organic matter (Finlay et al., 2006) and older carbon is released into the system. Holmes et al. (2008) found that the lability of DOC varies greatly throughout the seasons with up to 40% loss during the spring freshet, when the majority of labile DOC flux occurs. Average losses of DOC were approximately 30%-50% during mixing along the shelf and up to 20% removal occurred in surface waters, which tend to have shorter residence times (Alling et al., 2010). These findings have been supported by other studies that determined significant proportions of high-latitude riverine DOC are broken down by microbial and photochemical processes either in the water column or in sediments after burial (Del Giorgio et al., 1997, Cooper et al., 2005, van Dongen et al., 2008, Mann et al., 2012, Raymond and Spencer, 2015).

1.6 Objectives

The main objectives of this thesis are to provide a detailed analysis of the origins, transformations, and bioavailability of Arctic river DOM during different flow regimes.

Over the last several decades, the Arctic region has experienced disproportionate increases in mean annual air temperatures (MAAT) which are expected to rise further by 4-7°C in the next one hundred years (IPCC and Change, 2007). The warming climate has affected permafrost cover and river flow patterns in the Arctic, potentially mobilizing previously sequestered organic matter.

Approximately 50% of global soil organic carbon is stored in the permafrost of the Arctic River watersheds. Arctic rivers are the dominant pathways for the transport of terrestrial dissolved organic matter (DOM) to the Arctic Ocean, but knowledge of sources, transformations and transfer of organic carbon and nitrogen in Arctic river

watersheds is extremely limited. This study uses chemical analyses of enantiomeric amino acids and carbohydrates to investigate the chemical composition and bioavailability of DOM in five major Arctic river watersheds. In addition, existing measurements of lignin, mono/di-hydroxy benzenes, and radiocarbon measurements will be used to assess the bioavailability of DOM in Arctic rivers and correlate them with seasons, vegetation topography, and water residence time in the watersheds**.**

2. METHODS

2.1 Sample Collection

The Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments (PARTNERS) research group collected samples used for this study from the major Arctic rivers (Kolyma, Lena, Yenisey, Ob, Mackenzie) between 2003 and 2007. Samples were collected upstream from the Arctic Ocean (Figure 1) to represent

Figure 1 Top-view map of six major Arctic rivers surrounding Arctic Ocean and basin with sampling locations indicated by a dot. Image courtesy of PARTNERS. This study excludes data from the Yukon.

surface-to-bottom hydrography and cross-river chemistry with the exception of winter samples, which were collected from under ice (Amon et al., 2012). Samples were collected at Cherskiy discharge gauging station for the Kolyma, approximately 100km upstream from the Arctic Ocean; Zhigansk station for the Lena, approximately 850km upstream from the Arctic Ocean; Dudinka station for the Yenisey, approximately 600km upstream from the Arctic Ocean; Salekhard station for the Ob, approximately 1000km upstream from the Arctic Ocean; and Tsiigehtchic station for the Mackenzie, approximately 300km upstream from the Arctic Ocean (Amon et al., 2012). The

collection device was a torpedo shaped, Teflon coated, 60kg depth-integrated sampler (US D-96). The rivers we sampled at five different locations along a cross-channel transect and combined into one homogeneous sample using a Teflon churn. With the exception of winter samples, which were collected by drilling a hole in the ice, each water sample is representative of not only surface to bottom, but cross-channel chemistry. Water from the Teflon churn was then filtered (0.45 µm Pall Aquaprep 600 capsule filters) into acid-washed 1L polycarbonate bottle and frozen. Frozen samples were thawed and vacuum-filtered through pre-combusted (450°C) 47mm GF/F filters in 20mL aliquots into clean EPA vials before analyses.

2.2 THAA Analysis

Total hydrolysable amino acids (THAA) aspartic acid (Asx), glutamic acid (Glx), serine (Ser), histidine (His), glycine (Gly), threonine (Thr), arginine (Arg), alanine (Ala), tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Ile), leucine (Leu), lysine (Lys), and hydroxyproline (Hyp)) were analyzed on an Agilent 1260 Infinity HPLC system with a fluorescence detector using a modified method developed by Woodward et al. (2007). Samples were hydrolyzed with 6M HCl at 110°C for 20 hours and dried under UHP N_2 gas. During hydrolysis, L-isomers of asparagine and glutamine become D- and L-isomers of aspartic and glutamic acids, denoted as Asx, and Glx, respectively (Kaiser and Benner, 2008). Amino acids were separated using a 1.8µm reversed-phase C18 column (ZORBAX Eclipse Plus C18 Rapid Resolution HT 4.6x50mm 1.8 micron). Phenylalanine could not be reliably quantified in river samples and was excluded.

An aqueous buffer and an organic mobile phase were used for chromatographic separation. Two liters of aqueous buffer were prepared in a pre-combusted (450°C) glass amber bottle with 9.7 mM dibasic Na_2PO_4 and 9.7 mM H_3BO_3. The pH was adjusted to 8.17 with 19M NaOH. The organic phase was acetonitrile: methanol (MeOH): MQ water (45:45:10 v/v).

Primary amino acids were derivatized with o-phthaldialdehyde (OPA) and secondary amino acids with 9-fluorenylmethyl chloroformate (FMOC) for separation and detection. OPA was prepared in three steps: an OPA stock, an OPA reagent, and a

working reagent. The reagent stock was prepared with 36mg of phthaldialdehyde dissolved into 2.5 mL of MeOH. The final OPA reagent was made from 630 µL of OPA reagent mixed with 22 µL of 3-mercaptopropionic acid dissolved into 0.5M borate buffer (pH 10.2). The working reagent was a 1:3 solution ratio by volume of OPA reagent: 0.5M borate buffer. FMOC was prepared by dissolving 42mg of 9-fluorenylmethyl chloroformate into 1.0mL of acetonitrile. After derivatization a diluent (pH = 1.5) prepared with 33mL of mobile phase A and 0.5mL of concentrated H_3PO_4 was added to lower the pH of the reaction solution below 7 before injection.

2.3 DLAA Analysis

Enantiomers of Asx, Glx, Ser, His, Gly, Thr, Arg, Ala, Tyr, Val, Phe, Ile, Leu, and Lys were analyzed according to the method developed by Kaiser and Benner (2005). Samples were hydrolyzed with 6M HCl at 110°C for 20 hours and dried under UHP N_2 gas. An OPA/isobutyryl-L-cysteine (IBLC) reagent was used for analysis. The amino acids were separated using a Poroshell 120, EC-C18, 4.6 x 100 mm, 2.7 µm column. A binary gradient was used for separation. A 40mM K_2HPO_4 aqueous buffer at pH 6.12 and an organic solution of MeOH: acetonitrile (30:1 v/v) were used as mobile phases. Measured values of enantiomeric amino acids were corrected for acid-catalyzed racemization according to Kaiser and Benner (2005). Only D-Asx, D-Glx, D-Ser, and D-Ala were detected.

2.4 Neutral Sugar Analysis

Seven total hydrolysable neutral sugars (THNS) (fucose (Fuc), rhamnose (Rha), arabinose (Ara), galactose (Gal), glucose (Glc), mannose (Man), xylose (Xyl)) were analyzed according to Skoog and Benner (1997) with modifications. Samples were hydrolyzed in 1.2M H_2SO_4 and neutralized with a self-absorbed ion retardation resin (Kaiser and Benner, 2000). After desalting with a mixture of cation and anion exchange resins, neutral sugars were isocratically separated with 25 mM NaOH on a PA1 column in a Dionex 500 system with a pulsed amperometric detector (PAD). Detector settings are analogous to (Skoog and Benner, 1997).

2.5 Bacterial Contribution to Riverine DOM

Bacterial processing of riverine DOM is reflected by C-normalized concentrations of D-Asx , D-Glx , D-Ser , and D-Ala (Kaiser and Benner, 2008, Tremblay and Benner, 2009). Contributions of bacteria to carbon in DOM were determined by comparing C-normalized biomarker yields in field samples to average yields in freshly-produced bacterial DOM (Kawasaki and Benner, 2006, Kaiser and Benner, 2008). The percentages of bacterial C and bacterial N in riverine DOM were calculated as follows:

$$\text{Bacterial DOC or DON (\%)} = \frac{Biomarker\ _{DOM}}{Biomarker_{bacterial\ DOM}} * 100$$

where $Biomarker_{DOM}$ is the C- or N-normalized concentration of a specific biomarker in riverine DOM and $Biomarker_{bacterial\ DOM}$ is the C- or N-normalized concentration in bacterial DOM. Average D-amino acid yields (nmol mgC^{-1}) from incubation experiments in two freshwater systems— Lake Murray (Kawasaki and Benner, 2006) and groundwater (Shen et al., 2015)—were used as endmembers for 100% bacterial DOM (Table 2). D-Ser was excluded in this study because this enantiomer is not as prevalent as the others (McCarthy et al., 1998).

Table 2 D-amino acid endmembers in freshly-produced bacterial DOM from two freshwater systems.

	D-Asx (nmol mgC^{-1})	D-Glx (nmol mgC^{-1})	D-Ala (nmol mgC^{-1})	Reference
Bacterial DOM-Lake Murray	11.2	4.5	8.9	Kawasaki and Benner (2006)
Bacterial DOM- Groundwater	5.8 ± 3.3	15 ± 7.8	24 ± 11	Shen et al. (2015)

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2.6 Annual Load Calculation

Annual loads for THAA and THNS for each river were calculated using the US Geological Survey LoadEstimator (LOADEST) program (Runkel et al., 2004) coupled with the LoadRunner interface (Booth et al., 2007) to automate runs. Daily discharge data between 2003 and 2007 for the five Arctic rivers in this study were obtained from the Arctic Great Observatory and PARTNERS (NSF-1107774). Annual load outputs were converted to Tg yr^{-1}.

3. RESULTS

3.1 Discharge, Concentrations and Yields

DOC concentrations were averaged and weighted to discharge in each river. Averages of THNS (μmol L^{-1}), THAA (μmol L^{-1}), D-AA (μmol L^{-1}), Hyp (nmol L^{-1}), THNS (%OC), and THAA (%OC) were weighted to river discharge and DOC (Table 3). The Lena had the highest concentrations of DOC, THNS, and D-AA (Table 3). The Ob had the highest concentrations of Hyp and the highest yields of THNS and THAA organic carbon (Table 3). The Yenisey had the highest average concentration of THAA (Table 3). All biochemical concentrations and yields were lowest in the Mackenzie except percent D-AA, which was highest in this river (6.8%±1.16). Pulses of THAA and THNS occurred during times of peak discharge each spring freshet, while lowest concentrations occurred during periods of low discharge (Figure 2).

The five Arctic rivers in this study export a combined total of 0.187 TgC yr^{-1} of amino acid carbon (AA-C) and 1.13 TgC yr^{-1} of neutral sugar carbon (NS-C) annually. The Lena accounts for >30% of total DOC exported in the Arctic while the Mackenzie accounts for <5%. Ratios of AA/DOC and NS/DOC are lower in the Mackenzie than any other river and ratios across the Siberian Rivers are similar regardless of river discharge or length (Table 3).

Table 3 Weighted average concentrations of dissolved organic carbon (DOC) to river discharge; total hydrolysable neutral sugar (THNS) concentrations to DOC and discharge; total hydrolysable amino acid (THAA) concentrations to DOC and discharge; average concentrations of D-amino acids (D-AA) weighted to DOC and river discharge; average concentrations of hydroxyproline (Hyp) weighted to DOC and river discharge; average THNS yields of organic carbon (%OC); average THAA yields of organic carbon (%OC); and average percent D-AA. Discharge and DOC data provided by the Arctic Great Rivers Observatory (NSF-1107774). Annual loads of DOC, AA carbon (AA-C), and NS carbon (NS-C) calculated using LOADEST with LoadRunner (Runkel et al., 2004, Booth et al., 2007).

	Kolyma	Lena	Ob	Yenisey	Mackenzie
DOC (μmol L^{-1})	597.2	921.5	842.2	842.4	384.8
THNS (μmol L^{-1})	1.34±0.06	1.81±0.12	1.68±0.09	1.16±0.06	0.29±0.01
THAA (μmol L^{-1})	1.63±0.12	2.26±0.16	2.31±0.16	2.34±0.16	0.64±0.05
D-AA (μmol L^{-1})	0.07±0.02	0.11±0.02	0.11±0.02	0.09±0.02	0.04±0.01
Hyp (nmol L^{-1})	6.02	8.38	9.90	4.63	3.07
THNS (%OC)	1.05±0.71	1.02±0.96	1.20±0.50	0.88±0.62	0.51±0.18
THAA (%OC)	0.92±0.29	0.76±0.37	0.97±0.26	0.87±0.26	0.55±0.19
D-AA (%)	4.72±0.57	5.42±1.05	5.00±1.00	4.01±0.57	6.8±1.16
DOC load (TgC yr^{r})	0.86	6.66	3.91	4.65	1.15
AA (TgC yr^{-1})	0.012	0.061	0.044	0.063	0.007
NS (TgC yr^{-1})	0.070	0.398	0.281	0.351	0.030
DOC Total (%)	4.99	38.66	22.70	27.00	6.68
AA-C (%)	5.49	32.69	23.88	33.97	3.97
NS-C (%)	6.21	35.20	24.84	31.06	2.69
AA/DOC	0.012	.009	0.011	0.014	0.006
NS/DOC	0.082	0.060	0.072	0.076	0.026
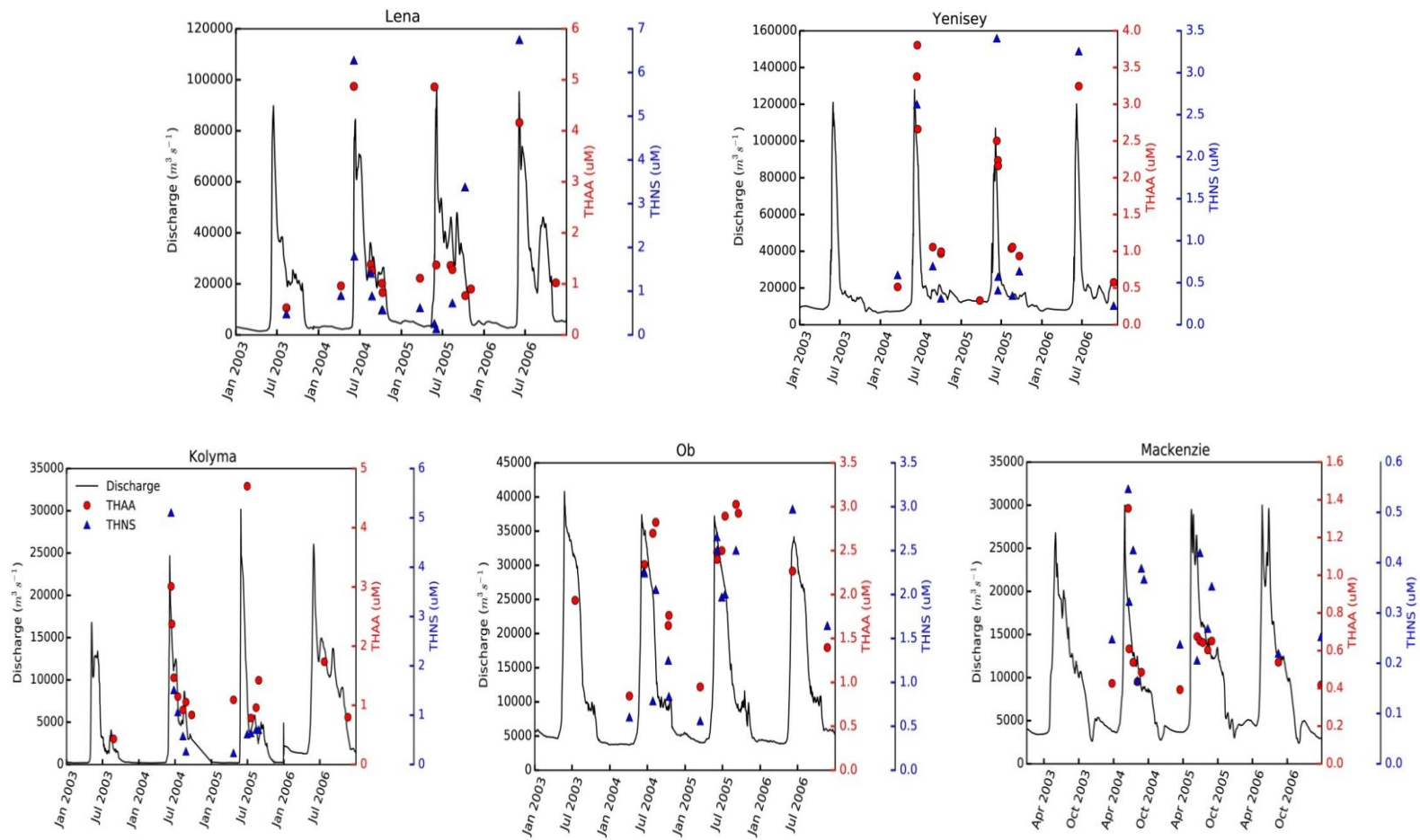
Figure 2 Seasonal discharge (m^3 s^{-1}) and concentrations (μmol L^{-1}) of total hydrolysable amino acids (THAA) and total hydrolysable neutral sugars (THNS) in five major Arctic rivers between 2003 and 2007.

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3.2 Molecular Composition of Arctic Riverine DOM

Season and flow-averaged molecular composition of amino acids and neutral sugars showed minor variability across all rivers. The dominant amino acids in all rivers were Gly, Ala, Asx, Glx, and Ser. Glc was the dominant neutral sugar in all rivers except the Lena, where Rha was most abundant (Figure 3).

Compositional variations between THAA and THNS among rivers and flow regimes were explored using principal component analyses (Figure 4). A weak separation of THAA relative abundance by river was detected (Figure 4, left). Gly (mol%) was enriched primarily in the Mackenzie River. The high flow and low flow regimes showed a difference in composition driven by Gly, and the mid flow shares compositional similarities between high and low flow (Figure 4B, left). Relative abundances of THNS were distributed similarly across all rivers and all flow regimes (Figure 4, 5, right).
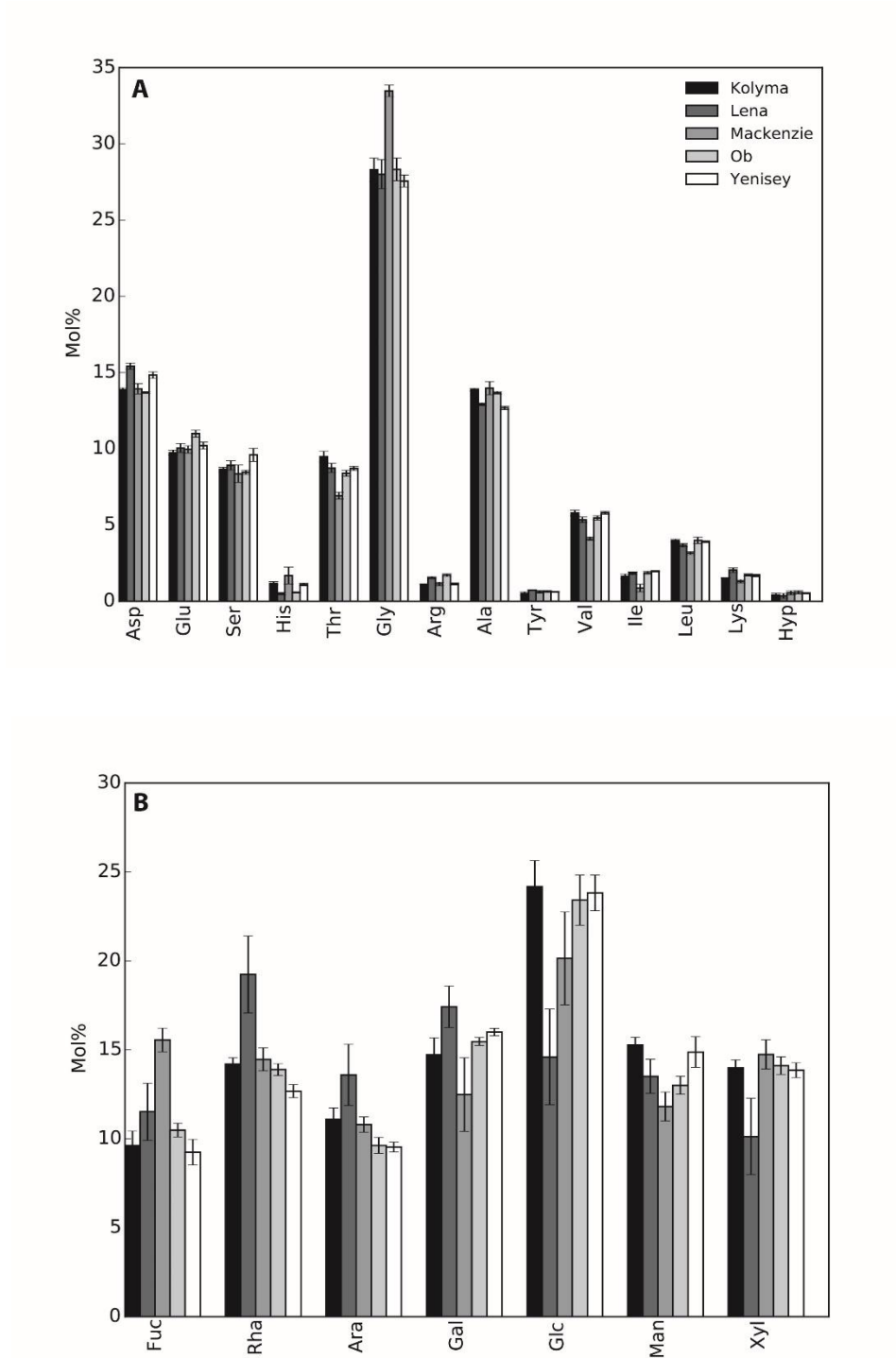
Figure 3 Relative abundances in mole percent (mol%) of THAA and THNS for five Arctic rivers. Averages weighted to discharge ($m^3\ s^{-1}$) and dissolved organic carbon (DOC) concentrations ($\mu mol\ L^{-1}$).
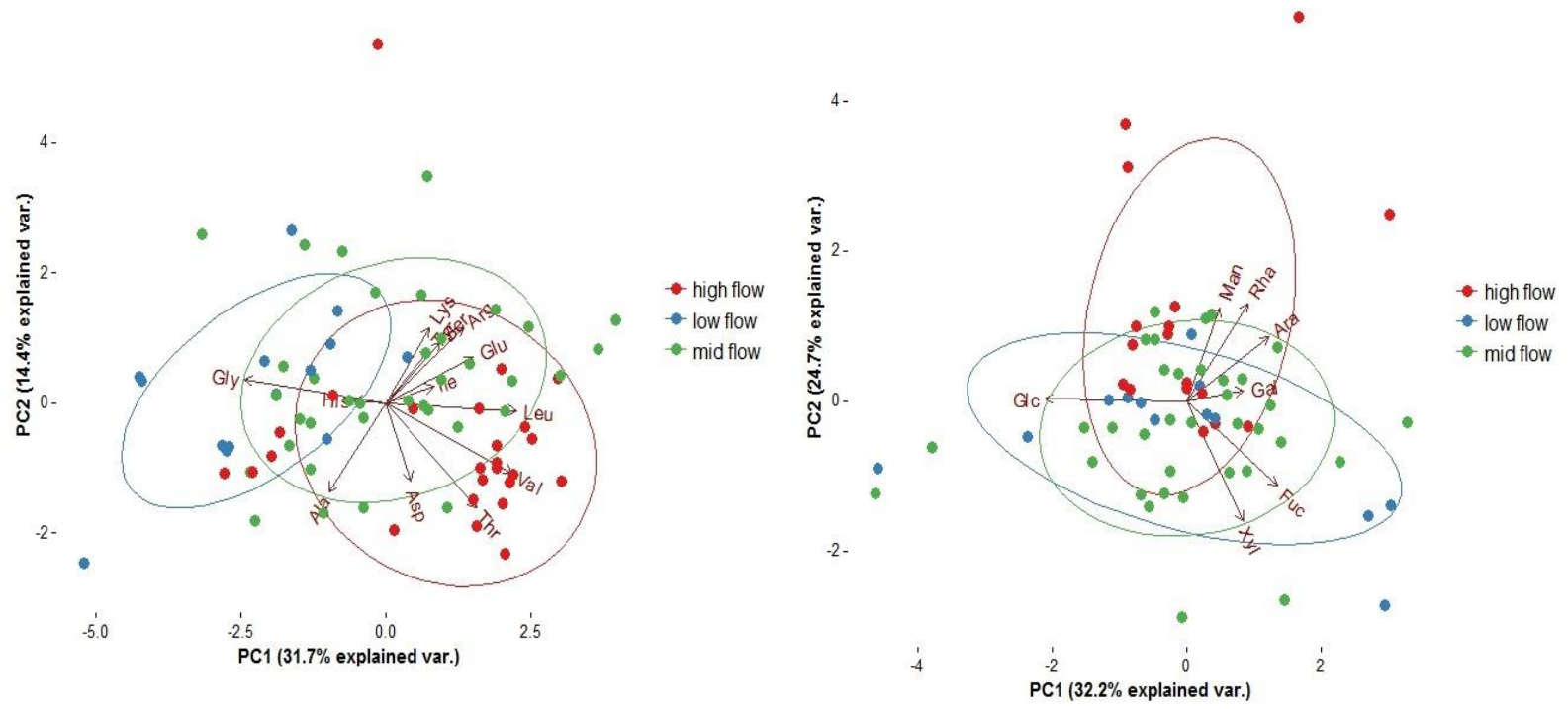
Figure 4 Principal component analysis (PCA) biplots of relative abundance of THAA (left) and THNS (right) per flow regime.
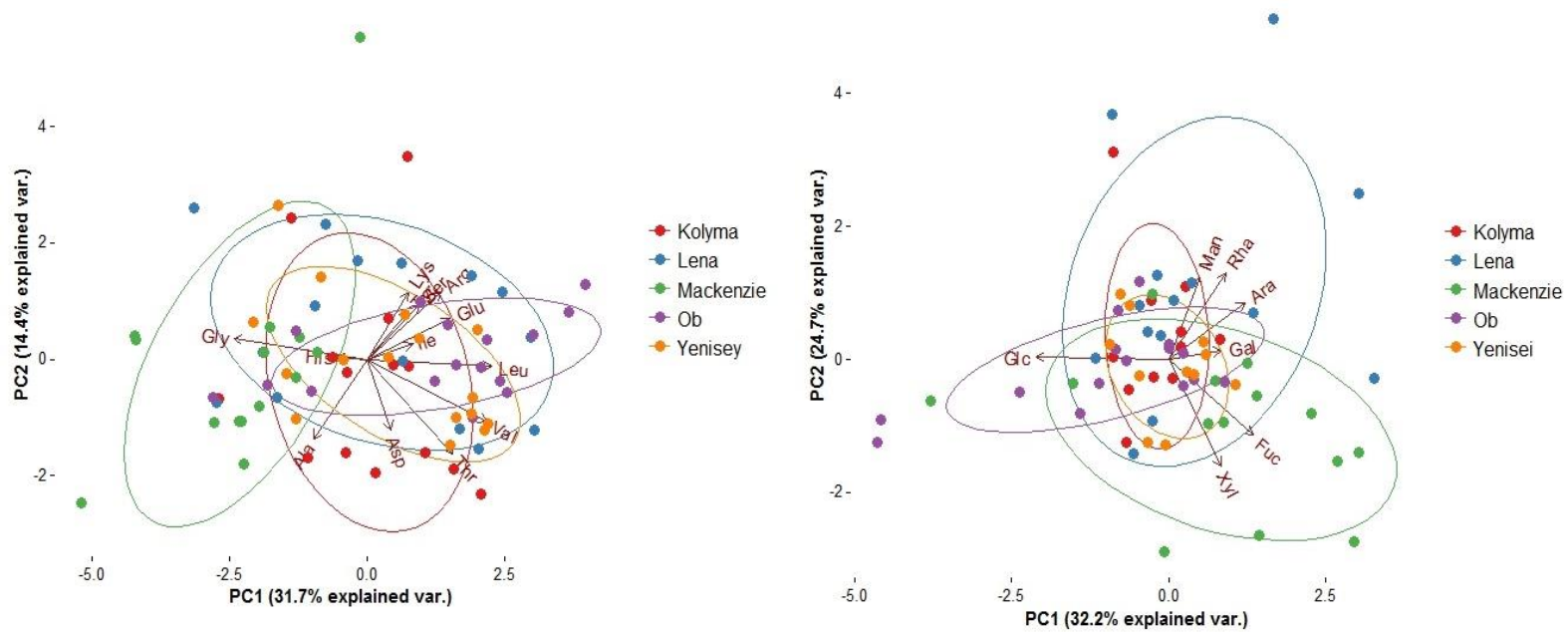
Figure 5 Principal component analysis (PCA) biplots of relative abundance of THAA (left) and THNS (right) per river.
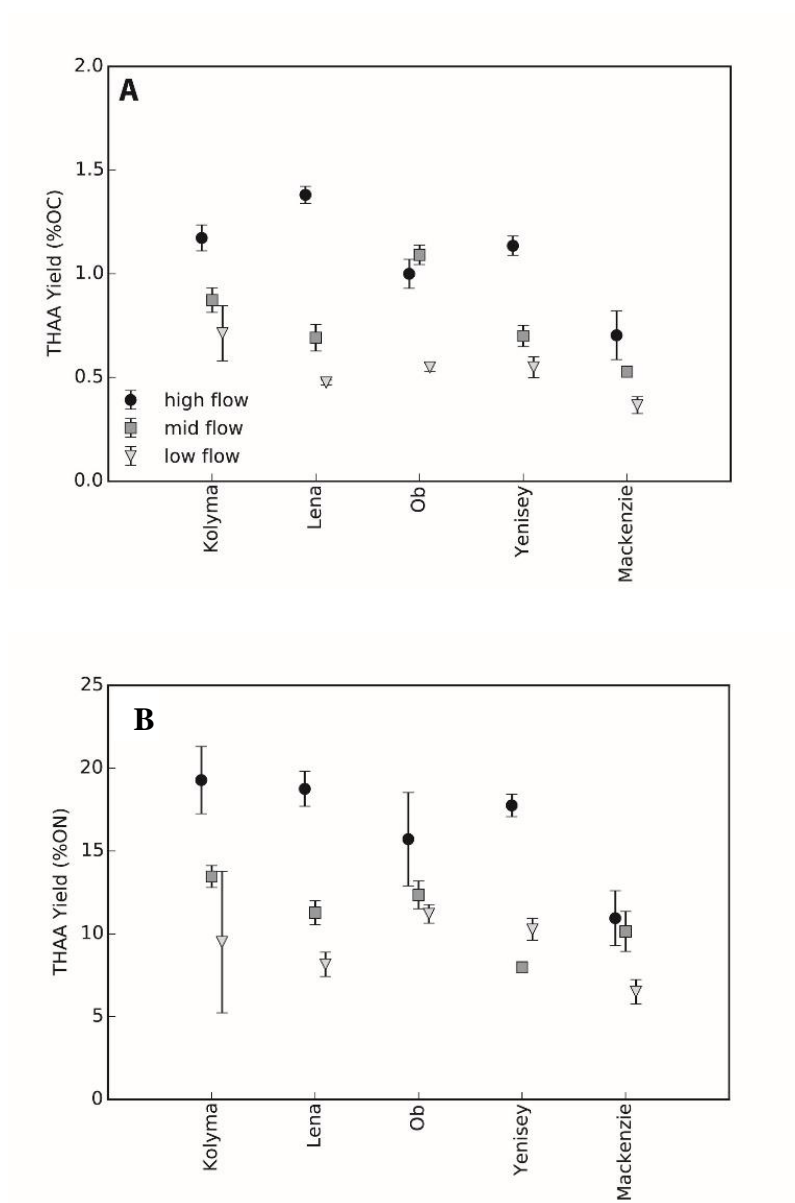
Figure 6 A) C-normalized yields of THAA in percent organic carbon (%OC); C) N-normalized yields of THAA in percent organic nitrogen (%ON) for five Arctic rivers across three flow regimes between 2003 and 2007.

Carbon-normalized yields of organic THAA and THNS depended on flow (Figure 6, 7). All rivers showed elevated C-normalized yields of THAA during the high flow regime except the Ob, which shows a slightly higher yield during the mid-flow period (Figure 6). The Siberian Rivers showed elevated concentrations of C-normalized yields of THNS during the high flow period, while the Mackenzie showed consistently lower yields across all flow regimes (Figure 7). Average C-normalized yields of THAA in percent organic carbon (%OC) across all flow regimes were highest for the Ob (0.973 %OC) and lowest for the Mackenzie (0.551 %OC). Average concentrations of THNS across all flow regimes were highest for the Ob (1.20 %OC) and lowest for the Mackenzie (0.508 %OC). The Siberian Rivers showed elevated N-normalized yields of organic nitrogen during the high flow regime and lower yields during low flow (Figure 6B). The Mackenzie showed no significant difference between high flow and low flow yields of organic nitrogen, but did show lower yields during low flow.
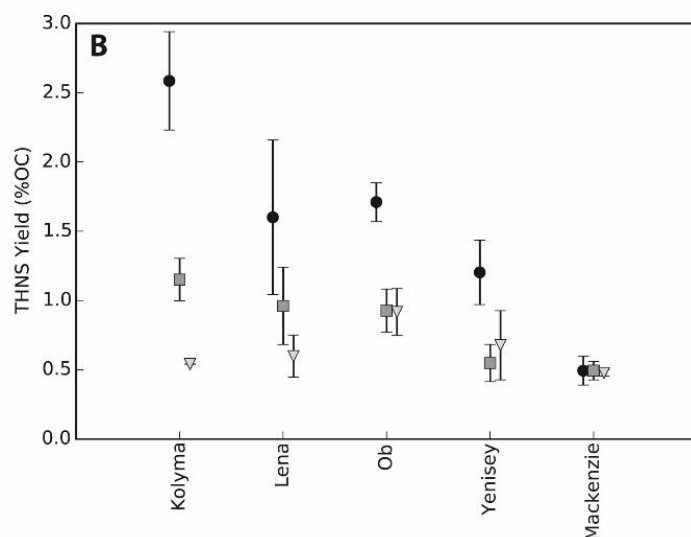
Figure 7 C-normalized yields of THNS in percent organic carbon (%OC) for five Arctic rivers across three flow regimes between 2003 and 2007.

3.3 Sources of DOM in Arctic Rivers

        C-normalized concentrations (nmol mgC^{-1}) of D-amino acids showed a uniform distribution across all flow regimes in all rivers (Figure 8A). C-normalized concentrations of Hyp were elevated during the high flow period in the Siberian Rivers and uniformly distributed across all flow regimes in the Mackenzie (Figure 8A). C-normalized yields of D-amino acids (nmol mgC^{-1}) showed similar distribution across all flow regimes for all rivers (Figure 9A). Percent D-AA is defined as the sum of the concentrations (µmol L^{-1}) of four D-enantiomers (D-Asx, D-Glx, D-Ser, and D-Ala) divided by the sum of all L- and D-amino acids analyzed in this study and multiplied by 100. All rivers showed similar percentages of D-AA across all flow regimes (Figure 9A). The Mackenzie had consistently higher D-AA percentages than the Siberian Rivers (Figure 9A, Table 3).

        Bacterial contribution to DOM was calculated based on previous incubation experiments conducted in freshwater and groundwater (Table 2). Yields obtained from a lacustrine and groundwater system represent a surface freshwater regime and a freshwater soil regime. The average of these endmembers was used to calculate 100% bacterial DOM. Biomarker calculations indicated that bacteria contribute 23-37% of DOC in Artic River DOM. Bacterial DOC in the Kolyma accounts for ~35% of DOC during high flow, ~29% during mid flow, and ~34% during low flow. In the Lena, bacteria contribute ~28% of OC during high flow, ~23% during mid flow, and ~25% during low flow; ~33% of DOC during high flow in the Ob is bacterially derived, ~37% during mid flow, and ~31% during high flow. The Yenisey accounts for ~27% of bacterially derived DOC during the freshet, ~24% during mid flow, and ~20% during winter low flow (Figure 9B). Percentages of bacterial C were uniformly distributed across all flow regimes in all rivers (Figure 9B). Bacterial nitrogen contribution could not be reliably calculated due to high inorganic N content.
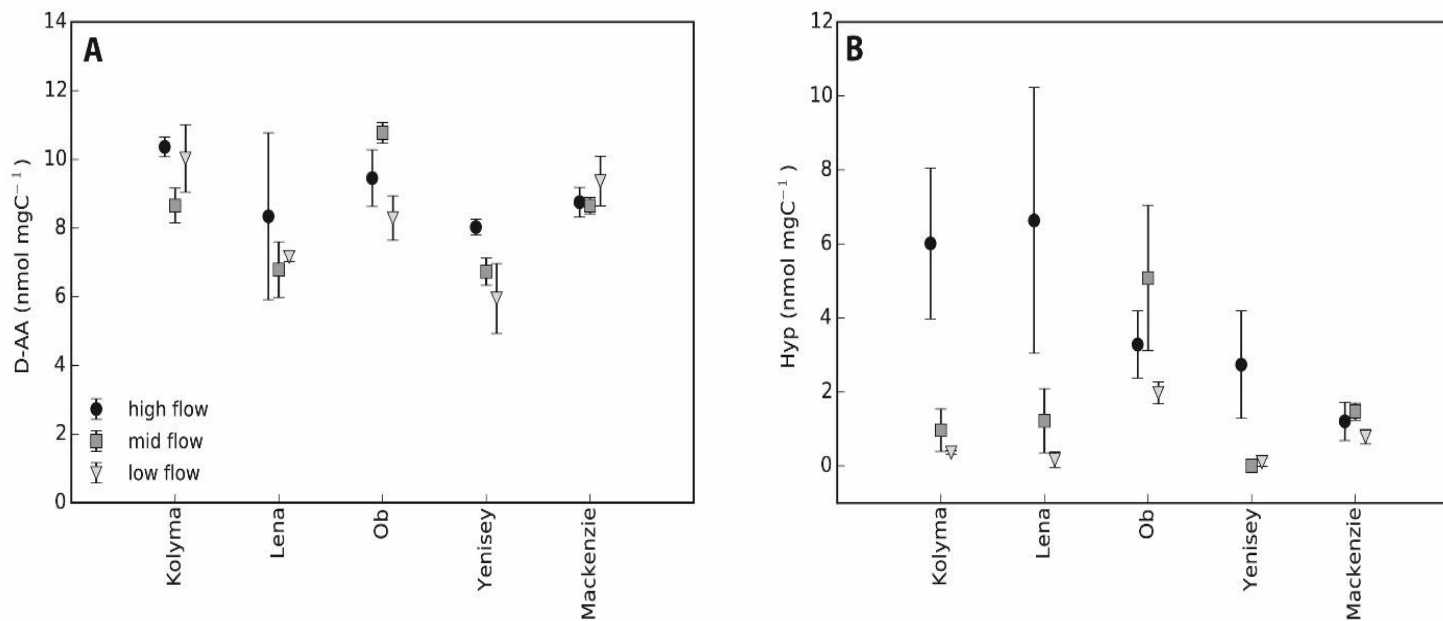
Figure 8 C-normalized D-amino acid (D-AA) and hydroxyproline (Hyp) concentrations (nmol mgC^{-1}) for five Arctic rivers across three flow regimes between 2003-2007.
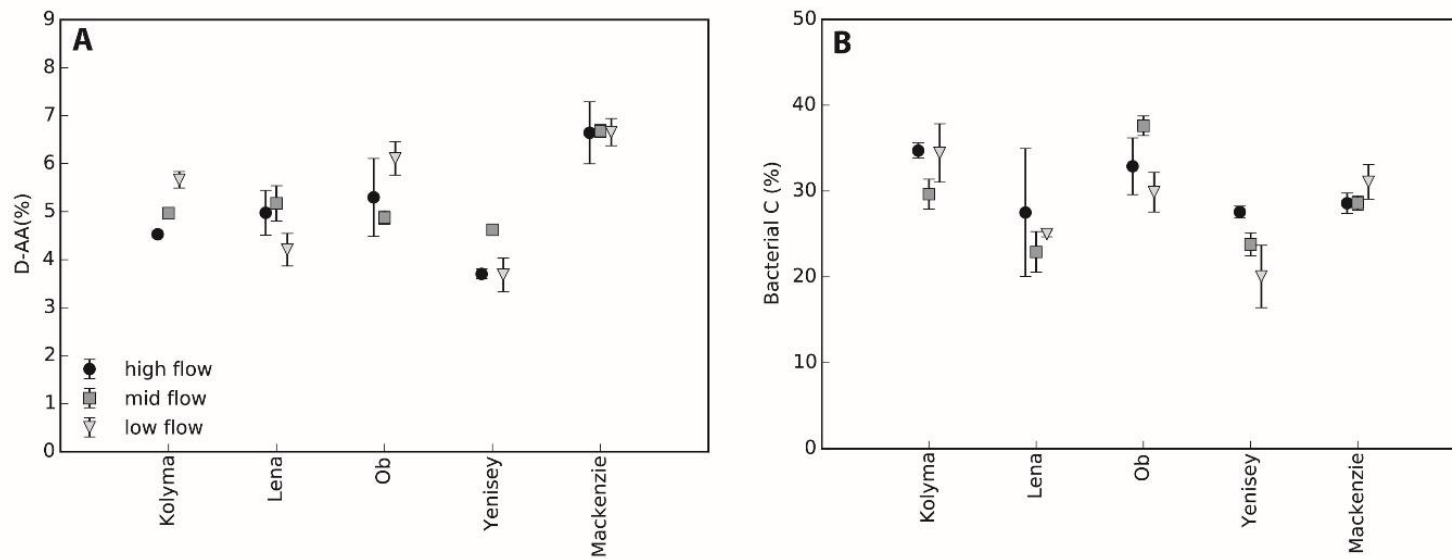
Figure 9 A) Percent D-AA (%) contribution to riverine DOM; B) percent bacterial C (%) contribution to riverine DOM in five Arctic rivers across three flow regimes between 2003 and 2007.

3.4 Diagenetic Indicators in Arctic Rivers

Common diagenetic indicators of DOM and radiocarbon (Δ^{14}DOC) measurements were compared using a Spearman's rank correlation and hierarchical clustering (Figure 10). Indices in clusters are more similar to each other. Clusters in boxes have statistically significant positive correlations, while clusters outside the boxes have significant negative ones. Numerical values represent non-significant p-values. Bacterial indicators (FI, BIX, D-AA, and Gly) are more similar to each other, while vascular plant indicators (TDLP, Ad/Al$_{v,s}$, THAA, and DI) are more similar. FI was not significantly correlated to any index. Carbohydrates (THNS, Glc) are clustered together but are not significantly correlated with any other index. There was a significant positive relationship between Δ^{14}DOC and the vascular plant indices, and a significant negative correlation between Δ^{14}DOC and the bacterial indices.
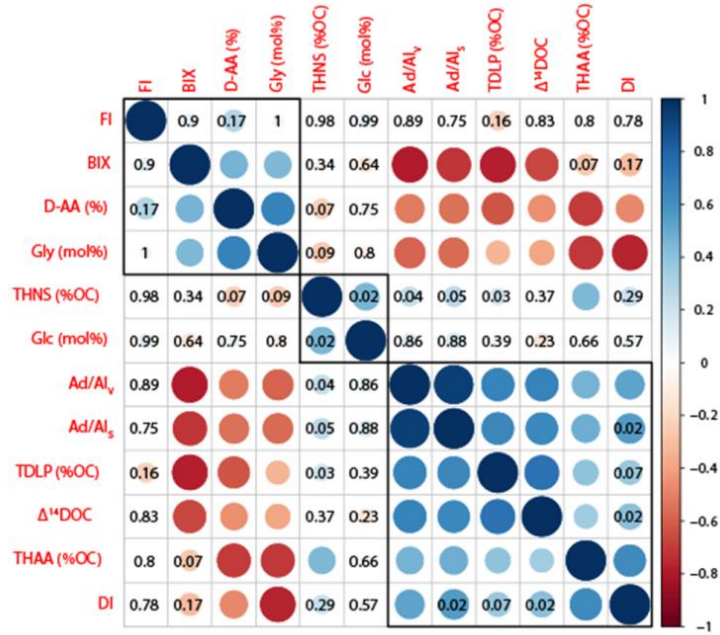
Figure 10 Comparison of common diagenetic indicators for riverine DOM. Spearman's rank correlations calculated at 99% significance. Numeric values indicate non-significant p values. Significantly-correlated parameters are sorted in hierarchical clustering; red circles show significant negative correlations and blue circles show significant positive ones.

4. DISCUSSION

4.1 Abundance of DOC, THAA and THNS in World River Systems

The majority of global river discharge is attributed to only a small number of rivers. The Amazon is the largest river in the world in terms of water discharge, accounting for 34.6% of the total global river discharge, followed by the Congo, which contributes to 6.9% (Commission on Geosciences, 1994). The Mississippi is the largest river in North America and the sixth largest river in the world (Dai and Trenberth, 2002, Shen et al., 2012). The major Siberian Rivers are comparable in size and water discharge to the Mississippi, and the Yenisey and Lena follow closely as the largest Arctic rivers and the seventh and ninth largest rivers in the world, respectively. (Dai and Trenberth, 2002). The three largest Siberian Rivers (Yenisey, Lena, and Ob) contribute to cover ~76% of the total catchment area and contribute to over 50% of riverine discharge to the Arctic Ocean (Amon et al., 2012).

The major Arctic rivers export annually a combined total of ~25 Tg C yr^{-1} (nearly 40% of global river DOC discharge) as DOC (Dittmar and Kattner, 2003, Raymond et al., 2007, Manizza et al., 2009, Amon et al., 2012, Holmes et al., 2012). The Siberian rivers contribute to >80% of the annual DOC discharge to the Arctic Ocean (Amon et al., 2012). DOC in temperate and tropical rivers is strongly influenced by interactions with the soil and varies greatly in age (Hedges et al., 1986, Raymond and Bauer, 2001, Benner et al., 2004). Climate, vegetation, and soil composition play a major role in DOM fluxes in rivers (Meybeck, 1982, Neff and Hooper, 2002, Kawahigashi et al., 2006), although knowledge of the specific control mechanisms is still limited. In colder climates, higher DOC concentrations have been observed in taiga and tundra rivers, followed by rivers in wet tropics and temperate zones (Meybeck, 1982, Neff and Hooper, 2002). Neff and Hooper (2002) found that DOC fluxes are strongly influenced by variations in vegetation type. DOC release is greatest from soils in tundra regions dominated by shrubs, followed by tussock tundra, spruce and wet sedge tundra soils, while DON fluxes are highest in tussock tundra zones and lowest in regions dominated by wet sedge vegetation (Neff and Hooper, 2002). DOC removal was observed to be

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greater in areas dominated by spruce and shrubs compared to tussock and sedge (Neff and Hooper, 2002), which is consistent with Arctic watershed biomes. In comparison, the lower part of the Amazon— the most biodiverse watershed in the world (Wright, 2002)—is dominated by evergreen broadleaf forests and grasses (Junk, 1973, Jordan, 1982, Hedges et al., 1986). DOM in this watershed tends to have low concentrations of nitrogen, amino acids, and neutral sugars mostly due to soil partitioning (Hedges et al., 1994, Neff and Hooper, 2002).

The Mississippi and Atchafalaya rivers export ~1% of global DOC discharge, with the Atchafalaya carrying more bioavailable DOM than the Mississippi (Shen et al., 2012). DOC concentrations in major rivers usually range between 250-750μmol L^{-1} (3-9 mg L^{-1}) (Benner, 2003) but DOC in Artic rivers has been measured between 330-1000 μmol L^{-1} (4-13 mg L^{-1}; Table 4). This discrepancy could be explained by increased hydrological connectivity during the spring freshet and the distinct pulse of DOM associated with peak discharge (Shen et al., 2012). The Lena exports the greatest amount of DOC annually (5.7 Tg C yr^{-1}) in the Arctic, while the Kolyma exports the least (0.7 Tg C yr^{-1}) (Dai and Trenberth, 2002). The Amazon River exports about five times more DOC than the Lena, despite the Amazon's annual water discharge being over 11 times greater than the Lena (Table 4). The Amazon and Congo Rivers contribute the majority of global DOC, while the rest of the world's rivers transport < 6 Tg C yr^{-1} each (Table 4). The three largest Arctic Rivers (Lena, Ob, and Yenisey) export a combined total of ~14.5 Tg C yr^{-1} as DOC, which is almost equivalent to the DOC load of the Congo River, greater than seven times the load of the Mississippi River, and about half that of the Amazon (Table 4).

Based on the limited THAA and THNS data available for rivers, we observe that the Atchafalaya, Mississippi, and Congo Rivers have the highest concentrations of amino acid and neutral sugar carbon, followed by the Amazon (Table 4). Carbon-normalized concentrations of THAA and THNS (nmol mgC^{-1}) in the Arctic Rivers were generally lower than reported values for other major world rivers (Table 4). The relative abundance of THAA and THNS was expected to vary significantly by river in

representation of the vegetation diversity in each watershed. Philben et al. (2014) measured the C-normalized concentrations of neutral sugars in representative vascular plants and mosses for Arctic ecosystems. Glucose was observed to be the most abundant sugar in all the studied plants, which our data reflects. The *Sphagnum sp.* mosses were rich in Rha (Philben et al., 2014), which would be expected in the Ob (peat bog) (Wagner, 1997, Zhulidov and Brannen, 1997, Gordeev et al., 2004, Amon et al., 2012), Yenisey (tundra) (Zhulidov and Brannen, 1997, Amon et al., 2012), and Mackenzie (Timoney et al., 1993, Amon et al., 2012). On the other hand, vascular plants lacked Rha but were abundant in mannose and xylose (Philben et al., 2014), which were expected in the larch-dominated Lena (Wagner, 1997, Walter and Breckle, 2002), Kolyma (Wagner, 1997, Amon et al., 2012), and Yenisey (taiga) (Zhulidov and Brannen, 1997, Walter and Breckle, 2002, Amon et al., 2012). Fucose enrichment, characteristic of phytoplankton sources rather than vascular plants in lacustrine systems (Aspinall, 1970, Percival, 1970, Bianchi and Canuel, 2011), suggests that the elevated relative abundance of fucose in the Mackenzie river could be indicative of DOM derived from the extensive lakes dominating this watershed. Contrary to expectations, relative abundance of THAA and THNS was similar across all rivers, suggesting that DOM undergoes extensive degradation within the watersheds and does not reflect source. Additionally, uniformity of relative abundance across all flow regimes indicates that DOM of similar composition is discharged throughout each river regardless of seasonality (Figure 5).

Table 4 Geographical properties and biogeochemical measurements of organic carbon in global rivers. All values normalized to match units in this study. THAA measurements for the Congo River were performed in our laboratory and were C-normalized using initial DOC values from (Spencer et al., 2012).

	Average Discharge[a,c] (km³ yr⁻¹)	Basin Area[a,c] (10⁶ km²)	DOC Flux (Tg yr⁻¹)	Global DOC Flux[c] (%)	DOC Load[c] (gC m² yr⁻¹)	DOC[d,f] (mg L⁻¹)	TOC[f] (mg L⁻¹)	THNS (nmol mgC⁻¹)	THAA (nmol mgC⁻¹)
Arctic									
Kolyma	136.0	0.7	1.2[f]	0.3	1.3	9.6[f]	8.1[f]	151.1	184.7
Lena	588.0	2.5	3.5[f]	2.3	2.3	6.6	7.7	142.2	146.6
Mackenzie	316.0	1.8	1.7[f]	0.6	0.8	4.5	12.5	72.4	136.0
Ob	427.0	3.0	2.9[f]	1.6	1.4	7.1	8.0	186.0	202.1
Yenisey	673.0	2.5	5.2[f]	1.9	1.8	8.5	8.8	139.9	179.8
Yukon	208.0	0.8	1.8[f]	0.6	1.8	8.8	14.0	-	-
Indigirka	54.0	0.3	0.3[f]	0.1[*]	-	4.8	7.7	-	-
Pechora	164.0	0.3	1.7[f]	0.7[*]	-	12.7[f]	13.0	-	-
S. Dvina	104.0	0.3	1.3[f]	0.5[*]	-	11.6	15.3	-	-
Khatanga	108.0	0.3	-	-	-	-	6.3	-	-
Yana	39.0	0.2	0.1[f]	0.04[*]	-	2.8	6.7	-	-
Olenek	48.0	0.2	0.2[f]	0.1[*]	-	6.4	7.2	-	-
Taz	43.0	0.2	-	-	-	-	-	-	-
Pur	32.0	0.1	-	-	-	-	-	-	-
S. America									
Amazon	6590.0	6.1	26.9[c]	10.8	4.4	5.0	7.0	166.1[b]	246.8[b]
Orinoco	1135.0	1.1	5.0[c]	2.0	4.5	2.9	-	-	-
Parana	568.0	2.8	5.9[c]	2.4	2.1	6.1	7.4	-	-
Magdalena	237.0	0.2	0.5[c]	0.2	2.0	-	-	-	-
Essequibo	178.0	0.2	0.9[c]	0.4	5.4	-	-	-	-
Tocantins	372.0	0.8	1.2[c]	0.4	1.5	-	-	-	-
Uruguay	145.0	0.2	0.5[c]	0.2	2.1	3.2	-	-	-
Africa									
Congo	1325.0	3.7	12.4[c]	5.0	3.4	10.7[j]	12.0[j]	-	435.5

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Table 4 Continued

	Average Discharge[a,c] (km³ yr⁻¹)	Basin Area[a,c] (10⁶ km²)	DOC Flux (Tg yr⁻¹)	Global DOC Flux[c] (%)	DOC Yield[c] (gC m² yr⁻¹)	DOC[d,f] (mg L⁻¹)	TOC[f] (mg L⁻¹)	THNS (nmol mgC⁻¹)	THAA (nmol mgC⁻¹)
Ogooue	150.0	0.2	1.3[c]	0.5	6.1	-	-	-	-
Niger	154.0	1.2	0.5[c]	0.2	0.4	2.9	6.3	-	-
Asia									
Amur	344.0	1.9	2.5[c]	1.0	1.3	-	-	-	-
Yangtze	928.0	1.8	1.6[c]	0.6	0.9	12.4	-	-	
Brahmaputra	510.0	0.6	1.9[c]	0.8	3.3	3.2	-	-	-
Ganges	493.0	1.1	1.7[c]	0.7	1.6	4.6	-	-	-
Irrawaddy	486.0	0.4	0.9[c]	0.4	2.2	-	-	-	-
Mekong	467.0	0.8	1.1[c]	0.4	1.4	-	-	-	-
Salween	211.0	0.3	0.2[c]	0.1	0.7	-	-	-	-
Zhujiang	280.0	0.4	0.4[c]	0.2	0.9	-	-	-	-
Europe									
Danube	207.0	0.8	0.6[c]	0.2	0.7	4.7	8.8	-	-
Rhone	53.0[h]	0.1[h]	0.1[h]	0.1[*]	-	-	-	87.8[h]	-
N. America									
Mississippi	552.6[g]	3.0	2.1[c]	0.8	0.7	3.6[g]	7.4	385.7[g]	278.7[g]
St. Lawrence	337.0	1.8	1.6[c]	0.6	0.9	4.9	5.4	-	-
Columbia	236.0	0.7	0.4[c]	0.2	0.6	2.7	3.3	-	-
Atchafalaya	252.4[g]	0.2[j]	1.0[g]	0.4[*]	-	5.3[g]	-	441.4[g]	409.1[g]

[a] Holmes et al. (2013)
[b] Hedges et al. (1994). Measurements for Obidos tributary used due to its distance downstream.
[c] Raymond and Spencer (2015)
[d] Artemyev (1996)
[e] Gordeev and Kravchishina (2009)
[f] McGuire et al. (2009)
[g] Shen et al. (2012)
[h] Panagiotopoulos et al. (2012)
[i] Spencer et al. (2012)
[*] Calculated based on total global DOC as per Hedges et al. (1997) and Raymond and Spencer (2015)

4.2 Chemical Composition and Bioavailability of Arctic Riverine DOM

Amino acid composition in all the rivers is dominated by Gly, Ala, Asx, Glu, Ser, and Thr (Figure 4), which is consistent with other major rivers (Hedges et al., 1994, Dittmar et al., 2001, Duan and Bianchi, 2007). Amino acid carbon accounts for 1.1% of the total annual DOC load in the major Arctic rivers (Table 3). Principal component analysis shows that the THAA composition of the rivers is similar across all the rivers, with the Mackenzie being enriched in Gly (Figure 5B, left). However, there seems to be variation in THAA composition across flow regimes (Figure 5A, left). Gly dominates during the low flow, when more degraded DOM is present, and Leu, Val, Thr, and Asx are more abundant during the high flow, when more bioavailable matter is released.

Neutral sugars account for 6.6% of the annual DOC load in the major Arctic rivers (Table 3). Glucose is the most abundant neutral sugar in all rivers, except the Lena (Figure 4). A possible explanation could be that the Lena has been observed to contain the greatest amount of fresh OM (Amon et al., 2012), possibly lowering the relative abundance of Glc. PCA shows that there is no distinct compositional difference across the rivers or flow regimes (Figures 5A, B, right), suggesting that THNS undergo rapid and extensive degradation in the watersheds and are not indicative of source. The Mackenzie is slightly enriched in Fuc and Xyl (Figure 4D) but overall, the THNS composition in Arctic rivers is uniform.

Amon et al. (2012) determined the lignin phenol composition in the major Arctic rivers to have a strong seasonal correlation as well. Ad/Al ratios are highest during the spring freshet period when DOM is derived from fresh plant material, and lowest during winter base flow. Lignin composition indicates that gymnosperm-derived DOM dominates the freshet flow regime while periods of low flow are dominated by *p*-hydroxybenzenes, typically indicative of moss and peat sources (Amon et al., 2012).

Carbon- and nitrogen- normalized THAA yields in the major Arctic rivers are distinctly elevated during the spring freshet than during periods of low flow (Figure 6). The Mackenzie is the only river without any significant distinction across the flow

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regimes, indicating that the DOM in this river has been extensively degraded by the time it reaches the sampling site due to this river's greater residence time. THNS yields also exhibit a distinct seasonal pattern: higher yields characterize the spring freshet while lower yields dominate periods of low flow (Figure 7).

4.3 Sources of DOM

Previous studies have suggested DOM in the major Arctic rivers originates mainly from soils and vascular plants (Hedges et al., 1994), while autochthonous production is low (Cauwet and Sidorov, 1996, Sorokin and Sorokin, 1996, Dittmar et al., 2001, Benner, 2003). Radiocarbon ages ($\Delta^{14}C$) in Arctic Rivers indicate that DOC in these systems is mostly derived from fresh plant litter and surface or near-surface soil regimes (Benner et al., 2004, Neff et al., 2006). DOC age corresponds closely to seasonal variability; younger, fresher OM characterizes the spring freshet period while older material is more prominent during winter low flow (Benner et al., 2004). The contribution of litter (surface run-off) and vascular plants to Arctic river DOM was estimated to be about 70% based on C/N ratios. Estimates using lignin phenol yields suggested vascular plant derived DOC contributed 16-87% of DOC in the major Arctic rivers varying with flow regime (Amon et al., 2012).

Cowie and Hedges (1994) suggested that neutral sugars could provide useful information about specific terrestrial sources. Although the general sugar composition of plants is similar, relative abundance varies depending on source. For example, mannose and xylose can be used to differentiate between angiosperm and gymnosperm plants, while arabinose is indicative of woody plants or mangroves (Cowie and Hedges, 1984, Cowie and Hedges, 1994, Bianchi and Canuel, 2011). Uniform THNS compositions across all Arctic rivers suggest the relative distributions of neutral sugars are controlled by diagenetic processes and do not reflect source in Arctic rivers (Figure 4, 5). Extensive microbial processing of riverine DOM is consistent with low THNS yields. Bacterial contributions to DOM were estimated based on carbon-normalized concentrations of D-Asx, D-Glx, and D-Ala. Our study indicates that bacteria contribute an important fraction of riverine DOM in the form of DOC (20-40%). The bacterial

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contribution to DOC in Arctic rivers is similar to that in the ocean (~25%) (Kaiser and Benner, 2008) and comparable to estimates for streams (Shen et al., 2015) but lower than estimates for lake water (Kawasaki et al., 2013). High bacterial DOC contributions indicate microbial transformations play an active role in shaping organic matter compositions in Arctic rivers, and compositions do not merely reflect the mixing of materials from various sources. The relatively uniform contribution of bacterial organic matter to bulk DOM across rivers and flow regimes is surprising given the perceived seasonal gradients of microbial activity in Arctic regions. A possible explanation for this pattern may be linked to similar processing histories in Arctic rivers that remove labile fractions of DOM immediately after leaching in soils or in the upper reaches of the watersheds. Samples were collected close to the river mouth allowing sufficient time for extensive processing of DOM even during the spring melt when microbial activity is low.

DON sources in Arctic rivers were variable across seasons alternating between higher contributions of plant-derived proteins during the spring freshest and DON derived from microbial sources and soil-derived humic and fulvic acids. The bacterial contribution to DON was not quantified due to high concentrations of inorganic N in river systems but is expected to be comparable or even higher than what was observed in marine environments (~50%). Higher contributions of reactive DON from plant-protein during the spring freshet suggest this DON may provide an important nutrient subsidy to Arctic shelves potentially supporting enhanced primary production.

4.4 Indicators of Diagenetic State of Riverine DOM

The present data provide a unique opportunity to test the performance of chemical and optical indicators for riverine DOM. Some optical indicators include tracing chromophoric dissolved organic matter (CDOM) absorbance, measuring the fluorescence index (FI), specific UV absorbance (SUVA), and the autochthonous—bacterial—index (BIX) (Stedmon et al., 2000, McKnight et al., 2001, Stedmon et al., 2011, Walker et al., 2013, Fichot et al., 2016, Mann et al., 2016). Biochemical indicators have also been used to trace diagenetic alterations of DOM. Some approaches include

mole percent and yields of THAA, D-AA, THNS, and lignin; lignin phenol ratios, and the degradation index (DI) (Cowie and Hedges, 1994, Dauwe and Middelburg, 1998, Dittmar et al., 2001, Amon and Benner, 2003, Davis et al., 2009, Amon et al., 2012). We compared a few of the most common optical and biochemical indicators and DOC age in a correlation matrix (Figure 10) to find significant correlations and validate the efficiency of these indicators.

The fluorescence index is defined by McKnight et al. (2001) as the "ratio of emission intensity (450 nm/500 nm) at 370 nm-excitation." This ratio is useful in differentiating terrestrial and bacterial sources: a ratio of ~1.9 determines a microbial source while a ratio of ~1.4 indicates terrestrial origins (McKnight et al., 2001). Thus, we can infer that FI values indicating microbially-derived DOM are also indicative of more degraded DOM. According to our results, however, the FI had no significant correlation with any other indicator (Figure 10), suggesting that other indicators may be more efficient as diagenetic tracers.

The biological/autochthonous index (BIX) is assessed by the presence of a previously identified terrestrial peak (C) and a microbial peak (M) within the fluorescence spectrum (McKnight et al., 2001, Walker et al., 2013). BIX is defined as the "ratio of emission wavelengths at 380 nm to that at 430 nm, at a fixed excitation wavelength at 310 nm" (Huguet et al., 2009, Walker et al., 2013). BIX values between 0.8 and 1.0 indicate microbially-derived DOM while values below 0.6 correspond to DOM derived from allochthonous sources (Birdwell and Engel, 2010, Walker et al., 2013).

High carbon-normalized yields and relative abundances of THAA and THNS characterize freshly produced OM, making these biochemicals useful for tracing the diagenetic state of DOM as they are abundant and preferentially utilized during decomposition (Cowie and Hedges, 1994, Biddanda and Benner, 1997, Amon et al., 2001, Benner, 2002, Amon and Benner, 2003, Benner and Kaiser, 2003). Davis et al. (2009) found that C-normalized yields are most useful for early stages of decomposition. Our results indicate that THNS and Glc mole percentages were not significantly

correlated with any other indicator (Figure 10), suggesting that these biochemicals become degraded too rapidly during diagenesis and are best used as qualitative indicators rather than quantitative.

D-enantiomers of Asx, Glx, Ser, and Ala (D-AAs)—found in the cell wall matrix of bacteria—accumulate during diagenesis because they are less accessible to degradation than bulk OM , thus serving as useful tracers of bacterial OM (Tanoue et al., 1995, Nagata et al., 1998, Kawasaki and Benner, 2006). We can therefore assume that a higher yield of D-AAs is indicative of more highly degraded OM in rivers, because it represents greater bacterial presence, and bacteria are the primary decomposers of OM (Dittmar et al., 2001, Kaiser and Benner, 2008).

The degradation index (DI) for Arctic rivers was calculated according to Peter et al. (2012) using an average of groundwater and marine indices as a representative value for river systems. More positive DI values are indicative of fresher DOM, while more negative values indicate greater decomposition (Davis et al., 2009, Kaiser and Benner, 2009, Peter et al., 2012). Davis et al. (2009) observed that DI scores did not correspond to amino acid decomposition rates and suggested that the solubilization of particulate organic matter (POM) or the production of bacterial OM could account for this discrepancy. Therefore, changes in DI are not reliable indicators of OM diagenesis during the early stages of decomposition and are most effective when used during intermediate stages of decomposition that occur in surface waters over annual to decadal time scales (Davis et al., 2009).

Lignin phenols are unique tracers of vascular plant material and high concentrations of these biochemical characterize freshly produced DOM and are a well-established biomarker of DOM freshness, source, and diagenetic state (Hedges and Prahl, 1993, Opsahl and Benner, 1997, Benner, 2003, Amon et al., 2012). The concentration of lignin phenols increases in river water during the spring freshet, confirming the presence of fresher, younger, newly released DOM. Vanillic acid to vanillin $(Ad/Al)_v$ and syringic acid to syringealdehyde $(Ad/Al)_s$ ratios have been used as diagenetic indicators for soil, particulate, and dissolved organic matter in aquatic

systems (Amon et al., 2012). Ad/Al ratios typically increase with increasing degradation state of soil organic matter but the opposite trend has been observed in DOM from Arctic rivers (Amon et al., 2012). Some studies have suggested that fractionation of OM during vascular plant leaching is responsible for this phenomenon (Hernes et al., 2007). In the Arctic Ocean, DOC has been observed to decrease as lignin concentrations increase (Benner et al., 2004).

The Δ^{14}DOC age was compared to all indicators to further investigate the diagenetic state of Artic river DOM and exhibits a significant positive correlation between Ad/Al ratios in these rivers and Δ^{14}DOC, indicating that a significant portion of riverine DOM comes from recently produced vascular plant and litter leachates during the spring freshet. The overall trend indicates that younger matter is more labile and more bioavailable and is exported during the spring freshet. During winter base flow, most matter is older and appears to be recalcitrant. However, some studies theorize that older matter that has been preserved in the permafrost will be reactive and readily available for decomposition if released (Neff and Hooper, 2002, Striegl et al., 2005).

Arctic soils contain a large pool of labile carbon (9-41%) "that could be easily decomposed given optimal conditions," (Neff and Hooper, 2002). Bioavailability of OM in temperate and high-latitude rivers varies seasonally with an increase in OM lability during peak discharge corresponding to increased precipitation and snowmelt (Buffam et al., 2001, Holmes et al., 2008, Fellman et al., 2009, Ward et al., 2012). Peak discharge during the freshet period is characterized by pulses of DOM in all Arctic rivers (Figure 2), suggesting that during the spring flow fresh terrestrial litter leaches into the rivers, elevating the concentrations of these biochemicals. Additionally, some studies have shown that a relative increase in dissolved amino acid concentrations farther downstream and during low flow periods is indicative of refractory DOM (Duan and Bianchi, 2007). Thus, DOM released during high flow periods can be assumed to be labile. The Siberian Rivers show elevated carbon-normalized yields of THAA and THNS during the high flow period, indicating export of bioavailable DOM, agreeing with previous studies (Holmes et al., 2008, Amon et al., 2012). The Mackenzie shows consistently lower

yields across all flow regimes (Figure 2, Table 4), indicating exported DOM is highly degraded within this watershed due to its greater residence time. Water residence time exerts a strong control on the export of bioavailable DOM to the Arctic Ocean by allowing microorganisms more time to decompose the organic matter.

Understanding the relative abundance of amino acids in rivers provides important information about organic matter lability and biogeochemical cycling (Hedges et al., 1994, Bianchi and Canuel, 2011). Yamashita and Tanoue (2003) found that relative abundance of glycine and alanine increased as organic matter became more degraded, while valine, phenylalanine, and isoleucine decreased. In this study, the Mackenzie River was expected to contain more degraded material due to the river's high residence time. PCA showed that the relative abundance of gly (mol%) was highest in the Mackenzie (Figure 4), in agreement with previous studies (Yamashita and Tanoue, 2003). Gly was also more abundant during the low flow regime in all rivers (Figure 4), suggesting that DOM released during this time is more degraded than material exported during the freshet. PCA 1 accounted for >30% of the variability in all rivers and has been attributed to diagenetic processes and the degradation index (Dauwe and Middelburg, 1998, Dauwe et al., 1999, Amon et al., 2001, Yamashita and Tanoue, 2003).

Vegetation is the dominant factor controlling decomposition rates of soil organic matter and DOC lability (Neff and Hooper, 2002). Variations in plant chemistry, in interactions between different plant types and the soil matrix, and in microbial communities across different vegetation types (Coulson and Butterfield, 1978, Verhoeven and Toth, 1995). Thus, differences in vegetation communities regulate diagenesis.

A Spearman's rank correlation matrix sorted into hierarchical clusters suggests that there is a stronger relationship among bacterial indicators (BIX, DAA, Gly) and among vascular plant indicators (Ad/Al, THAA, TDLP, DI) (Figure 10). THNS and Glc serve best as qualitative indicators of OM "freshness" but are degraded too quickly for reliable quantification. These relationships suggest that diagenetic indices should be used

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in conjunction with others for a more complete understanding of OM diagenetic state because sources, structure, and phase of diagenesis influence their effectiveness.

5. CONCLUSION AND BROADER IMPACTS

The Arctic basin only accounts for approximately 1% of global seawater volume yet receives over 10% of the total global riverine discharge (Shiklomanov et al., 2000, Amon and Meon, 2004). The Arctic region is particularly vulnerable to warming global temperatures; as temperatures rise, permafrost thaws and fluvial flow paths deepen, increasing hydrologic connectivity and runoff, which could potentially mobilize previously sequestered reserves of ancient organic matter (Jorgenson et al., 2001, Peterson et al., 2002, Hinzman et al., 2005, White et al., 2007, Alling et al., 2010, McGuire et al., 2010, Serreze, 2010, Holmes et al., 2012, Holmes et al., 2013). Over the last several decades, warming rates have accelerated, resulting in increased freshwater discharge from Arctic watersheds and declining permafrost cover. (Peterson et al., 2002, IPCC and Change, 2007).

Eastern Siberia and the adjacent seas are predicted to experience the highest increase in temperature on Earth as climate changes (Zwiers, 2002). Freshwater runoff has been observed to increase substantially in the region (Peterson et al., 2002), as well as increased thawing of permafrost. Understanding the composition, bioavailability, and sources of riverine DOM is therefore crucial for predicting the effects of future changes due to climate change and furthering insight of biogeochemical cycles on these vast shallow shelf regions.

Increasing temperatures leading to the thawing of permafrost and deepening of the active layer could have unforeseen repercussions on the Arctic freshwater system related to increased river discharge, alterations in precipitation, hydrological connectivity, and organic and inorganic matter storage (White et al., 2007, McGuire et al., 2009, McGuire et al., 2010). Changes in the freshwater system could have complex consequences, thus understanding the cycling of DOM in this sensitive region could provide answers about future impacts of increasing global temperatures.

Through this study, we can conclude that DOM in Artic rivers is more bioavailable during the spring freshet, when the majority of organic matter is derived from fresh plant litter, while DOM released during winter low flow is refractory. We

also observe that extensive degradation of DOM occurs within the watersheds, before it reaches the Arctic Ocean shelves. Most of the DOM in the Mackenzie River appears more degraded than the DOM in the Siberian Rivers, due to its longer residence time.

Finally, we conclude that bacteria are an important source of DOM in Arctic rivers across all flow regimes, contributing up to 40% of DOC in the major rivers.

Despite the significant role that Arctic watersheds play in the land-sea interaction processes and the transport and transformations of terrestrially exported organic matter (Alling et al., 2010), information on the composition and bioavailability of DOM is limited. Therefore, further studies on the variability of DOM coupled with other parameters are crucially needed to understand and predict the effects of a changing climate on Arctic watersheds and biogeochemical cycles on the Arctic coastal shelves.

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