# Dissolved organic matter sources in large Arctic rivers

R.M.W. Amon[a,b,*], A.J. Rinehart[b†], S. Duan[a‡], P. Louchouarn[a,b], A. Prokushkin[c], G. Guggenberger[d], D. Bauch[e], C. Stedmon[f], P.A. Raymond[g], R.M. Holmes[h], J.W. McClelland[i], B.J. Peterson[j], S.A.Walker[b], A.V. Zhulidov[k]

[a]Department of Marine Sciences, Texas A&M University at Galveston, Galveston, USA.

[b]Department of Oceanography, Texas A&M University, College Station, USA.

[c]V.N. Sukachev Institute of Forest SB RAS, Akademgorodok, Krasnoyarsk, Russia

[d]Institut für Bodenkunde, Leibniz-Universität Hannover, Hannover, Germany

[e]Leibniz Institute of Marine Sciences, University of Kiel (IFM-GEOMAR), Kiel, Germany

[f]Department of Marine Ecology, National Environmental Research Institute, University of Aarhus, Roskilde, Denmark.

[g]Yale School of Forestry and Environmental Studies, Yale University, Connecticut, USA

[h]The Woods Hole Research Center, Woods Hole, Massachusetts USA

[i]Marine Science Institute, University of Texas at Austin, Port Aransas, Texas USA

[j]Marine Biological Laboratory, Woods Hole, Massachusetts USA

[k]South Russia Centre for Preparation and Implementation of International Projects, Rostov-on-Don, Russia

[†] Current address: Institute of Arctic Biology, University of Alaska Fairbanks, Fairbanks, AK, USA.

[‡] Current address: Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD, USA

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## Abstract

The biomarker composition of dissolved organic carbon (DOC) of the six largest Arctic rivers was studied between 2003 and 2007 as part of the PARTNERS Project. Samples were collected over seasonal cycles relatively close to the river mouths. Here we report the lignin phenol and p-hydroxybenzene composition of Arctic river DOC in order to identify major sources of carbon. Arctic river DOC represents an important carbon conduit linking the large pools of organic carbon in the Arctic/Subarctic watersheds to the Arctic Ocean. Most of the annual lignin discharge (>75%) occurs during the two month of spring freshet with extremely high lignin concentrations and a lignin phenol composition indicative of fresh vegetation from boreal forests. The three large Siberian rivers, Lena, Yenisei, and Ob, which also have the highest proportion of forests within their watersheds, contribute about 90% of the total lignin discharge to the Arctic Ocean. The composition of river DOC is also characterized by elevated levels of p-hydroxybenzenes, particularly during the low flow season, which indicates a larger contribution from mosses and peat bogs. The lignin composition was strongly related to the average $^{14}C$-age of DOC supporting the abundance of young, boreal-vegetation-derived leachates during spring flood, and older, soil-, peat-, and wetland-derived DOC during groundwater dominated low flow conditions, particularly in the Ob and Yukon Rivers. We observed significant differences in DOC concentration and composition between the rivers over the seasonal cycles with the Mackenzie River being the most unique, the Lena River being similar to the Yenisei, and the Yukon being most similar to the Ob. The observed relationship between the lignin phenol composition and watershed characteristics suggests that DOC discharge from these rivers could increase in a warmer climate under otherwise undisturbed conditions.

## 1. INTRODUCTION

The watersheds of the six largest Arctic rivers (Ob, Yenisei, Lena, Kolyma, Yukon, and Mackenzie) cover more than $10x10^6$ $km^2$ of surface area (larger than Canada) including extended boreal forests, tundra, and wetlands. Approximately 76% of the combined watershed area is located in Eurasia (Zhulidov et al., 1997). Within these large watersheds lies an immense carbon reservoir, including biomass organic carbon in vegetation, soil organic carbon, and methane hydrates. A large portion of the soil organic carbon is trapped in permafrost soils with ~54% of this designated as continuous permafrost (Tarnocai et al., 2009). Among these large carbon pools, soil organic carbon is quantitatively the most important with 1400-1850 PgC, followed by 60-70 Pg biomass carbon, and 2–65 PgC as land-based methane hydrates (Tarnocai et al., 2009). The soil organic carbon in these watersheds represents roughly 50% of the global soil organic matter with 67% of it located in the Eurasian watersheds (Tarnocai et al., 2009). Biomass carbon in Arctic watersheds represents roughly 10-20% of the global vegetation carbon with about 73% of the high latitude vegetation carbon located in Eurasia (McGuire et al., 2009, 2010). The size of these carbon pools triggered the interest of researchers studying the global carbon cycle and its response to climate change. The Arctic has experienced a larger increase of mean annual air temperature (MAAT) over the last few decades (IPCC 2007) relative to the global average along with a shift in the total flow and distribution of flow in high latitude rivers (Peterson et al., 2002; Walvoord and Striegl, 2007). Temperature and moisture are key parameters governing the fate of organic matter by influencing vegetation, permafrost stability, peat formation and decomposition, and the frequency of forest fires. The transfer of carbon from high latitude watersheds to the Arctic Ocean and the atmosphere will be partitioned between gaseous forms ($CO_2$ and $CH_4$) and dissolved and particulate carbon in the rivers. Recent estimates for these fluxes indicate that the large Arctic watersheds are currently net sinks for $CO_2$ (200-400 $Tgyr^{-1}$; McGuire et al., 2009), net sources for $CH_4$ (33-46 $TgCyr^{-1}$; McGuire et al., 2009), and deliver between 25 and 36 $TgCyr^{-1}$ in the form of dissolved organic carbon (DOC) to the Arctic Ocean (Raymond et al., 2007, Holmes et al., 2011). How these large high latitude watersheds, with their immense carbon pools, will respond to climate change is still highly uncertain.

The large Arctic rivers have been the focus of numerous studies over the last few years establishing these rivers as important conduits of DOC and dissolved inorganic carbon (DIC) from the watersheds to the Arctic Ocean (Holmes et al., 2011, Prokushkin et al., 2011). The rivers are characterized by strong seasonal fluctuations in hydrology and high concentrations of DOC of predominantly modern age (Amon and Meon, 2004, Benner at al., 2005, Neff et al., 2006, Raymond et al., 2007). However, we still have a very limited understanding of what sources of organic matter predominate during the different stages of the hydrograph in each of the major Arctic rivers. Knowing the sources (vegetation, soil, peat etc.) of organic matter is crucial if we want to predict the effect that changing climate conditions will have on the transfer of carbon from land to sea. In this study we focus on the lignin phenol composition of river dissolved organic matter (DOM) from the six largest Arctic rivers in order to identify sources and seasonal differences of DOC inputs to these rivers with the purpose to relate the chemical composition of DOC to respective contributions of vegetation, bogs, and soils, and how this affects terrestrial DOC input to the Arctic Ocean.

## 2. METHODS:

### 2.1. Study area

The distribution and size of the six largest Arctic watersheds are shown in Fig. 1, with the dots indicating the approximate sampling location. Of the six rivers, four are located in Siberia (Ob, Yenisei, Lena and Kolyma), and two in North America (Mackenzie, and Yukon). Generally, snow and river ice begin to thaw in May with freshet occurring in late May, early June. Approximately 31-45% of the annual discharge occurs during the freshet period. The northernmost part of the watersheds is characterized by continuous permafrost, and shifts to discontinuous and then sporadic permafrost towards the south, with the exception of the Kolyma watershed, which is underlain by continuous permafrost throughout.

The Mackenzie River is the fourth largest river in terms of discharge (298 $km^3$ $yr^{-1}$) (Holmes et al., 2011) draining into the Arctic Ocean. The watershed is 1.78 x $10^6$ $km^2$ and stretches from the Great Slave Lake in the Northwest Territories of Canada to the Beaufort Sea. The Mackenzie supplies the Beaufort Sea with approximately 1.4 Tg of DOC per year (Raymond et al., 2007; Holmes et al., 2011). Sedimentary bedrock underlying the catchment consists of carbonates, shales, siltstones, mudstones and till is the dominant parent material. Dominant soil types include Orthic, Regosolic, and Gleysolic Turbic Cryosols (Timoney et al., 1993). Vegetation in the north consists of treeless tussock tundra with the dominant groups being legumes, carices and mosses (*Arctostaphylos rubra, Dryas integrifolia, Hedysarum alpinum, Lupinus arcticus, Ditrichum flexicaule*; Timoney et al., 1993). Boreal coniferous forest dominates the southern parts of the watershed with mainly white spruce (*Picea glauca*) in the north and black spruce (*Picea mariana*) in the south (Goni et al., 2000). The Mackenzie watershed is characterized by large lakes (covering 10% of the drainage basin area), 35% forest, 30% grassland, and 10% shrubland (Table 1).

The Yukon River in Alaska is the fourth largest river in North America. Its discharge averages 208 $km^3$ annually and the drainage basin covers 0.830 x $10^6$ $km^2$ (Table 1, Holmes et al., 2011). Of the 6 rivers studied in this project the Yukon is the only one that does not directly drain into the Arctic Ocean, but into the Bering Sea. DOC discharge of the Yukon is roughly 1.5 TgC per year (Raymond et al., 2007; Holmes et al., 2011). The watershed is situated between the Central and Eastern Brooks Range in the north and the Alaska Range and Wrangell-St. Elias Mountains to the south. The mountainous terrain creates a steeper mean slope (2.93 m $km^{-1}$), higher mean elevation (690 m) and higher maximum elevation (6100 m) than the other rivers studied here. Geology for the Yukon is complex reflecting the tectonic activity of the region (Brabets et al., 2000). Generally, the age of rocks range from Precambrian to Holocene and are composed of unconsolidated deposits and consolidated rocks (Brabets et al., 2000). Sedimentary rocks are primarily composed of sandstone, siltstone, shale and limestone but certain locations can contain smaller amounts of coal, mudstone, conglomerate, dolomite and chert (Brabets et al., 2000). Volcanic rocks have a variable composition ranging from rhyolite, andesite, basalt, sandstone, and chert (Brabets et al., 2000). Paleozoic metamorphic rocks are present over much of the Yukon-Tanana upland and are composed of gneiss, schist, phyllite, and quartzite (Brabets et al., 2000). The most abundant soil types within the Yukon watershed are Cryosols and Cambisols with minor amounts of Regosols, and Mollisols (Brabets et al., 2000). Approximately 20% of the catchment is covered by spruce forest, white (*Picea glauca*) in well drained sites and black (*Picea mariana*) in lowland sites (Brabets et al., 2000), about 40% by grassland, 20% by shrubland, and 8% by open water and wetlands (Table 1) associated with the low land areas. Note that other studies give higher estimates for the contribution of low-lying wetlands in the Yukon Basin (30%; O'Donnell et al., 2010).

The Ob River is the westernmost of the Siberian rivers studied in this project. Its discharge averages 427 km$^3$ yr$^{-1}$ or 15% of total freshwater flow into Arctic Ocean and the drainage basin is approximately 2.99 x 10$^6$ km$^2$ (Table 1; Holmes et al., 2011). DOC discharge totals 3.05–4.2 Tg yr$^{-1}$ (Raymond et al., 2007; Holmes et al., 2011). Of the Siberian rivers studied herein the Ob experiences the mildest climate and therefore has the least amount of permafrost (4-10%) within its catchment (Zhang et al., 1999). The source of this river is in the Altai Mountains and extends to the Kara Sea with a total length of 3977 km. Most of the lower reaches of the catchment are relatively flat with altitudes of 50-150 m (Astakhov, 1991) and slopes between 0-2% (Stolbovoi et al., 1997), which creates enormous flood plains. The mountainous region of the upper river has elevations of ~4000 m and a steeper slope (30-60%; Stolbovoi et al., 1997) creating an average slope of 1.28 m km$^{-1}$ (Table 1). The Ob River watershed is more populated relative to the Yenisei and Lena catchment, and is more influenced by industrial activities and agricultural development (Yang et al., 2004). The bedrocks include granites, clayey sandstone and limestone (Gordeev et al., 2004). Soils are mainly Gleysols, Podsols and Histosols with minor portions of Chernozems and Podzoluvisols (Stolbovoi et al., 1997). The Ob is unique among the other rivers because it contains within its watershed the largest peat bog system on the planet. The western Siberian lowlands extend over 900,000 km$^2$ (Kremenetski et al., 2003) and are a recognized source of methane (Smith et al., 2004). Vegetation is more variable in this watershed compared with the others because of its milder climate, but forests include pine and birch species with reed and sphagnum mosses being dominant in the peat bog system (Wagner, 1997; Zhulidov et al., 1997; Gordeev et al., 2004). Forests cover 39%, croplands 23%, grasslands 16%, and wetlands about 9% of the drainage basin (based on satellite derived vegetation maps, Table 1). However, based on the estimate of Kremenetski et al. (2003) the peat bog system would make up about 30% of the drainage basin.

The Yenisei is the longest river (4803 km), has the greatest discharge (averaging 636 $km^3yr^{-1}$) and largest watershed ($2.54 \times 10^6 km^2$) among all Arctic rivers (Table 1, Holmes et al., 2011). DOC discharge from the Yenisei is 4.69 Tg $yr^{-1}$ (Raymond et al., 2007, Holmes et al., 2011). The Yenisei originates in the Sayan Mountains and drains Lake Baikal through the Angara tributary. Along with the Ob the Yenisei flows north into the Kara Sea on the western edge of the Central Siberian Uplands. The mean elevation is 670 m and average slope is 1.94 m $km^{-1}$ (Table 1). Both elevation and slope classes are variable throughout the watershed but abruptly increase nearing the headwaters. Soils are dominated by Podzoluvisols, Cambisols, Podsols in the southern and central parts and have a larger contribution of Cryosols and Gleysols in the northern part (Stolbovoi et al., 1997). The climate is colder than in the Ob watershed, therefore 36-55% of its watershed is underlain with permafrost (Zhang et al., 1999). Vegetation varies from tundra, mixed taiga and pine forest from north to south. The tundra is dominated by dwarf birch (*Betula nana)*, sedges (*Carex canescens, Eriophorum vaginatum*) and mosses (*Hylocomium proliferum*, *Polytrichum commune* and *Sphagnum spp.;* Zhulidov et al., 1997*,* Šantrůčková et al., 2003). The boreal zone or taiga includes extensive areas with larches (*Larix sibiricaa, L. gmelinii),* spruce (*Picea obovata*), birch (*Betula sp.*) and pine *(Pinus sibirica, P. sylvestris*) as the dominant species and any number of subdominant plants including *Vaccinium spp., Ledum spp.,* horsetails (*Equisetum pratense* and *E. sylvaticum),* berries (*Rubus arcticus* and *R. chamaemorus)*, mosses (*Hylocomium proliferum*, *Pleurozium schreberi*, *Cladonia spp.*, and *Sphagnum spp)* and lichens *(Cetraria spp., Cladonia spp. Etc;* Zhulidov et al., 1997; Breckle, 2002*;* Šantrůčková et al., 2003). Towards the south there is a transition into Scots pine forests

(*Pinus sylvestris;* Šantrůčková et al., 2003) and dark conifer taiga near the headstream (Sayan Mountains). The extensive larch forests are unique to central and east Siberia, but are absent from the watersheds of North American rivers (Strassburger, 1983; Breckle, 2002). In general, vegetation in the Yenisei watershed is dominated by forests (68% of watershed area) with much smaller contributions of shrubland (9%), grassland (7%), and cropland (6%; Table 1).

The Lena is the second largest Arctic river in terms of discharge (averaging 581 $km^3$ $yr^{-1}$; Table 1) and provides the Laptev Sea with 5.6 - 5.8 Tg of DOC per year (Raymond et al., 2007; Holmes et al., 2011). The river is bound by the mountains of the Baikal region in the south, the Verkhoyansk Ridge to the east, the Central Siberian Uplands in the west and flows into the Laptev Sea through a complex braided network of channels (Zhulidov et al., 1997). The total length of the river is 4387 km and its watershed covers $2.46 \times 10^6$ $km^2$ (Table 1). The catchment's average slope is 1.83 m $km^{-1}$, and the mean and maximum elevations are 560 and 2830 m, respectively. Permafrost underlies 78-93% of the watershed (Zhang et al., 1999) with continuous permafrost extending down to 50° N in this region. The parent material of the northern to middle watershed is mostly Cambrian and Precambrian limestones, with Jurassic to Cretaceous aged terrigenous sediments and Quaternary alluvial deposits (Rachold, 1999). The southern parts of the watershed are composed of Proterozoic gneiss, shists, quartzites, and marbleized limestones (Rachold, 1999). Soils are mainly Cryosols, Cambisols, and Podsols with minor amounts of Fluvisols and Podzoluvisols (Stolbovoi et al., 1997). Severe climate limits the growth of most species in this region except for larch forests (*L. cajanderi),* which occupy much of the watershed (Wagner, 1997; Breckle, 2002). To the south where conditions are less severe, pine and birch forests become more abundant (Wagner, 1997; Zhulidov et al., 1997). The Lena watershed has the most extensive forest area (72% of the watershed) and about 12% of shrubland (Table 1).

The Kolyma is the smallest of the rivers studied in this project. Its discharge averages 111 $km^3$ annually and drains 0.65 x $10^6$ $km^2$ (Table 1, Holmes et al., 2011). The Kolyma River has the lowest DOC discharge of the rivers studied here with estimates ranging from 0.46 – 0.82 TgC per year (Rachold et al., 2004; Holmes et al., 2011). It is the easternmost Siberian river and is bounded by the Kolyma Mountains to the southeast and the Chersky Ridge to the southwest. The average slope is 2.16 m $km^{-1}$, and mean and maximum elevations are 490 and 2560 m, respectively. Soils are dominated by Cryosols and also include Gleysols, Cambisols, Podsols, and Histosols (Stolbovoi et al., 1997). Tree vegetation is limited to larch forests (*L. cajanderi)* which dominate most of the watershed (Wagner, 1997). Forest cover in the Kolyma watershed is 49%, however, lower estimates (10%) have also been reported depending on the satellite data source (see Table 1). Shrublands make up another important section of the watershed with about 35% (Table 1).

## 2.2. Sampling

The PARTNERS Project was coordinated by a core group at the Marine Biological Laboratory (MBL) in Woods Hole, USA. Sampling times and frequencies were planned by this group and executed by local collaborators following on-site training by core group members (McClelland et al., 2008; Holmes et al., 2011). Samples were filtered and preserved in the field before shipment to MBL. At the end of each season frozen samples were shipped to involved principal investigators.

Samples used in this study were collected during the years 2003-2007. Discharge data has been recorded from gauging stations since 1936 for the Ob, Yenisei, and Lena Rivers. Similar gauging stations were established on the Kolyma, Mackenzie and Yukon between 1968 and 1978 and each continues to generate data. PARTNERS samples were collected near these gauging stations at the following locations (Fig. 1); Tsiigehtchic for the Mackenzie River (about 300 km upstream from the Arctic Ocean), Pilot Station for the Yukon (about 200 km upstream from the Arctic Ocean), Salekhard for the Ob (about 1000 km upstream from the Arctic Ocean), Dudinka for the Yenisei (600 km upstream from the Arctic Ocean), Zhigansk for the Lena (850 km upstream from the Arctic Ocean) and Cherskiy for the Kolyma (about 100 km upstream the Arctic Ocean). Sampling was conducted at various times of the year to obtain a representative data set reflecting the changing seasonal hydrograph, including sampling under ice cover during winter. The collection device was a torpedo shaped, Teflon coated, 60 kg, depth integrated sampler (US D-96). The rivers were 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 not only of 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 1 liter polycarbonate bottles and frozen. All samples remained frozen and in the dark during shipment to MBL and final distribution to project participants. DOC and lignin phenol concentrations presented in this study were determined in these I liter samples.

### 2.3. Dissolved Organic Carbon

DOC concentrations were measured on a MQ-1001 TOC analyser (MQ-Scientific) according to the protocol of Qian and Mopper (1996) and Peterson et al. (2003). Potassium hydrogen phthalate was used for standards and a daily calibration curve was measured ranging from 200 to 2000 μM C. Deep sea reference (DSR) material supplied by D. Hansell (University of Miami) was run daily to assure proper instrument performance. The residual standard deviation on this instrument averaged 2.5 % for the river samples, and milliQ water blanks averaged 0.12 mg C $l^{-1}$. The DSR values varied between 40 and 55 μmol $l^{-1}$ C based on the "wide range" calibration curves.

## 2.4. Lignin Phenols

About 1 L of river water was filtered through a 0.2 μm pore size polycarbonate filter cartridge and acidified to pH 2.5 using concentrated HCl (reagent grade). Lignin phenols were extracted by solid phase extraction (SPE) using 60 CC/10 gram C18 bonded phase columns (Varian) that were pre-cleaned with 50 ml HPLC grade methanol followed by 100 ml acidified (pH 2.5) MQ water just before sample extraction, and then eluted with 35 ml HPLC grade methanol into a 250 ml precombusted flask (Louchouarn et al., 2000). The samples in the flasks were dried in a Savant SpeedVac (SC210A) for 12-24 hours and dissolved in 3ml 2N NaOH for CuO oxidation.

Alkaline CuO oxidation of DOM and quantification of lignin oxidation products (LOP) was performed according to the methods described in detail in Louchouarn et al. (2000, 2010) and Kuo et al. (2008). Briefly, each SPE eluent was sonicated twice with 1.5 mL of 8% NaOH (pre-sparged with Ar) to remove the isolated DOM and residues adhered to the Savant flasks. The two 1.5 ml aliquots of NaOH with DOM were then transferred to a reaction mini-vessels pre-loaded with CuO (~300 mg) and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (~50 mg) and then heated (155ºC for 3 h) in a customized Hewlett-Packard 5890 gas chromatograph. Trans-cinnamic acid (CiAD: 3-

phenyl-2-propenoic acid) and ethyl vanillin (EVAL: 3-ethoxy-4-hydroxybenzaldehyde) were used as surrogate standards and were directly added (~3-12 μg) to each mini-vessel after cooling. The CuO reaction products were re-dissolved in a small volume of pyridine (200-500 μL), and derivatized (75°C, 1 h) with *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS).

Separation and quantification of trimethylsilyl derivatives of CuO oxidation by-products were performed using gas chromatography-mass spectrometry (GC/MS) with a Varian Ion Trap 3800/4000 system fitted with a fused silica column (VF 5MS, 30 m x 0.25 mm i.d. or 60 m x 0.25 mm i.d.; Varian Inc.). Each sample was injected, under split less mode, into a deactivated glass liner inserted into the GC injection port; He was the carrier gas (~1.0 mL min$^{-1}$). The GC oven was programmed from 65°C (with a 2 min initial delay) to 300°C (held 10 min) using a 4°C/min temperature ramp. The GC injector and GC/MS interface were both maintained at 280°C and 270°C, respectively. The mass spectrometer was operated in the electron ionization mode (EI, 70 eV) using full scan (FS) in the 50-500 mass range. Compound identification was performed using GC retention times and by comparing full mass spectra with those of commercially available standards. Trimethylsilyl derivatives were detected using 3-5 ions for identification of each CuO oxidation product, but one for quantification. Cinnamic Acid (CiAD) was used for calculation of response factors and LOP concentrations. However, we monitored the ratio of EVAL/CiAD as a quality control parameter due to the sensitivity of aldehydes to degradation or vaporization compared to acids.

The analytical precision of the major CuO-oxidation products and related parameters was derived from replicate analyses of standard materials including estuarine sediments (NIST SRM 1944 and SRM 1941b) and dried fulvic acid (IHSS 1S101F). The average variability for all parameters was better than 10% (Louchouarn et al., 2010). Reagent blanks and SRMs were processed daily as additional quality control measures.  Analysis of SPE blanks found only trace contamination of the acidic groups (vanillic acid, syringic acid, *p*-hydroxybenzoic acid, 3,5 dihydroxybenzoic acid). With this approach we were confident to quantify the following CuO oxidation products: vanillin, vanillic acid, acetovanillone, syringealdehyde, syringic acid, acetosyringone, p-coumaric acid, ferulic acid, p-hydroxybenzaldehyde, p-hydroxyacetophenone, p-hydroxybenzoic acid, and 3,5 dihydroxybenzoic acid.

**2.5. Calculations**

Discharge-weighted-average concentrations presented in Table 2 were calculated as follows. The relationship between the available daily discharge and the different DOM parameters (17 observations per river) was used to derive the function with the best statistical fit. The equations were then used to derive values for each month of the year. The value for each month was then multiplied by the respective monthly discharge and then divided by the total annual discharge to derive a discharge-weighted mean.

The relative contributions of potential DOM sources (gymnosperm, angiosperm plants, mosses, soils, and peat) were estimated based on the following 4 equations.

$$\frac{\mathrm{fG}*\mathrm{SG}+\mathrm{fg}*\mathrm{Sg}+\mathrm{fA}*\mathrm{SA}+\mathrm{fa}*\mathrm{Sa}+\mathrm{fM}*\mathrm{SM}+\mathrm{fS}*\mathrm{SS}+\mathrm{fP}*\mathrm{SP}}{\mathrm{fG}*\mathrm{VG}+\mathrm{fg}*\mathrm{Vg}+\mathrm{fA}*\mathrm{VA}+\mathrm{fa}*\mathrm{Va}+\mathrm{fM}*\mathrm{VM}+\mathrm{fS}*\mathrm{VS}+\mathrm{fP}*\mathrm{VP}} = \mathrm{S/V}_{\mathrm{DOM}} \tag{1}$$

$$\frac{\mathrm{fG}*\mathrm{CG}+\mathrm{fg}*\mathrm{Cg}+\mathrm{fA}*\mathrm{CA}+\mathrm{fa}*\mathrm{Ca}+\mathrm{fM}*\mathrm{CM}+\mathrm{fS}*\mathrm{CS}+\mathrm{fP}*\mathrm{CP}}{\mathrm{fG}*\mathrm{VG}+\mathrm{fg}*\mathrm{Vg}+\mathrm{fA}*\mathrm{VA}+\mathrm{fa}*\mathrm{Va}+\mathrm{fM}*\mathrm{VM}+\mathrm{fS}*\mathrm{VS}+\mathrm{fP}*\mathrm{VP}} = \mathrm{C/V}_{\mathrm{DOM}} \tag{2}$$

$$\frac{\mathrm{fG}*\mathrm{PG}+\mathrm{fg}*\mathrm{Pg}+\mathrm{fA}*\mathrm{PA}+\mathrm{fa}*\mathrm{Pa}+\mathrm{fM}*\mathrm{PM}+\mathrm{fS}*\mathrm{PS}+\mathrm{fP}*\mathrm{PP}}{\mathrm{fG}*\mathrm{VG}+\mathrm{fg}*\mathrm{Vg}+\mathrm{fA}*\mathrm{VA}+\mathrm{fa}*\mathrm{Va}+\mathrm{fM}*\mathrm{VM}+\mathrm{fS}*\mathrm{VS}+\mathrm{fP}*\mathrm{VP}} = \mathrm{P/V}_{\mathrm{DOM}} \tag{3}$$

$$\frac{\mathrm{fG}*\mathrm{PnG}+\mathrm{fg}*\mathrm{Png}+\mathrm{fA}*\mathrm{PnA}+\mathrm{fa}*\mathrm{Pna}+\mathrm{fM}*\mathrm{PnM}+\mathrm{fS}*\mathrm{PnS}+\mathrm{fP}*\mathrm{PnP}}{\mathrm{fG}*\mathrm{PG}+\mathrm{fg}*\mathrm{Pg}+\mathrm{fA}*\mathrm{PA}+\mathrm{fa}*\mathrm{Pa}+\mathrm{fM}*\mathrm{PM}+\mathrm{fS}*\mathrm{PS}+\mathrm{fP}*\mathrm{PP}} = \mathrm{Pn/P}_{\mathrm{DOM}} \tag{4}$$

The fractions (f) in the equations were adjusted until all 4 equations returned similar percentages for the different sources. This was done by trial and error. We used 4 lignin oxidation derived parameters, the ratio of syringyl to vanillyl phenols (S/V), the ratio of cynamyl to vanillyl (C/V) phenols, the ratio of p-hydroxybenzenes to vanillyl phenols (P/V), and the ratio of p-hydroxyacetophenone to p-hydroxybenzenes (Pn/P), and 7 potential sources including gymnosperm wood (G), gymnosperm needles (g), angiosperm wood (A), angiosperm leaves (a), moss (M), soil (S), and peat (P). The endmember values for these sources are given in Table 4 and a detailed description of the parameters is given in the discussion.

## 3. RESULTS

DOC concentrations increased with discharge with elevated levels during the spring freshet and lowest concentrations during winter base flow conditions. In short, average DOC concentrations were highest in the Lena (11.4 – 11.9 mg $l^{-1}$) and lowest in the Mackenzie (4.2 – 4.4 mg $l^{-1}$; Table 2). The annual DOC load from these rivers varied considerably (Table 3) ranging from 6.47 Tg DOC $yr^{-1}$ (36% of the total) in the Lena River to 0.71 Tg DOC $yr^{-1}$ (3.9% of total) in the Kolyma. Together, the Eurasian rivers contribute about 84% of the annual DOC discharge to the Arctic Ocean.

Lignin phenol concentrations based on the sum of vanillyl, syringyl, and cinnamyl phenols ($\Sigma_8$) are, like DOC, strongly correlated with discharge, but not to the same extent in the different rivers. Similar to DOC, most lignin is discharged during the 2 months of spring freshet (49-78%; Table 3). While lignin increased by more than an order of magnitude during the freshet (from < 3ug $l^{-1}$ to >100 ug $l^{-1}$) in most rivers, the lignin levels in the Mackenzie only increased by a factor of 4 (from ~5 to ~25 ug $l^{-1}$). The relationship between lignin concentrations and discharge was different for the 6 rivers (Fig. 2) with some rivers (Yenisei and Mackenzie) displaying a strong linear relationship while other rivers (Ob, Lena, Yukon) suggested that DOM saturation or dilution effects occur towards the end of the peak flow period. Highest lignin concentrations were found in the Lena with freshet values exceeding 400 μg lignin phenols $l^{-1}$ ($\Sigma_8$), a mean value of 135 μg $l^{-1}$ and a discharge weighted mean of 102 μg $l^{-1}$ (Table 2). These freshet values are among the highest lignin concentrations reported in natural waters. The lowest lignin concentrations were detected in the Mackenzie with respective mean and discharge weighted mean values of 12.6 and 12.7 μg $l^{-1}$. Second largest lignin concentrations were found in the Yenisei with 109 and 86 μg $l^{-1}$ for the mean and discharge weighted mean, followed by the Ob with a mean concentration of 66 and a discharge weighted mean of 61 μg $l^{-1}$ which was very similar to concentrations in the Yukon and Kolyma (Table 2). The Lena is the single most important source of lignin to the Arctic Ocean with 91.6 Gg lignin per year (47.7%), followed by the Yenisei with 54.3 Gg lignin per year (28.3%). The Mackenzie on the other hand only contributes 3.6 Gg lignin per year (1.9%). Taken together the 3 largest Eurasian rivers, Lena, Yenisei and Ob contribute more than 87% of the lignin phenols to the Arctic Ocean and release 67% of the total annual pan-Arctic lignin discharge during the 2 month of spring freshet (Table 3). Lignin yield ($\Lambda_8$), a measure of the relative contribution of lignin to total DOC, is also strongly related to discharge (data not shown) with elevated values during freshet. The differences in the lignin yield between peak, intermediate, and low discharge periods, was least pronounced in the Mackenzie (Fig. 3B). Values ranged from < 0.2 to > 2.5 mg lignin 100mg$^{-1}$ DOC and the discharge weighted means were 0.20, 0.53, 0.55, 0.77, 0.77, and 2.14 mg lignin 100 mg$^{-1}$ DOC for Mackenzie, Ob, Yukon, Kolyma, Yenisei, and Lena, respectively (Table 2).

Lignin monomer ratios reflect a strong seasonal signal, related to discharge, but also differ among some of the rivers. The ratios of vanillic acid to vanillin $(Ad/Al)_v$ and syringic acid to syringealdehyde $(Ad/Al)_s$, often used as a diagenetic indicator, were highest during peak flow and consistently decreased from peak flow conditions to base flow conditions (Table 2, Fig. 3CD), contrary to the common diagenetic pattern. Discharge weighted means of $(Ad/Al)_v$ ratios were slightly lower in Yukon and Mackenzie (~0.8) than in the Eurasian rivers (1.0-1.1). The source indicator ratios S/V (syringyls/vanillyls) and C/V (cynnamyls/vanillyls) also display a seasonal change with lower ratios during the spring freshet except for S/V ratios in Ob and Mackenzie (Table 2, Fig. 3EF). S/V ratios were slightly higher in the Yukon, Ob and Kolyma (0.4-0.6), relative to the Mackenzie, Lena, and Yenisei (~0.3). The Yukon and the Ob rivers also stand out with respect to C/V ratios which are higher (>0.1) in these two rivers relative to the other four (<0.1). Yukon and Ob also had more elevated values for three, less commonly used, lignin indicators, the ratio of p-coumaric acid to ferulic acid (Cad/Fad), 3,5-dihydroxybenzoic acid/vanillyls (3,5Bd/V), and p-hydroxybenzenes to vanillyls (P/V). All of these typically increase from freshet to mid and base flow in all rivers, but in the Yukon and Ob this trend was especially pronounced (Table 2, Fig. 3G-I). Seasonal trends and differences among rivers were also found in lignin derived phenol parameters recently used as source indicators including the ratio of p-hydroxyacetophenone to total p-hydroxybenzenes (Pn/P) and the yield of Pn, both potential indicators for peat and moss contributions, which showed generally lower values during freshet in all rivers (Table 2, Fig. 3J,K). Pn yields were clearly elevated in Ob and Yukon, particularly during the low-flow seasons, but had high variability during that time. The vanillyl yield (Fig. 3L) has recently been used as a measure for vascular plant contribution in the Yukon

River (Spencer et al. 2009) and mirrors the $\Lambda_8$ values with much higher values during the spring flood, particularly in the Lena and Yenisei.

Lignin phenol concentrations and monomer composition are strongly related to the average $^{14}$C-age of DOC. All rivers except the Mackenzie show an increase of lignin phenol concentrations and yields with younger average DOC-age (Fig. 4). The relationship between the lignin concentration and $^{14}$C age of DOC is significant in all rivers except the Mackenzie (Fig 4). In the Mackenzie there is actually a negative trend, however, the relationship between lignin and DOC-age is not significant (Fig. 4E). Most of the lignin monomer ratios are also related to the average $^{14}$C-age of DOC (Fig. 5). While Ad/Al ratios increased with decreasing average DOC-age (contrary to the common believe; Fig 5A), the C/V, Cad/Fad, 3,5Bd/V, P/V, and Pn/P ratios all decreased in younger DOC (Fig. 5C-G). S/V ratios changed the least with age, except for the Ob, which has elevated S/V ratios at intermediate $^{14}$C-ages of DOC (Fig 5B). The yield of p-hydroxyacetophenone had a weaker negative relationship with $^{14}$C-age of DOC and increasing values with older DOC was only obvious in Ob and Yukon (Fig. 5H), while the yield of vanillyl phenols showed a strong positive exponential relationship with $^{14}$C-age across all the rivers (Fig. 5I).

## 4. DISCUSSION

### 4.1. Dissolved organic carbon

Dissolved organic carbon discharge from the large Arctic rivers sampled during the PARTNERS program has been discussed in several previous studies (Cooper et al., 2005; Raymond et al., 2007; Cooper et al., 2008; Holmes et al., 2011). The DOC data presented here were measured in the samples collected for lignin analysis and represent a replicate data set to the PARTNERS data. The two data sets return almost identical estimates for the total annual DOC export of ~18.25 Tg C $yr^{-1}$ for the six rivers (Table 3, Holmes et al., 2011). The vast majority (84%) of river DOC is discharged by the Eurasian rivers with a relatively small (16%) contribution from the large North American rivers. In addition, a significant portion of the North American river DOM is exported through the Canadian Archipelago (Guay et al., 2009; Macdonald et al., 2002) before entering the Canada Basin. This has important implications for the interpretation of the geographical distribution of terrestrial DOM within the Arctic Ocean.

### 4.2. Lignin phenols

The seasonal change of DOM composition has been documented for the Yukon (Striegl et al., 2005, 2007; Guo and Macdonald, 2006; Spencer et al., 2008, 2009) and Kolyma (Finlay et al., 2006; Neff et al., 2006) rivers indicating a general shift from recently produced DOM during freshet to more aged DOM during winter base-flow. While this general trend is also reflected in the other large Arctic rivers (Koehler et al., 2003; Raymond et al., 2007; Stedmon et al., 2011), we still have a very limited understanding of the sources of DOM and how they are affected by the changing hydrograph and the different watershed characteristics. Lignin phenols are produced by vascular plants and their presence in DOM can help to characterize and quantify sources in the overall DOM pool. Differences in lignin concentrations and compositions between rivers are important when estimating their relative contributions to the Arctic Ocean and interpreting the distribution of terrestrial organic matter within the Arctic Ocean.

The role of diagenetic and/or sorption processes for the lignin concentration and yield in the rivers is reflected in the relationships between the average $^{14}$C-age of DOC and lignin concentrations (Fig. 4). The younger or "fresher" the river DOM is, the higher is the concentrations of lignin. This is the most direct evidence that a large proportion of the DOM exported by large Arctic rivers during the spring freshet comes from recently produced vascular plant material with little exposure to microbial degradation and sub soils. The strong relationship between lignin concentration and $^{14}$C-age is consistent with previous observations in the Arctic Ocean where the age of DOC decreased with increasing concentrations of lignin (Benner et al., 2004). The Mackenzie was the only river showing a negative, albeit not significant, trend (Fig. 4E), which could be related to the rapid removal of fresh vascular plant derived DOM during freshet. $\Delta^{14}$C-values never exceeded 40‰ in the Mackenzie compared to $\Delta^{14}$C-values >70‰ in all the other rivers during freshet. Reasons for the markedly different lignin concentrations and lignin-$\Delta^{14}$C relationship in the Mackenzie River are not clear but could also involve the much higher concentration of suspended matter (SPM) in the Mackenzie, potentially leading to the removal of DOM through sorption onto particles. However, the depleted $\Delta^{14}$C values measured in suspended matter (SPM) from the Mackenzie (Goni et al., 2005) would limit the amount of fresh DOM that could be adsorbed onto SPM. The fact that part of the Mackenzie SPM is radiocarbon dead ($\Delta^{14}$C of -1000‰, Goni et al. 2005) would allow for a maximum of 30% modern carbon contribution to Mackenzie SPM (Goni et al., 2005). The rapid removal of dissolved lignin phenols due to adsorption on fine particles has been suggested in the Amazon River system (Ertel et al., 1986) where blackwater rivers (high in lignin) mix with white water rivers (high in SPM). The same mechanism could be important in the Mackenzie, which has the highest sediment load of all Arctic rivers. Alternatively, the unique abundance of lakes and wetlands in the Mackenzie watershed (the Mackenzie originates in the Great Slave Lake) could alter the proportion of DOM transported down the river. Lakes and wetlands contribute more than 55% to the water in the Mackenzie River (Yi et al., 2010). Because open water bodies generally act as a buffer for hydrologic events (Gibson and Prowse, 2002), they can increase the residence time for organic matter in these systems, potentially leading to larger losses of DOM due to degradation or burial before discharge (Cole et al., 2007).

The relative composition of lignin phenol monomers has been used as a source as well as a diagenetic indicator of terrestrial organic matter in aquatic and soil systems (Hedges and Mann, 1979; Benner et al., 1990; Goni and Hedges, 1992; Opsahl and Benner, 1995; Louchouarn et al., 1999; Opsahl et al., 1999; Hernes and Benner, 2002; Tesi et al., 2007; Houel et al., 2009). Vanillic acid to vanillin or $(Ad/Al)_v$ and syringic acid to syringealdehyde or $(Ad/Al)_s$ ratios have been used as diagenetic indicators for soil organic matter as well as particulate and dissolved organic matter in rivers, lakes, and the ocean. Usually, the Ad/Al ratios increase with increasing oxidative degradation of organic matter. However, the variation of Ad/Al ratios in different lignin sources is large and it has been suggested that leachates from vascular plant litter can also have elevated Ad/Al ratios (Guggenberger and Zech, 1994; Hernes et al., 2007). From our data set it is obvious that Ad/Al ratios are consistently affected by the hydrograph (Fig. 3CD) and also show a strong relationship to the radiocarbon age of DOC (Fig 5A). Ad/Al ratios are highest during spring freshet when the average $^{14}C$ age of DOC is young, indicating that a significant fraction of river DOM comes from recently produced vascular plant and litter leachates during the spring freshet in May and June. Each of the rivers displayed elevated Ad/Al ratios during the spring freshet relative to base flow. Based on discharge weighted mean Ad/Al ratios, the Yukon and the Mackenzie have slightly lower values than the Eurasian rivers, which may be related to the rapid removal of fresh lignin phenols with high Ad/Al ratios or the larger amount of SPM in the North American rivers. Sorption of DOM to the mineral phase has been connected to changing Ad/Al ratios in experimental studies (Hernes et al., 2007).

The ratio of syringyl to vanillyl phenols (S/V) is an indicator for the lignin phenol sources with high ratios indicating angiosperms sources and low S/V ratios indicating a gymnosperm source (Hedges and Mann 1979). Most rivers had lower S/V ratios during the spring freshet relative to the base flow values, except for the Ob, which displayed the opposite trend (Fig. 3E). Of all lignin parameters S/V ratios were the least affected by the change in DOC age (Fig. 5B), indicating that the shift in S/V ratios during the different hydrographic stages reflected a shift in sources as well as diagenetic state. Overall, low S/V ratios indicate gymnosperm vegetation as the most important source of lignin in these rivers, which reflects the dominant form of vegetation in these watersheds. The seasonal variation in S/V ratios is almost as big as the differences among rivers, but based on the discharge weighted means the Lena, Yenisei, and Mackenzie have very similar (0.28 -0.31) and relatively low S/V ratios, while the Kolyma, Yukon and Ob have relatively higher S/V ratios (0.38-0.58, Fig. 4E). The Ob watershed has the warmest climate of all with a relatively larger contribution from angiosperms as well as an extensive bog system with abundant mosses (Table 1; Breckle, 2002; Strassburger, 1983; Opsahl et al., 1999). Elevated S/V ratios in the Kolyma and Yukon are less obvious, but a study by Lobbes et al. (2002) suggests that rivers that drain mainly higher latitudes and altitudes including the Arctic tundra are characterized by elevated S/V ratios. The fact that a large portion of the Yukon and Kolyma watersheds are north of the Arctic Circle with a general shift to flowering tundra plants could explain the elevated S/V ratios. Elevated values of S/V have been reported from high altitude tundra vegetation and soils in northern Alaska (Ugolini et al., 1981).

The watersheds of the Yukon and Kolyma also share extended shrubland areas with 20% and 32%, respectively (Table 1).

The ratio of cynamyl to vanillyl (C/V) phenols has been used to distinguish woody lignin from other lignin sources with higher ratios indicating herbaceous plants or sphagnum moss sources. C/V ratios varied less with the hydrograph than the other lignin parameters except in the Yukon and the Ob, which showed increasing C/V ratios during mid and low flow conditions (Fig. 3F). Overall, the C/V ratios were low (<0.1) for most rivers except for the Yukon and Ob which had C/V ratios >0.1 throughout the year. This indicates significant input of woody plant material as a source of lignin phenols. It has been indicated that C/V ratios decrease with progressive degradation, but in our data set the C/V ratios were actually higher in older DOC (Fig. 5C) potentially reflecting different sources and/or varying sorption behavior of the V and C phenols. As with S/V ratios, elevated C/V ratios have been reported for high altitude soils and tundra vegetation (Ugolini et al., 1981) and the Yukon watershed has the highest mean elevation of all the large Arctic rivers. Both, Yukon and Ob watersheds also have a significant contribution of wetland vegetation and grassland (Table 1, O'Donell et al., 2010) likely contributing to slightly elevated C/V values. It is noteworthy that C/V ratios doubled in the Yukon River during base flow conditions relative to the freshet.

Ratios of p-coumaric acid to ferulic acid (CAD/FAD) have also been used as a diagenetic indicator in lake sediments (Houel et al. 2006) due to the preferential degradation of ferulic acid. In addition, p-coumaric acid is believed to be more soluble (Sanger et al., 1997). Both of these processes lead to higher CAD/FAD ratios in river DOM. In this data set the CAD/FAD ratios stayed fairly constant over the different hydrographic stages except for the Yukon and Ob, which showed increasing ratios during winter base flow conditions (Fig. 3G) and had the highest average values among all rivers. Most rivers, except the Mackenzie, showed a significant negative correlation between CAD/FAD and $\Delta^{14}$C-DOC (Fig. 5D) indicating increasing CAD/FAD ratios in older DOC. Elevated CAD/FAD ratios have also been reported in leaves, needles, wetland vegetation (Table 4), and from tundra soils relative to boreal forest soils (Ugolini et al., 1981). p-coumaric acid is also a significant component in sphagnum moss and wetland soils (Williams et al., 1998) indicating that sources as well as the diagenetic state of organic matter can influence the observed trends in CAD/FAD ratios.

We also included a number of cupric oxide oxidation products that do not necessarily originate from lignin but have been used along with lignin-derived phenols in soil and aquatic geochemistry. 3,5-dihydroxybenzoic acid (3,5Bd) likely originates from terrestrial sources such as tannins and flavonoids (Goni and Hedges, 1995). Due to the recalcitrant nature of tannins, 3,5Bd/V ratios have been used as diagenetic indicator for organic matter in soils and sediments (Houel et al., 2006). Alternatively, increasing 3,5Bd/V ratios could indicate more effective sorption of vanillyls relative to 3,5Bd. This is consistent with our data which show a shift in 3,5Bd/V ratios from low values during freshet to higher values during mid and base flow conditions (Fig. 3H) and a strong relationship to average DOC age (Fig.5E). The 3,5Bd/V ratios (discharge weighted means) were slightly higher in the Yukon , Ob, and Mackenzie than in the Yenisei, Lena, and Kolyma with maximum values above 1.5. Such high values have been reported for mineral soil horizons of boreal forest soils (Houel et al., 2006) as well as from alpine tundra soils in northern Alaska (Ugolini et al., 1981).

p-hydroxybenzenes can have several sources, while p-hydroxyacetophenone (Pn) is lignin-derived, p-hydroxybenzaldehyde (Pl) and p-hydroxybenzoic acid (Pd) can also be derived from proteins and polysaccharides during cupric oxide oxidation (Goni et al., 2000). High concentrations of all three p-hydroxybenzenes have been detected in different Sphagnum species as well as in certain peat soils (Williams et al., 1998). Moss and peat are especially enriched in Pn which make up more than 60% of the sum of all p-hydroxybenzenes in mosses and 30-60% in peat samples (Williams et al., 1998). In contrast, published Pn/P ratios are typically lower for vascular plants (0.18; Hedges et al., 1982), vascular wetland plants (0.22; Williams et al., 1998), boreal lake sediments (<0.15; Teisserenc et al., 2010; Houel et al., 2006) and boreal soils (0.14-0.40; Houel et al. 2006). Published information on p-hydroxybenzenes in DOM is sparse but the few available data also indicate rather low Pn/P ratios for the Amazon River (0.21; Ertel et al., 1986), a North American river (0.26; Benner and Kaiser, 2010), and in boreal forest lake DOM (~ 0.18, Ouellet et al., 2009). In contrast to the available literature data, we measured elevated concentrations of p-hydroxybenzenes and specifically Pn/P ratios in Arctic river DOM (Table 2, Fig. 3J). The fact that Pn/P ratios never dropped below about 0.22, suggests p-hydroxybenzenes are largely lignin-derived in these rivers. Pn/P ratios in Arctic rivers range from 0.24 to 0.47 with increasing ratios during base flow conditions and highest values in Yukon and Ob (Fig. 3J). Relative to the few published Pn/P values in freshwater DOM, it seems that large Arctic rivers are characterized by elevated values of p-hydroxyacetophenone. P/V ratios in the 6 rivers ranged from 0.26 to 5.0 with a pronounced decrease during the spring freshet (Fig. 3I). P/V ratios in the Amazon (0.68; Ertel et al., 1986), a north American river (0.44; Benner and Kaiser, 2010), and boreal forest lakes (0.68; Ouellet et al., 2009) are similar to average values in the 6 largest Arctic rivers during freshet (Table 2) but lower than P/V ratios measured during mid and base flow conditions. P/V ratios were highest (>2.0) during base flow in the Yukon and Ob (Fig. 4I), representing another similarity between these two rivers. P/V and Pn/P values indicate a considerable contribution of mosses or peat to the riverine DOM pool, particularly during mid and low flow conditions.

## 4.3. Sources of Arctic river DOM

Discharge of DOC and lignin to the Arctic Ocean changes dramatically during the seasons with more than 2/3rd of the annual discharge occurring during the two months of spring freshet. Hence, understanding the sources for this quantitatively dominant DOM pool is most important. Potential sources of DOM in rivers include vascular plants and algae. The vascular plant source can enter the river as part of the surface run-off after snowmelt or as part of the subsurface run-off (groundwater) after percolating the upper soil horizons. The highly elevated concentrations of lignin phenols during the spring freshet suggest vascular plants and fresh litter as a dominant source, which agrees with the modern $^{14}$C-age (Raymond et al., 2007) and the relatively high C/N ratios of peak flow DOM (44; Holmes et al., 2011). C/N ratios also allow to roughly distinguish algae-derived DOM (C/N=14; Amon and Meon 2004) and soil-derived DOM (C/N=14-25; Kaiser et al., 2004; Kawahigashi et al., 2006) from vascular plant sources (C/N~54; Amon and Meon, 2004). Based on the reported C/N ratios during peak flow in these rivers (Holmes et al., 2011), vascular plants and litter (surface run-off) contribute about 70% of the DOM and a combination of algae and soil derived DOM contributes the other 30% of the DOM (soil and algae DOM cannot be distinguished based on C/N ratios). An alternative approach to estimate the vascular plant contribution to river DOM was introduced by Hernes et al. (2007) and Spencer et al. (2009) based on the yield of vanillyl phenols. Spencer et al (2009) estimated that 5-55% of DOM in the Yukon is vascular plant derived depending on the season, with higher percentages during the freshet. If we assume a source endmember of 1.6 mg/100mg

DOC, as given in Hernes et al. (2007), the vascular plant contribution to peak-flow DOM in our study varies between 16% (Mackenzie) and 87% (Lena). Based on our V-yield data during peak flow conditions, vascular plants make up most of the riverine DOM. Lowest yields were found in the Mackenzie River and during the late winter base flow, potentially because of selective sorption of LOPs to the mineral phase in soils and rivers (Guggenberger and Zech, 1994; Kaiser et al., 2004). Algae probably contribute little to river DOM during the cold and dark period of the year when the V-yield is the lowest, but mosses, peat, and soil DOM also have low V-yields and are likely important DOM sources during that time. Clearly, the vanillin yield is affected by degradation (Fig. 5I) and sorption processes. Its use as a source indicator is therefore hampered by multiple challenges including endmember characterization and potential changes in yield during degradation/sorption processes.

The classical property-property plot of C/V and S/V (Fig. 6A) underlines the dominance of gymnosperms as a source of Arctic river DOM. Especially, the Lena and Yenisei peak flow values plot very close to the gymnosperm wood endmember (Fig. 6A). Peak flow values are very low but still show slightly elevated S/V and C/V values relative to a pure gymnosperm wood source. Because gymnosperm wood and needles are devoid of syringyl phenols, the slightly elevated S/V values point to additional plant sources. Field observations indicate that moss biomass exceeds shrub biomass by a factor of 10 (Prokushkin et al., 2006) suggesting the most likely source with elevated S/V values in northern taiga and larch woodlands of Siberia are mosses rather than angiosperms (Prokushkin et al., 2006). However, angiosperms become abundant in the tundra regions of the watersheds as well as in the alpine regions and likely contribute to some degree to the DOM found in the rivers. A prominent moss contribution is consistent with the observed values for Pn-yields (Fig. 5H), P/V and Pn/P (Fig. 6B). A mixture of gymnosperm wood and needles with moss would be able to explain the observed river DOM values of Pn-yields, P/V and Pn/P, while a mixture with angiosperm wood and leaves would not. Based on the S/V, C/V, P/V, and Pn/P ratios it seems reasonable to assume that most of the Arctic River DOM during peak flow is derived from relatively fresh vegetation. We would thus expect a strong relationship between biomass and DOM export in the different watersheds under undisturbed conditions (no forest fires). The Lena and Yenisei, which have by far the highest lignin discharge (and the lowest S/V and C/V values), also have the largest fraction of boreal forests within their watersheds (Table 1). A positive relationship exists between the annual lignin export from the rivers and the percentage of forest cover in the respective watersheds (data not shown). A compilation for boreal forest biomass, based on new satellite data (Envisat) is currently under way and expected to be available sometime in 2012 (Schmullius et al. pers. Comm.). DOM collected from a boreal forest lake (Ouellet et al., 2009) resembles the peak flow river DOM very closely (Fig. 6AB), also suggesting that boreal forest vegetation is a dominant source of DOM for Arctic rivers during the snow-melt driven peak flow. Based on the observed lignin monomer ratios (Fig 6AB) and the endmember values given in Table 4 we performed a simple endmember mixing calculation (Ertel and Hedges, 1985) for the freshet in Lena and Ob, representing the two rivers which had the least resemblance in terms of lignin monomer composition, as well as for the low flow situation in the Yukon (as the most unique example during winter). For this rough estimate we calculated the relative contribution of gymnosperms, angiosperms, mosses, soil, and peat based on each of the following lignin parameters, S/V, C/V, P/V, and Pn/P. The relative contribution of each source was adjusted in equations 1-4 until all 4 equations returned similar results to the measured river values. Based on such estimate, the Lena freshet-DOM signal could be derived predominantly (70%) from gymnosperm vegetation and fresh litter with lesser contributions from angiosperm vegetation and litter (15%), and mosses and peat (13%). The lignin composition of freshet-DOM in the Ob on the other hand, could be comprised of 45% gymnosperm, 23% angiosperm, and 25% moss and peat contributions. The base-flow situation is quite different and more challenging to describe in terms of DOM sources because the origin of groundwater, which dominates the river flow in late winter in these rivers, is poorly understood. DOM transported during that time has obviously penetrated the deeper soil layers and experienced sorption/desorption and degradation processes which changes the lignin fingerprint. In addition, base-flow DOM contributes only about 5% to the annual lignin discharge and might represent more localized sources (e.g. wetlands, taliks; Gibson pers. com.). In order to account for the lignin composition found in Yukon and Ob base-flow DOM one would need a mixture of approximately 1/3rd vegetation or litter (gymnosperm plus angiosperm), 1/3rd soil and peat and about 1/3rd of an unidentified source with highly elevated levels of p-hydroxybenzenes and p-coumaric acid. The unique lignin composition in base flow DOM in Yukon and Ob was not represented in any of the endmembers identified in this study (Table 4) but it obviously is characterized by very high contributions of p-hydroxybenzenes which are most abundant in mosses and peat.

The use of endmembers derived from different plants (Hedges and Mann, 1979) for describing the sources of river DOM based on lignin monomer ratios is not straightforward. A shift in the lignin monomer ratios has been observed during leaching and sorption processes (Hernes et al., 2007). Significant differences in the lignin composition have also been observed between soil organic matter and the corresponding soil DOM fraction (Prokushkin and Guggenberger pers. comm) as well as between leachates from litter, surface soils, and subsurface soils (Kaiser et al., 2004). In addition to phase change effects, we need to consider diagenetic effects which become more important during the mid and especially during base flow conditions. Some of the endmembers given in Table 4 are from leachates of plant material but the influence of sorption/desorption and degradation are still poorly constrained in our endmembers, like moss- and peat-derived DOM. The estimates given above are therefore rough estimates useful only for providing order of magnitude proportions. In order to understand the DOM sources during base flow conditions we need to develop a better understanding of the influence of leaching, sorption, desorption, and degradation on the lignin phenol composition of DOM in the different watersheds. In the property-property plots (Fig. 6AB) we compiled some of the available data on endmembers and put them in perspective to the river DOM values.

Sorption and desorption becomes more important in the late summer, fall, and winter as a larger fraction of river water comes from groundwater (Gibson and Prowse, 2002; Gibson pers. com.) and has therefore percolated through the soils. Hence, most of the low flow DOM has been in contact with different surface and subsurface soil layers. Typically, DOM in subsurface soils has a lower lignin yield than surface soils (Kaiser et al., 2004). Soil studies in the Yenisei watershed have directly shown that soil organic matter is different from soil DOM with a rapid decline in lignin yields, and an increase in S/V and C/V ratios, especially in DOM from subsurface soils (Prokushkin et al. in prep.). These trends are consistent with what we see in most rivers as they transition from snowmelt driven surface run-off to groundwater driven base flow. The general shift to lower lignin yields, higher S/V and C/V ratios along with elevated values of other lignin based diagenetic indicators (CAD/FAD; 3,5Bd/V; P/V), and DOM age between peak flow and low flow indicate that we are either seeing changes in the relative contribution from different DOM sources, differences in the relative contribution of DOM that has undergone processing either in the terrestrial environment or during transport, or a combination of the two. P/V ratios were particularly elevated during base flow in the Yukon and the Ob, which are also the two rivers with the oldest base flow DOM (Raymond et al., 2007). The only sources that could explain such high P/V values are mosses, soils, and peat bogs. The concentrations of p-hydroxybenzenes are significantly correlated to the Pn/P ratio, which never drops below 0.22. This argues against a significant contribution of p-hydroxybenzenes from the conversion of protein or carbohydrates during CuO oxidation. In addition, proteins and carbohydrates are typically not retained by the C18 resins used in this study to isolate lignin from the river samples. We think that the abundance of p-hydroxybenzenes in the river samples is a valid indicator for a significant moss and peat contribution to the DOM pool. Pn-yields are elevated in all rivers throughout the year, but particularly during base flow in Ob and Yukon. During freshet mosses are the most likely reason for elevated Pn-yields, while peat bogs and wetlands will become more important Pn sources during base flow.

A recent study (Jensco et al., 2009) pointed to the importance of hydrologic connectivity of a stream to its watershed when it comes to solute transport. This connectivity changes during seasons, with high connectivity during freshet (including hill slopes, valley bottoms, and lowlands) and low connectivity during winter low flow (hill slopes are largely disconnected) conditions. Translated to the large rivers studied here it would mean that during the freshet most of the watershed is hydrologically connected to the streams and therefore organic matter can derive from all parts of the watershed including hill slopes where most of the boreal forest biomass resides. During low flow conditions large parts of the watershed are isolated from the stream network, especially in watersheds with mountainous regions. This restricts organic matter sources to valley bottoms and lowlands, including wetlands. The lignin signature we found in the rivers indicates that such a shift is most pronounced in the Ob and Yukon. While in the Ob watershed one can expect a significant contribution from mosses and peat because it contains the largest peat bog system on earth, the shift in the Yukon River is less obvious. We think the reason we see a strong shift in the Yukon River has to do with the abundance of mountainous regions and lowland wetlands in the watershed and it seems that during low flow in winter much of the water and organic matter is contributed by those lowland wetlands. This does not agree with the satellite based vegetation data presented in Table 1, but would be consistent with a recent study stating that 30% of the Yukon watershed are covered by low lying wetlands (O'Donnell et al., 2010). The existing vegetation maps based on vegetation continuous field data (VCF-MODIS) or global land cover (GLC) data are not specific enough to completely resolve watershed differences and don't always agree with ground observations. Improved maps for watershed vegetation are needed to better understand carbon transport in a changing climate.

Due to the many poorly constrained factors influencing the lignin composition during base flow we feel it is premature to assign exact percentages to the different potential DOM sources for each river during the different seasons beyond the approximate breakdown for the most extreme situations given above. The main reason is that each watershed differs in terms of climate, vegetation, land use, topography, and hydrologic connectivity, and that sources and hydrology change in a different way in each watershed during the seasons. In general terms it appears that soil and peat DOM from wetlands contribute a dominant portion to the river DOM pool during low flow periods, but one has to keep in mind that only about 5% of the annual lignin load is discharged during the 6 month of low flow. During freshet, which contributes ~75% of the annual lignin load, vegetation and fresh litter from boreal forests seems to be by far the dominant source of river DOM.

### 4.4. Fate of river DOM in the Arctic Ocean

The input of terrigenous DOM to the Arctic Ocean has a strong geographic and seasonal bias. The Eurasian shelves receive ~90% of the total annual lignin discharge, while the Alaskan and Canadian shelves only receive 10% of the annual Arctic lignin load. Additionally, about 75% of the annual load is discharged during freshet. This uneven input has important implications for the distribution of lignin and our interpretation of its fate in the Arctic Ocean. After discharge, the general path of the bulk of terrigenous DOM in the Eurasian Arctic follows the Eurasian shelf to the East Siberian Sea where it enters the open Arctic Ocean in the Transpolar Drift and crosses the central Arctic towards Fram Strait and the Canadian Archipelago (Opsahl et al., 1999; Guay et al., 1999; Amon et al., 2003; Morrison et al., 2012; Amon et al. in prep.). Because of the strong seasonal discharge variation the distribution of terrigenous DOM will not be homogeneous along that path but rather reflect patches of elevated terrigenous DOM. A large proportion of the terrigenous DOM from North American rivers is transported east in the Alaskan Coastal Current and leaves the Arctic through the Canadian Archipelago (Macdonald et al., 2002). The smaller input of lignin to the Canada Basin is reflected in much lower lignin concentrations found in its surface waters, while the Transpolar Drift surface waters are characterized by very high lignin concentrations (Amon et al. in prep).

Terrestrial DOM has been used as a tracer of water masses in the Arctic Ocean (Guay et al., 1999; Amon et al., 2003; Benner et al., 2005; Walker et al., 2009; Gueguen et al., 2011) and its fate is therefore of interest to the wider Arctic oceanographic community. During the transit from the watersheds to the Arctic Ocean exit gateways a portion of the terrigenous DOM will be degraded, reducing the strong seasonal variation. The amount of degradation has been a matter of debate over the last few years but the rapid seasonal changes observed in river DOM concentration and composition indicate very strong temporal variability in sources (Fig. 3 and 5). For some lignin parameters, like the lignin yield, the shift in concentrations is very rapid (< 1 month) and it is therefore very difficult to determine a representative endmember concentration for Arctic rivers, especially when including the estuarine mixing zone. Early studies (Cauwet et al., 1996; Kattner et al., 1999; Koehler et al., 2003; Amon, 2004) have reported the conservative behavior of DOC during estuarine mixing in the late summer. More recent studies on the degradability of DOM in small Arctic rivers (Kawahigashi et al., 2004; Holmes et al., 2008) have indicated that a substantial fraction of the soil DOM and freshet DOM in the rivers is actually degradable on a time scale of a few weeks to months. Both studies indicate that 30-40% can be degraded during incubations with the bulk of the degradation happening during the first few weeks. Independent estimates for degradable DOC can be derived indirectly by comparing the peak flow DOC concentrations, determined in the PARTNERS Project, to theoretical river endmember DOC values derived from earlier studies in the Ob and Yenisei estuaries (Kara Sea; Koehler et al., 2003). However, to derive reasonable endmembers from the salinity-DOC relationships we corrected the DOC data for dilution caused by sea-ice melt (Figure 7). This is accomplished by using the existing estimates for sea ice melt, based on salinity and stable oxygen isotope values determined for each sample (Bauch et al., 2003). This correction increases DOC values in the low salinity regions resulting in a steeper slope of the linear regression, relating salinity to DOC concentrations, and therefore elevated theoretical river endmember concentrations (Fig. 7). Based on the corrected DOC values, the theoretical endmembers are 710 µM DOC for the Ob and 736 µM DOC for the Yenisei (Fig. 7) with corresponding freshet DOC concentrations of 925µM for the Ob and 1120 µM DOC for the Yenisei (Amon unpubl. data). Because the samples from the quantitatively most important rivers were collected >600 km upstream of the confluence with the Arctic Ocean (a time span of several weeks) a loss of lignin and terrigenous DOC in general could have occurred which could significantly lower the DOC input estimates to the Arctic Ocean.

Another argument in favor of rapid removal of freshet DOM can be found in the strong difference between the Mackenzie River and the other rivers. The Mackenzie seems to lack the large spike in lignin phenols (with young ages) during freshet. Because there is no logical reason to assume that the Mackenzie watershed would not produce the same type and amount of young, vegetation-derived DOM during freshet we propose that the lack of the spring peak can be explained by rapid removal during DOM transport from the watershed to the downstream sampling station. As explained above the Mackenzie watershed is unique in terms of the abundance of large lakes and other water bodies (Table 1), which increases the residence time or transit time of DOM within the watershed during which a significant fraction of labile components can be removed.

The reason for the differences between the bioavailability of freshet DOM and mid flow DOM must have to do with the difference in the chemical composition. Freshet DOM is characterized by very high lignin yields with elevated acid/aldehyde ratios indicating freshly leached vascular plant DOM. It is possible that a significant fraction of the plant leachates during spring freshet are free lignin phenols and ligno-cellulose compounds (Prokushkin et al., 2007), rather than structural lignin phenols, and the free lignin phenols could be degraded faster. This could explain the significant, but short-lived spike in lignin phenol yields during freshet and lignin yield could be an indicator for riverine DOM bioavailability, analogous to what has been observed for the neutral sugar yield (Cowie and Hedges, 1982; Skoog and Benner, 1997; Amon et al., 2001). If these assumptions are correct a significant portion of freshet DOM could be removed before passing the estuaries into the Arctic Ocean, which will affect our estimates for input, distribution, export, and processing of terrestrial DOM in the Arctic Ocean.

## 5. CONCLUSIONS

The lignin phenol and p-hydroxybenzene composition of Arctic river DOM indicate a strong seasonal change in DOM sources with fresh vegetation, mainly boreal forests, dominating during spring freshet and contributing 75% of the annual lignin load, while base flow DOM contains a significant fraction of peat/moss derived DOM (>30%). DOM from different watersheds can be distinguished from each other reflecting the variations in climate, vegetation, topography, and hydrologic connectivity in the watersheds. All rivers except the Mackenzie showed comparable patterns in lignin signatures with strong relationships to the $^{14}$C-age of DOM. With a warming climate, increased precipitation and hydrologic connectivity, and a northward extension of the boreal forests, one can expect an increase in DOM transport to the Arctic Ocean in the future. During spring freshet such an increase will be caused by more biomass production in the watersheds. For the base flow conditions increasing hydrologic connectivity in the high latitude watersheds could be the key parameter for increasing DOM fluxes during that time. Increased frequency of forest fires, on the other hand, would decrease the biomass in the watersheds and as a consequence decrease the DOM export. Our data suggest that current descriptions of watershed characteristics, especially the distribution of vegetation in these large watersheds could be improved in terms of forest cover and wetland contributions.

DOC input to the Arctic Ocean has a very high temporal and geographical variability with a strong bias towards the large Eurasian Rivers and the freshet period. The large and rapid temporal variability paired with complex estuarine DOC dynamics (ice formation and melt) make it difficult to choose representative river DOC input estimates which have a disproportionate effect on our understanding of DOC export and fate in the Arctic Ocean.

## REFERENCES

Abaimov A.P. (2010) Geographical distribution and genetics of Siberian Larch species. In: Permafrost ecosystems: Siberian Larch forests (Eds. Osawa A., Zyryanova O.A., Matsuura Y., Kajimoto T., Wein R.W.) Springer. NY. pp. 41-58.

Amon R. M. W., Fitznar H.-P., Benner R. (2001) Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. *Limnol. Oceanogr*. **46**, 287-297.

Amon RMW. (2004) The role of dissolved organic matter for the organic carbon cycle in the Arctic Ocean. In: Stein R., MacDonald R. (editors.) The organic carbon cycle in the Arctic Ocean. Berlin, Springer; 2003. p83−99.

Amon R. M. W., Budeus G., Meon B. (2003) Dissolved organic carbon distribution and origin in the Nordic Seas: Exchanges with the Arctic Ocean and the North Atlantic. *J. Geophys. Res*. **108** (C7, 3221): doi:10.1029/2002JC001594.

Amon R. M. W. and Meon B. (2004) The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean System. *Marine Chemistry* **92**, 311-330.

Bauch, D., Erlenkeuser H., Stanovoy V., Simstich J., Spielhagen R. F. (2003) Freshwater distribution and brine waters in the southern Kara Sea. Siberian river run-off in the Kara Sea. Stein R., Fahl K., Fütterer D. K., Galimov E. M. and Stephanets O. V. Amsterdam, Elsevier. **6**, 73-91.

Benner R., Weliky K., Hedges J. I. (1990) Early diagenesis of mangrove leaves in a tropical estuary - molecular-level analyses of neutral sugars and lignin-derived phenols. *Geochimica Et Cosmochimica Acta* **54**, 1991-2001.

Benner R. and Opsahl S., (2001) Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi River plume. *Organic Geochemistry* **32**(4), 597-611.

Benner R., Benitez-Nelson B., Kaiser K., and Amon R. M. W. (2004) Export of young terrigenous dissolved organic carbon from rivers to the Arctic Ocean. *Geophysical Research Letters* **31**, L05305, doi:10.1029/2003GL019251

Benner R., Louchouarn P. and Amon R. M. W., 2005. Terrigenous dissolved organic matter in the Arctic Ocean. *Global Biogeochemical Cycles* **19**, GB2025, doi:10.1029/2004GB002398

Benner R. and Kaiser K. (2010) Biological and photochemical transformations of amino acids and lignin phenols in riverine dissolved organic matter. *Biogeochemistry* **102**, 209-222.

Brabets T. P., Wang B., and Meade R. H. (2000) Environmetnal and hydrological overview of the Yukon River Basin, Alaska and Canada, U.S. Geological Survey Water Resources Investment Report. 99-4209, 106 pp.

Breckle S. (2002) Walter's vegetation of the Earth. Berlin, Heidelberg, Springer.

Cauwet G., and Sidorov I. (1996) The biogeochemistry of Lena River: Organic carbon and nutrients distribution. *Marine Chemistry* **53**, 211-227.

Cole J. J., Prairie Y. T., Caraco N. F., McDowell W. H., Tranvik L. J., Striegl R. G., Duarte C. M., Kortelainen P., Downing J. A., Middelburg J. J. and Melack . (2007) Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems* **10**(1), 171-184.

Cooper L. W., Benner R., McClelland J. W., Peterson B. J., Holmes R. M., Raymond P. A., Hansell D. A., Grebmeier J. M., and Codispotti L. A. (2005) Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. *J. Geophys. Res*. **110**, G02013, doi:10.1029/2005JG000031, 2005.

Cooper L. W., McClelland J. W., Holmes R. M., Raymond P. A., Gibson J. J., Guay C. K. and Peterson B. J. (2008) Flow-Weighted values of runoff tracers (d18O, DOC, Ba, alkalinity) from the six largest Arctic rivers. *Geophys. Res. Lett*. **35**. L18606, doi:10.1029/2008GL035007

Cowie G. L. and Hedges J. I. (1984). Carbohydrate sources in a coastal marine environment. *Geochimica et Cosmochimica Acta* **48**, 2075-2087.

Ertel J. R. and Hedges J. I. (1984) The lignin component of humic substances - distribution among soil and sedimentary humic, fulvic, and base-insoluble fractions. *Geochimica Et Cosmochimica Acta* **48**, 2065-2074.

Ertel J. R., Caine J. M. and Thurman E. M. (1993) Biomarker compounds as source indicators for dissolved fulvic-acids in a bog. *Biogeochemistry* **22**(3), 195-212.

Ertel J. R., Hedges J. I., Devol A., Richey J. E. and de Nazare Goes Ribeiro M. (1986) Dissolved humic substances of the Amazon River system. *Limnology and Oceanography* **31**(4): 139-154.

Finlay J., Neff J., Zimov S., Davydova A., and Davydov S. (2006) Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC. *Geophysical Research Letters* **33**, L10401, doi:10.1029/2006GL025754

Gibson J. J and Prowse T. D., (2002) Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance. *Hydrological Processes* **16**, 873-890.

Goñi M. A. and Hedges J. I. (1992) Lignin Dimers - Structures, Distribution, and Potential Geochemical Applications. *Geochimica Et Cosmochimica Acta*, **56**(11), 4025-4043.

Goñi M. A. and Hedges J. I. (1995) Sources and Reactivities of Marine-Derived Organic-Matter in Coastal Sediments as Determined by Alkaline Cuo Oxidation. *Geochimica Et Cosmochimica Acta*, **59**(14), 2965-2981.

Goñi M. A. and Montgomery, S. (2000) Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. *Analytical Chemistry*, **72**(14): 3116-3121.

Goni M. A., Yunker M. B., Macdonald R. W., and Eglington T. I. (2000) Distribution and sources of organic biomarkers in arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry* **71**, 23-51.

Goni M. A., Yunker M. B., Macdonald R. W., and Eglington T. I. (2005) The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean. *Marine Chemistry* **93**, 53-73.

Gordeev V. V. (2006) Fluvial sediment flux to the Arctic Ocean. *Geomorphology* **80**, 94-104.

Gordeev V. V., Rachold V., and Vlasova I. E. (2004) Geochemical behaviour of major and trace elements in suspended particulate material of the Irtysh river, the main tributary of the Ob river, Siberia. *Applied Geochemistry* **19**, 593-610.

Granskog M. A., Stedmon C. A., Dodd P. A., Amon R. M. W., Pavlov A., Hansen K. (2012) Fate of terrestrial colored dissolved organic matter in the Arctic Ocean: exported or removed? *Geophysical Research Letters* (submitted)

Guay, C. K. H., McLaughlin F. A., and Yamamoto-Kawai M. (2009) Differentiating fluvial components of upper Canada Basin waters on the basis of measurements of dissolved barium combined with other physical and chemical tracers, *J. Geophys. Res.,* **114**, C00A009, doi:10.1029/2008JC005099.

Guéguen, C., McLaughlin F. A., Carmack E. C., Itoh M., Narita H., Nishino S. (2011) The nature of colored dissolved organic matter in the southern Canada Basin and East Siberian Sea. *Deep Sea Res. II* doi:10.1016/j.dsr2.2011.05.004

Guggenberger G. und Zech W. (1994) Composition and dynamics of dissolved carbohydrates and lignin-degradation products at spruce forest sites, Bavaria, Germany. *Soil Biol. Biochem.* **26**, 19-27.

Guo L. D., and Macdonald R. W. (2006) Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (delta C-13, Delta C-14, and delta N-15) composition of dissolved, colloidal, and particulate phases. *Global Biogeochemical Cycles* **20**: DOI:10.1029/2005GB002593

Hedges J. I. and Parker P. L. (1976) Land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta* **40** 1019-1029.

Hedges J. I. and Mann D. C. (1979) Characterization of Plant-Tissues by Their Lignin Oxidation-Products. *Geochimica et Cosmochimica Acta* **43**(11), 1803-1807.

Hedges J. I. and Ertel J. R. (1982) Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry* **54**, 174-178.

Hedges J. I., Ertel J. R. and Leopold E. B. (1982) Lignin geochemistry of a Late Quaternary sediment core from Lake Washington. *Geochimica et Cosmochimica Acta* **46**(10), 1869-1877.

Hedges J. I., Keil R. G. and Benner R. (1997) What happens to terrestrial organic matter in the ocean? *Organic Geochemistry*, **25**(5/6), 195-212.

Hedges J. I., Mayorga E., Tsamakis E., McClain M.E., Aufdenkampe A.K., Quay P.D., Richey J.E., Benner R., Opsahl S. (2000) Organic matter in Bolivian tributaries of the Amazon River: A comparison to the lower mainstream. *Limnology and Oceanography* **45**(7), 1449-1466.

Hernes P. J. and Benner R. (2002) Transport and diagenesis of dissolved and particulate terrigenous organic matter in the North Pacific Ocean. *Deep-Sea Research Part I*-Oceanographic Research Papers **49**, 2119-2132.

Hernes P. J., Robinson A. C. and Aufdenkampe A.K. (2007) Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters*, **34**(17), L17401, doi:10.1029/2007GL031017

Holmes R. M., McClelland J. W., Peterson B. J., Shiklomanov I. A., Shiklomanov A. I., Zhulidov A. V., Gordeev V. V., and Bobrovitskaya N. N. (2002) A circumpolar perspective on fluvial sediment flux to the Arctic Ocean. *Global Biogeochemical Cycles* **16**, 1098, doi:10.1029/2001GB001849.

Holmes R. M., McClelland J. W., Raymond P. A., Frazer B. B., Peterson B. J., Stieglitz M. (2008) Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophys. Res. Lett.* **35**, L03402, doi:10.1029/2007GL032837.

Holmes R. M., McClelland J. W., Peterson B. J., Tank S. E., Bulygina E., Eglinton T. I., Gordeev V. V., Gurtovaya T. Y., Raymond P. A., Repeta D. J., Staples R., Striegl R. G., Zhulidov A. V., and Zimov S. A. (2011) Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. *Estuaries and Coasts*, DOI 10.10007/s12237-011-9386-6.

Houel S., Louchouarn P., Lucotte M., Canuel R. and Ghaleb B. (2006) Translocation of soil organic matter following reservoir impoundment in boreal systems: Implications for in situ productivity. *Limnology and Oceanography* **51**, 1497-1513.

Jencso K. G., McGlynn B. L., Gooseff M. N., Wondzell S. M., Bencala K. E. and Marshall L. A. (2009) Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale, *Water Resour. Res.*, ***45***, W04428, doi:10.1029/2008WR007225.

Kaiser K., Guggenberger G. and Haumaier L. (2004) Changes in dissolved lignin derived phenols, neutral sugars, uronic acids, and amino sugars with depth in forested Haplic Arenosols and Rendzic Leptosols. *Biogeochemistry* **70**, 135-151.

Kattner G., Lobbes J., Fritznar H. P., Engbrodt R., Lara R. J. (1999) Tracing dissolved organic substances and nutrients from the Lena River through Laptev Sea (Arctic). *Mar. Chem.* **65**, 25-39.

Kawahigashi M., Kaiser K., Kalbitz K., Rodionov A. and Guggenberger G. (2004) Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. *Global Change Biology* **10**, 1576-1586.

Kawahigashi M., Kaiser K., Rodionov A. and Guggenberger G. (2006) Sorption of dissolved organic matter by mineral soils of the Siberian forest tundra. *Global Change Biology* **12**, 1868-1877.

Koehler H., Meon B., Gordeev V. V., Spitzy A. and Amon R. M. W. (2003) Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara-Sea, Russia. *Proceedings in Marine Science* **6**, 281-309.

Kremenetski K. V., Velichko A. A., Borisova O. K., MacDonald G. M., Smith L. C., Frey K. E. and Orlova L. A. (2003) Peatlands of the Western Siberian lowlands: Current knowledge on zonation, carbon content and Late Quaternary history. *Quaternary Science Reviews* **22**, 703–723.

Kuo L.-J., Herbert B. E. and Louchouarn P. (2008a) Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? *Organic Geochemistry* **39**, 1466-1478.

Kuo L.-J., Louchouarn P. and Herbert B. E. (2008b) Fate of CuO-derived lignin oxidation products during plant combustion: Application to the evaluation of char inputs to soil organic matter. *Organic Geochemistry* **39**, 1522–1536.

Lobbes J. M., Fitznar H. P. and Kattner G. (2000) Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. *Geochimica Et Cosmochimica Acta* **64**, 2973-2983.

Louchouarn P., Opsahl S. and Benner R. (2000) Isolation and quantification of dissolved lignin from natural waters using solid-phase extraction and GC/MS. *Analytical Chemistry* **72**, 2780-2787

Louchouarn P., Amon R. M. W., Duan S., Pondell C., Seward S. M. and White N. (2010) Analysis of lignin-derived phenols in standard reference materials and dissolved organic matter by gas chromatography/tandem mass spectrometry. *Marine Chemistry* **118**, 85–97.

Macdonald, R. W., McLaughlin F. A. and Carmack E. C. (2002) Freshwater and its sources during the SHEBA drift in the Canada Basin of the Arctic Ocean. *Deep-Sea Research I.* **49**(10), 1769-1785.

McClelland J. W., Holmes R. M., Peterson B. J., Amon R. M. W., Brabets T., Cooper L., Gibson J., Gordeev V.V., Guay C., Milburn D., Raymond P.A., Shiklomanov I., Staples R., Striegl R., Zhulidov A.T., Gurtovaya T., Zimov S. (2008) Development of a Pan-Arctic Database for River Chemistry. *EOS* **89**(24), 217−218.

McGuire A. D., Anderson L. A. Christensen T.R., Dallimore S., Guo L., Hayes D.J., Heimann M., Lorenson T.D., Macdonald R.W., Roulet, N. (2009) Sensitivity of the carbon cycle in the Arctic to climate change. *Ecological Monographs* **79**(4), 523-555.

McGuire A. D., Macdonald R. W., Schuur E. A. G., Harden J. W., Kuhry P., Hayes D. J., Christensen T. R., and Heimann M. (2010) The carbon budget of the northern cryospere region. *Current opinion in Environmental sustainability* **2**, 231-236.

Morison J., Kwok R., Peralta-Ferriz C., Alkire M., Rigor I., Andersen R. and Steele, M., 2012. Changing Arctic Ocean freshwater pathways. *Nature* **481**, 66-70.

Neff J. C., Finlay S. A., Zimov S. P., Davydov J. J. Carrasco E., Schuur A. G. and Davydova A. I. (2006) Seasonal changes in the age and structure of dissolved organic carbon in

Siberian rivers and streams. *Geophysical Research Letters* **33**, L23401, doi: 10.1029/2006GL028222

Opsahl S. and Benner R. (1995) Early diagenesis of vascular plant-tissues - lignin and cutin decomposition and biogeochemical implications. *Geochimica Et Cosmochimica Acta* **59**, 4889-4904.

Opsahl S. and Benner R. (1997) Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature* **386**, 480-482.

Opsahl S. and Benner R. (1998) Photochemical reactivity of dissolved lignin in river and ocean waters. *Limnology and Oceanography* **43**, 1297-1304.

Opsahl S., Benner R. and Amon R. M. W. (1999) Major flux of terrigenous dissolved organic matter through the Arctic Ocean. *Limnology and Oceanography* **44**, 2017-2023.

Ouellet J., Lucotte M. Teisserenc R., Paquet S., Canuel R. (2009) Lignin biomarkers as tracers of mercury sources in lakes water column. *Biogeochemistry* **94**, 123-140.

Peterson B. J., Holmes R. M., McClelland J. W., Vorosmarty C. J., Shiklomanov I. A., Shiklomanov A. I., Lammers R. B. and Rahmstorf S. (2002) Increasing river discharge to the Arctic Ocean. *Science* **298**, 2171-2173.

Peterson M. L., Lang S. Q., Aufdenkampe A. K. and Hedges J. I. (2003) Dissolved organic carbon measurement using a modified high-temperature combustion analyzer. *Marine Chemistry* **81**, 89-104.

Prokushkin S. G., Abaimov A. P., Prokushkin A. S., Masyagina O. V. (2006) Biomass of ground floor vegetation and understory in larch forests of cryolythozone of Central Siberia.

*Sibirskiy Ekologicheskiy zhurnal* (Contemporary Problems of Ecology) **2**, 131-139. (In Russian)

Prokushkin A. S., Gleixner G., McDowell W. H., Ruehlow S. and Schulze E.-D. (2007) Source and substrate-specific export of dissolved organic matter from permafrost-dominated forested watershed in central Siberia. *Global Biogeochemical Cycles,* **21**, GB4003, doi: 10.1029/2007GB002938.

Prokushkin A. S*.,* Pokrovsky O.S., Shirokova L. S., Korets M.A., Viers J., Prokushkin S. G., Amon R. M. W., Guggenberger G. and McDowell W.H. (2011) Sources and the flux pattern of dissolved carbon in rivers of the Yenisey basin draining the Central Siberian Plateau. *Environ. Res. Lett.* **6** 045212 (14pp) doi:10.1088/1748-9326/6/4/045212.

Qian J. G., and Mopper K. (1996). Automated high performance, high-temperature combustion total organic carbon analyzer. *Analytical Chemistry* **68**, 3090-3097

Rachold, V. (1999) Major, trace and rare earth element geochemistry of suspended particulate material of east siberian rivers draining to the arctic ocean. In Land-ocean systems in the Siberian Arctic dynamics and history. Eds: Kassens, H., Bauch H.A., Dmitrenko I.A., Eicken H., Hubberten, H.W. Melles, M. Thiede, J., Timokhov, L.A.. Springer-Verlag, New York.

Rachold V., Eicken H., Gordeev V.V., Brigoriev M.N., Hubberten M.-W., Lisitzin A.P., Shevschenko V.P. and Schirrmeister L. (2004) Modern terrigenous organic carbon input to the Arctic Ocean. In: The organic carbon cycle in the Arctic Ocean. Eds: Stein, R. and Macdonald, R.W. pages 33-54.

Raymond P. A., McClelland J. W., Holmes R. M., Zhulidov A. V., Mull K., Peterson B. J., Striegl R. G., Aiken G. R. and Gurtovaya T. Y. (2007) Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers, *Global Biogeochem. Cycles* **21**: GB4011, doi:10.1029/2007GB002934.

Sanger L. J., Anderson J. M., Little D. and Bolger T. (1997) Phenolic and carbohydrate signatures of organic matter in soils developed under grass and forest plantations following changes in land use. *European Journal of Soil Science* **48**, 311-317.

Šantrůčková H., Bird M. I., Kalaschnikov Y. N., Grund M., Elhottová D., Šimek M., Grigoryev S., Gleixner G. (2003) Microbial characteristics of soils on a latitudinal transect in Siberia. *Global Change Biology*. **9**, 1106-1117

Schiff S. L., Aravena R., Trumbore S. E., Hinton M. Elgood J., R., Dillon P. J. (1997) Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from 13C and 14C, *Biogeochemistry* **36**, 43-65

Smith L. C., MacDonald G. M., Velichko A. A., Beilman D. W., Borisova O. K., Frey K. E., Kremenetski K. V. & Sheng Y. (2004) Siberian peatlands a net carbon sink and methane source since the early Holocene. *Science* **303**, 353–356

Spencer R. G. M., Aiken G. R., Butler K. D., Dornblaser M. M., Striegl R. G., Hernes P. (2009) Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon river, Alaska, *Geophys. Res. Lett.*; **36**, L06401, doi:10.1029/2008GL036831.

Spencer R. G. M., Aiken G. R., Wickland K. P., Striegl R. G., Hernes P. J. (2008) Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon river basin, Alaska. *Global Biogeochem*. *Cycles*. **22**, GB4002, doi:10.1029/2008GB003231.

Skoog A. and Benner R. (1997) Aldoses in various size fractions of marine organic matter: Implications for carbon cycling. *Limn. Oceanogr*. **42**, 1803-1813.

Stedmon C. A., Amon R. M. W., Rhinehart A. J., Walker S. A. (2011) The supply and characteristics of colored dissolved organic matter (CDOM) in the Arctic Ocean. *Marine Chemistry* **124**, 108-118. DOI:10.1016/j,marchem.2010.12.007

Stolbovoi V. 2002. Carbon in Russian soils. *Climatic Change* **55**, 131-156.

Stolbovoi V., Fischer G., Ovenkin V.S. and Rozhkova S. (1998) Soils of Russia-correlated with the revised legend of the FAO soil map of the world, IIASA Interim Report IR-97-070, International Institute for Applied Systems Analysis, Laxenburg, Austria.

Strasburger E., Noll F., Schenck H., Schimper A. F. W. Denffer D., Ziegler H., Ehrendorfer F., Bresinsky A. (1983). Lehrbuch der Botanik. Stuttgard, Gustav Fisher Verlag. (in German).

Striegl R. G., Aiken G. R., Dornblaser M. M., Raymond P. A., and Wickland K. P. (2005) A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. *Geophysical Research Letters* **32**, DOI:10.1029/2005GL024413

Striegl R. G., Dornblaser M. M., Aiken G. R., Wickland K. P. and Raymond P. A. (2007) Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001-2005. *Water Resources Research* **43**, DOI:10.1029/2006WR005201

Tareq S. M., Tanaka N. Keiichi O. (2004) Biomarker signature in tropical wetland: lignin phenol vegetation index (LPVI) and its implications for reconstructing the paleoenvironment. *Science of the Total Environment* **324**, 91-103.

Tarnocai C., Canadell J. G., Schuur E. A. G., Kuhry P., Mazhitova G., Zimov S. (2009) Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochemical cycles*; **23**, GB2023, doi:10.1029/2008GB003327.

Teisserenc R., Lucotte M., Houel S., Carreau J. (2010) Integrated transfer of terrigenous organic matter to lakes at their watershed level: A combined biomarker and GIS analysis. *Geochim. Cosmochim. Acta* **74**, 6375-6386.

Timoney K. P., Laroi G. H., Zoltai S. C. and Robinson A. L. (1993) Vegetation communities and plant-distributions and their relationships with parent materials in the forest-tundra of northwestern Canada. *Ecography* **16**, 174-188.

Ugolini F. C., Reanier R. E., Rau, G. H., Hedges J. I. (1981) Pedological, isotopic, and geochemical investigations of the soils at the boreal forest and alpine tundra transition in northern Alaska. *Soil Science* **131**(6), 359-374.

Wagner V. (1997) Analysis of a Russian Landscape map and landscape classification for use in computer-aided forestry research. IIASA Interim Report I97-54, International Institute for Applied Systems Analysis, Laxenburg, Austria.

Walvoord M. A. and Striegl R. G. (2007) Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen. *Geophysical Research Letters* **34**, L12402, doi:10.1029/2007GL030216

Walker S. A., Amon R. M. W., Stedmon C., Duan S. and Louchouarn P. (2009) The use of PARAFAC modeling to trace dissolved organic matter and fingerprint water masses in coastal Canadian Arctic surface waters. *J. Geophys. Res*., **114**, G00F06, doi:10.1029/2009JG000990.

Williams C. J., Yavitt J. B., Kelman Wieder R. and Cleavitt N. L. (1998) Cupric oxide oxidation products of northern peat and peat-forming plants. *Can. J. Bot* **76**, 51-62.

Yang D. Q., Ye B. S. and Shiklomanov A. (2004) Discharge characteristics and changes over the Ob River watershed in Siberia. *Journal of Hydrometeorology* **5**, 595-610.

Yi Y., Gibson J. J., Hélie J., Dick T. A. (2010) Synoptic and time series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003-2006. *Journal of Hydrology* **383**, 223-232.

Zhang T., Barry R. G. and Knowles K. (1999) Statistics and characteristics of permafrost and ground-ice distribution in the northern hemisphere. *Polar Geography* **23,** 132-154.

Zhulidov A. V., Headley J. V., Robarts R. D., Nikanorov A. M. and Ischenko A. A. (1997) Atlas of Russian Wetlands: Biogeography and Metal Concentrations. Editor M. J. Brannen. Foreword R.G. Wetzel. National Hydrology Research Institute, Canada, 309 pp.

**Figure legends**

Figure 1. Map of the watersheds of Ob, Yenisei, Lena, Kolyma, Yukon, and Mackenzie with the respective sampling locations indicated by a dot in the lower reaches of the rivers.

Figure 2. Seasonal discharge and lignin phenol concentrations (ug/L) in the 6 rivers between 2003 and 2007.

Figure 3. Average Lignin phenol concentrations and monomer ratios during the freshet, mid flow and base flow periods in the 6 rivers.

Figure 4. Relationship of lignin phenol concentrations to $\Delta^{14}C$ (‰) of dissolved organic carbon (DOC) in the six rivers.

Figure 5. Relationship of lignin phenol monomer ratios and lignin yield to $\Delta^{14}C$ (‰) of dissolved organic carbon (DOC).

Figure 6. Property-property plots of lignin phenol monomer ratios (A, S/V versus C/V and B, p-hydroxybenzenes/V versus p-hydroxyacetophenone/P) in river dissolved organic matter (DOM) relative to different source materials. G-Gymnosperm wood, g-gymnosperm needles, A-angiosperm wood, a-angiosperm leaves, BFL-boreal forest lake, B-soil B horizon.

Figure 7. Distribution of DOC along the salinity gradient in the Ob and Yenisei estuaries relative to the measured freshet DOC values in the rivers (shown at 0 salinity). The difference between

the theoretical riverine DOC endmember, based on a linear relationship of DOC and salinity, and the freshet DOC values is considered degradable DOC. However, during freshet the estuaries and coastal ocean is still frozen and the massive discharge of relatively warm riverwater will result in significant sea ice melt which dilutes the DOC concentrations. In order to correct for this dilution we estimated the amount of sea ice melt based on stable oxygen isotope values of water (Bauch et al. 2003) measured in the same samples as DOC. Stable oxygen isotopes of water along with salinity can be used in mass balance equations to calculate the contribution of river water, sea ice melt, and sea water, respectively (Bauch et al. 2003). Correcting for sea ice melt increases the DOC concentration. The same approach can be used to correct for the influence of brine, produced in the previous winter, which has the opposite effect on DOC concentrations. Linear regression used to estimate the theoretical endmembers are shown for both the uncorrected and the corrected DOC data set. The uncertainty for theoretical endmembers was ± 27.9 µM DOC for the Ob River and ± 13.5 µM DOC for the Yenisey River.

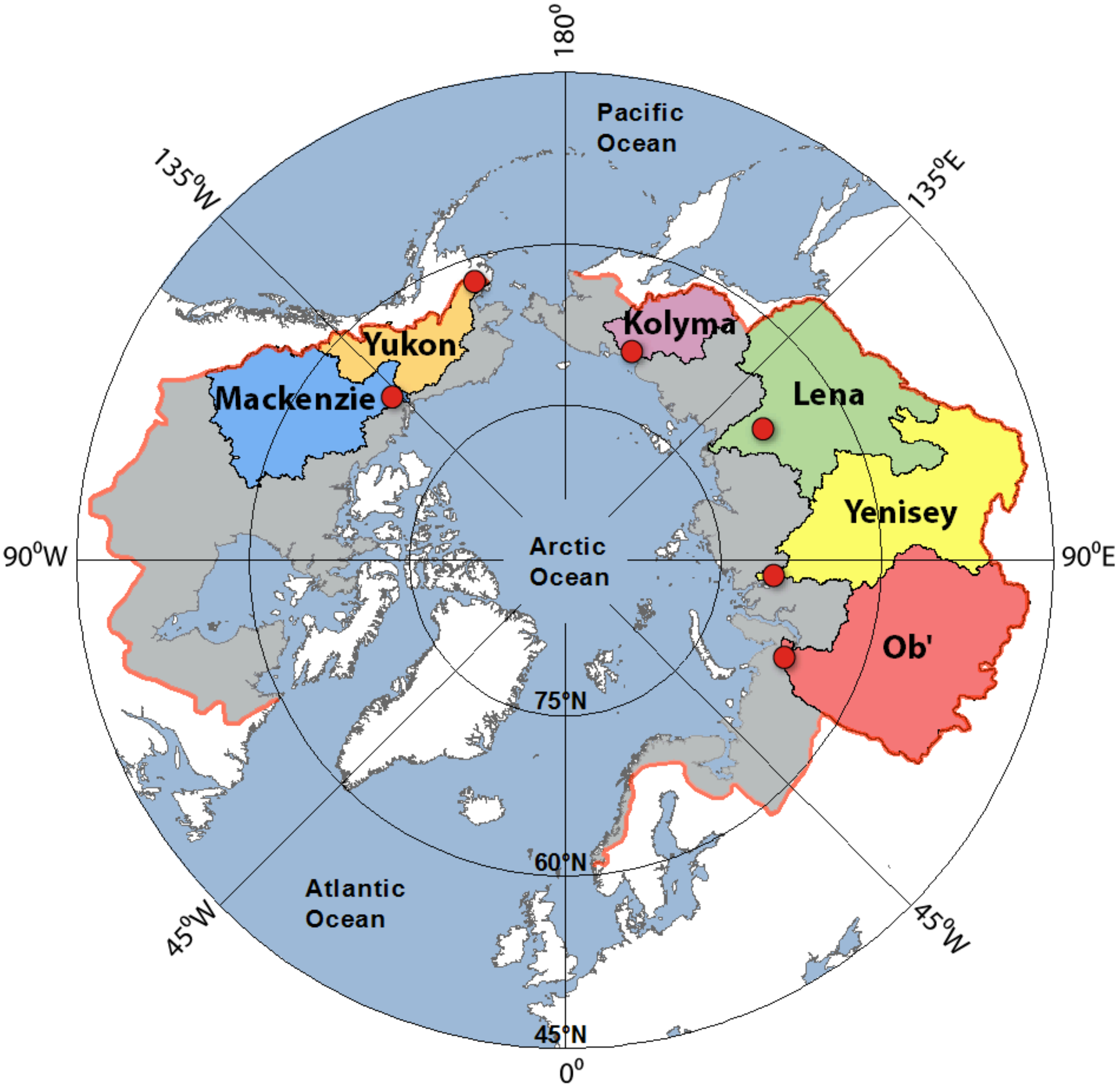
180°
Pacific Ocean
135°W
135°E
Kolyma
Yukon
Lena
Mackenzie
Yenisey
90°W
Arctic Ocean
90°E
Ob'
75°N
60°N
Atlantic Ocean
45°W
45°W
45°N
0°

Figure 1

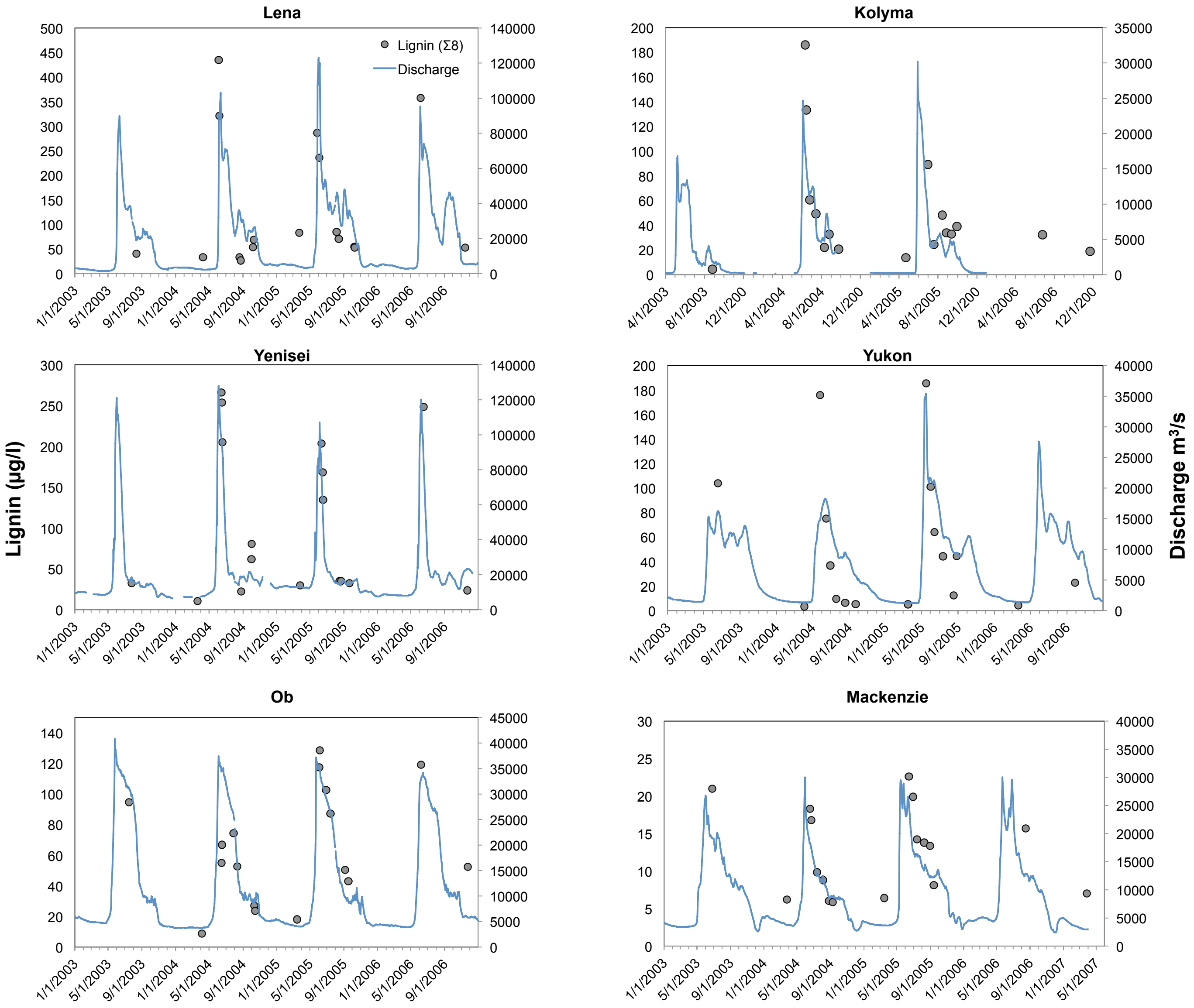
Lena
Lignin (Σ8)
Discharge
0 50 100 150 200 250 300 350 400 450 500
0 20000 40000 60000 80000 100000 120000 140000
1/1/2003 5/1/2003 9/1/2003 1/1/2004 5/1/2004 9/1/2004 1/1/2005 5/1/2005 9/1/2005 1/1/2006 5/1/2006 9/1/2006
Kolyma
0 20 40 60 80 100 120 140 160 180 200
0 5000 10000 15000 20000 25000 30000 35000
4/1/2003 8/1/2003 12/1/200 4/1/2004 8/1/2004 12/1/200 4/1/2005 8/1/2005 12/1/200 4/1/2006 8/1/2006 12/1/200
Yenisei
0 50 100 150 200 250 300
0 20000 40000 60000 80000 100000 120000 140000
1/1/2003 5/1/2003 9/1/2003 1/1/2004 5/1/2004 9/1/2004 1/1/2005 5/1/2005 9/1/2005 1/1/2006 5/1/2006 9/1/2006
Yukon
0 20 40 60 80 100 120 140 160 180 200
0 5000 10000 15000 20000 25000 30000 35000 40000
1/1/2003 5/1/2003 9/1/2003 1/1/2004 5/1/2004 9/1/2004 1/1/2005 5/1/2005 9/1/2005 1/1/2006 5/1/2006 9/1/2006
Lignin (µg/l)
Discharge m³/s
Ob
0 20 40 60 80 100 120 140
0 5000 10000 15000 20000 25000 30000 35000 40000 45000
1/1/2003 5/1/2003 9/1/2003 1/1/2004 5/1/2004 9/1/2004 1/1/2005 5/1/2005 9/1/2005 1/1/2006 5/1/2006 9/1/2006
Mackenzie
0 5 10 15 20 25 30
0 5000 10000 15000 20000 25000 30000 35000 40000
1/1/2003 5/1/2003 9/1/2003 1/1/2004 5/1/2004 9/1/2004 1/1/2005 5/1/2005 9/1/2005 1/1/2006 5/1/2006 9/1/2006 1/1/2007 5/1/2007

Figure 2

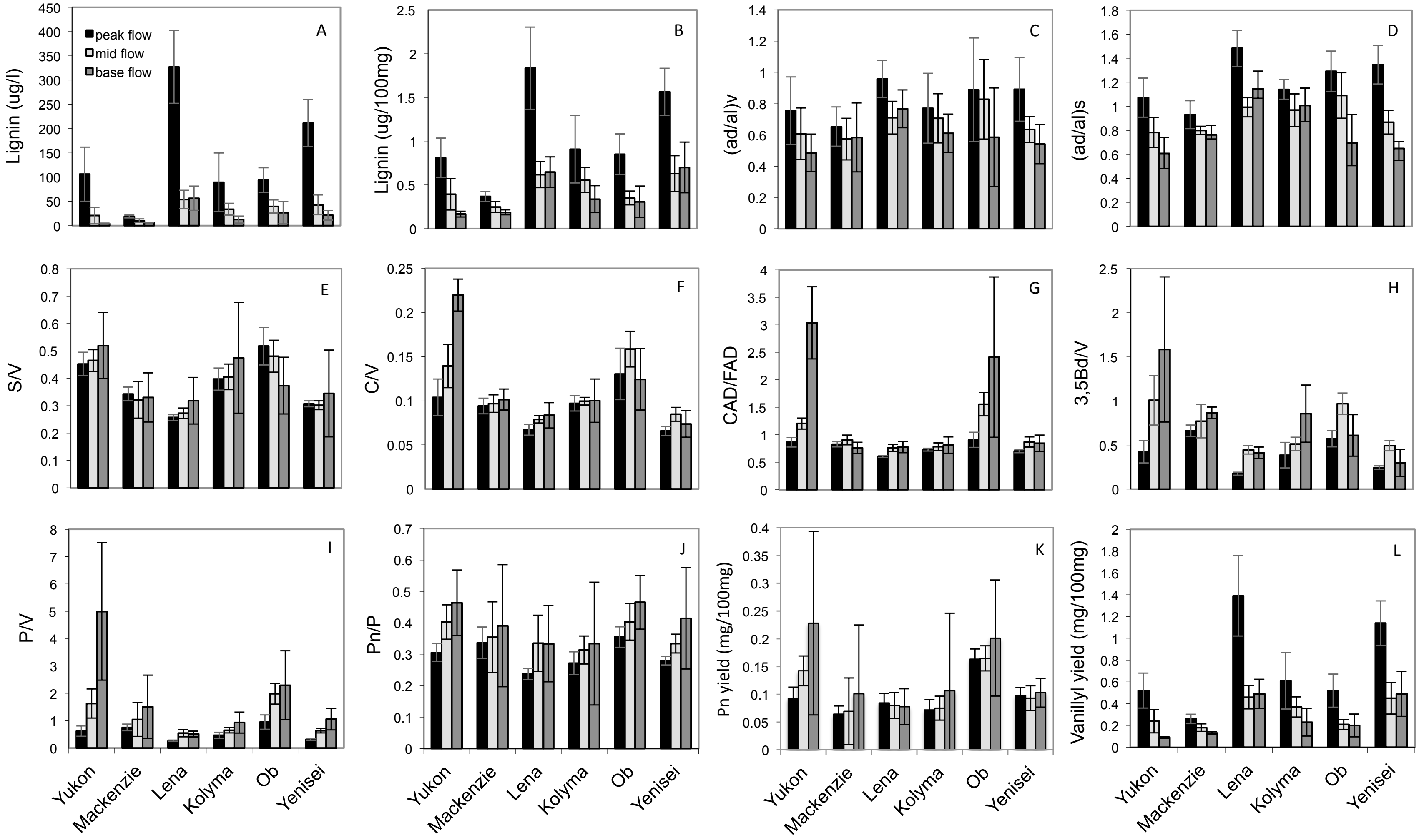
A
Lignin (ug/l)
0
50
100
150
200
250
300
350
400
450
■ peak flow
□ mid flow
▨ base flow
B
Lignin (ug/100mg)
0
0.5
1
1.5
2
2.5
C
(ad/al)v
0
0.2
0.4
0.6
0.8
1
1.2
1.4
D
(ad/al)s
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
E
S/V
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
F
C/V
0
0.05
0.1
0.15
0.2
0.25
G
CAD/FAD
0
0.5
1
1.5
2
2.5
3
3.5
4
H
3,5Bd/V
0
0.5
1
1.5
2
2.5
I
P/V
0
1
2
3
4
5
6
7
8
J
Pn/P
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
K
Pn yield (mg/100mg)
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
L
Vanillyl yield (mg/100mg)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Yukon
Mackenzie
Lena
Kolyma
Ob
Yenisei

Figure 3

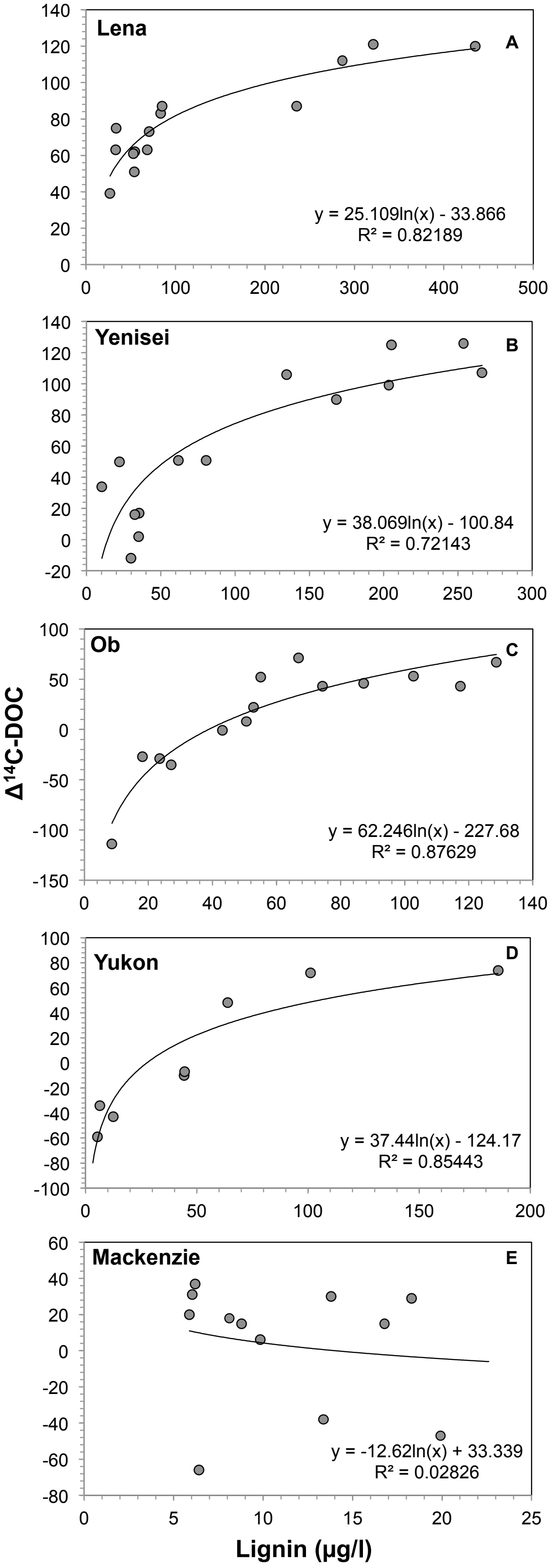
Lena
A
y = 25.109ln(x) - 33.866
R² = 0.82189
0
20
40
60
80
100
120
140
0
100
200
300
400
500
Yenisei
B
y = 38.069ln(x) - 100.84
R² = 0.72143
-20
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300
Ob
C
y = 62.246ln(x) - 227.68
R² = 0.87629
-150
-100
-50
0
50
100
0
20
40
60
80
100
120
140
Δ14C-DOC
Yukon
D
y = 37.44ln(x) - 124.17
R² = 0.85443
-100
-80
-60
-40
-20
0
20
40
60
80
100
0
50
100
150
200
Mackenzie
E
y = -12.62ln(x) + 33.339
R² = 0.02826
-80
-60
-40
-20
0
20
40
60
0
5
10
15
20
25
Lignin (µg/l)

Figure 4

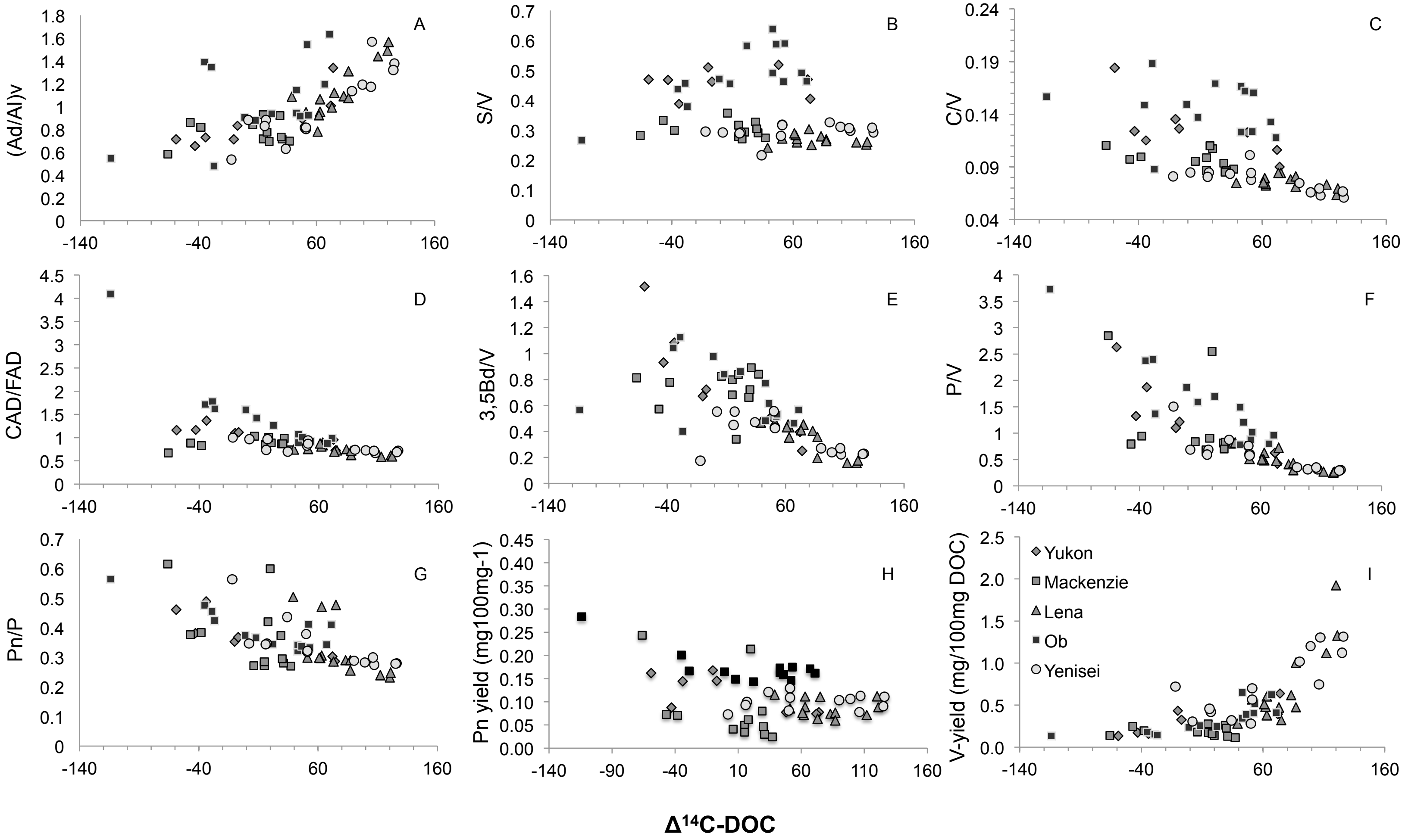
A
(Ad/Al)v
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
B
S/V
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
C
C/V
0.04
0.09
0.14
0.19
0.24
D
CAD/FAD
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
E
3,5Bd/V
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
F
P/V
0
0.5
1
1.5
2
2.5
3
3.5
4
G
Pn/P
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
H
Pn yield (mg100mg-1)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
-140
-90
-40
10
60
110
160
I
V-yield (mg/100mg DOC)
0.0
0.5
1.0
1.5
2.0
2.5
-140
-40
60
160
Yukon
Mackenzie
Lena
Ob
Yenisei
Δ14C-DOC

Figure 5

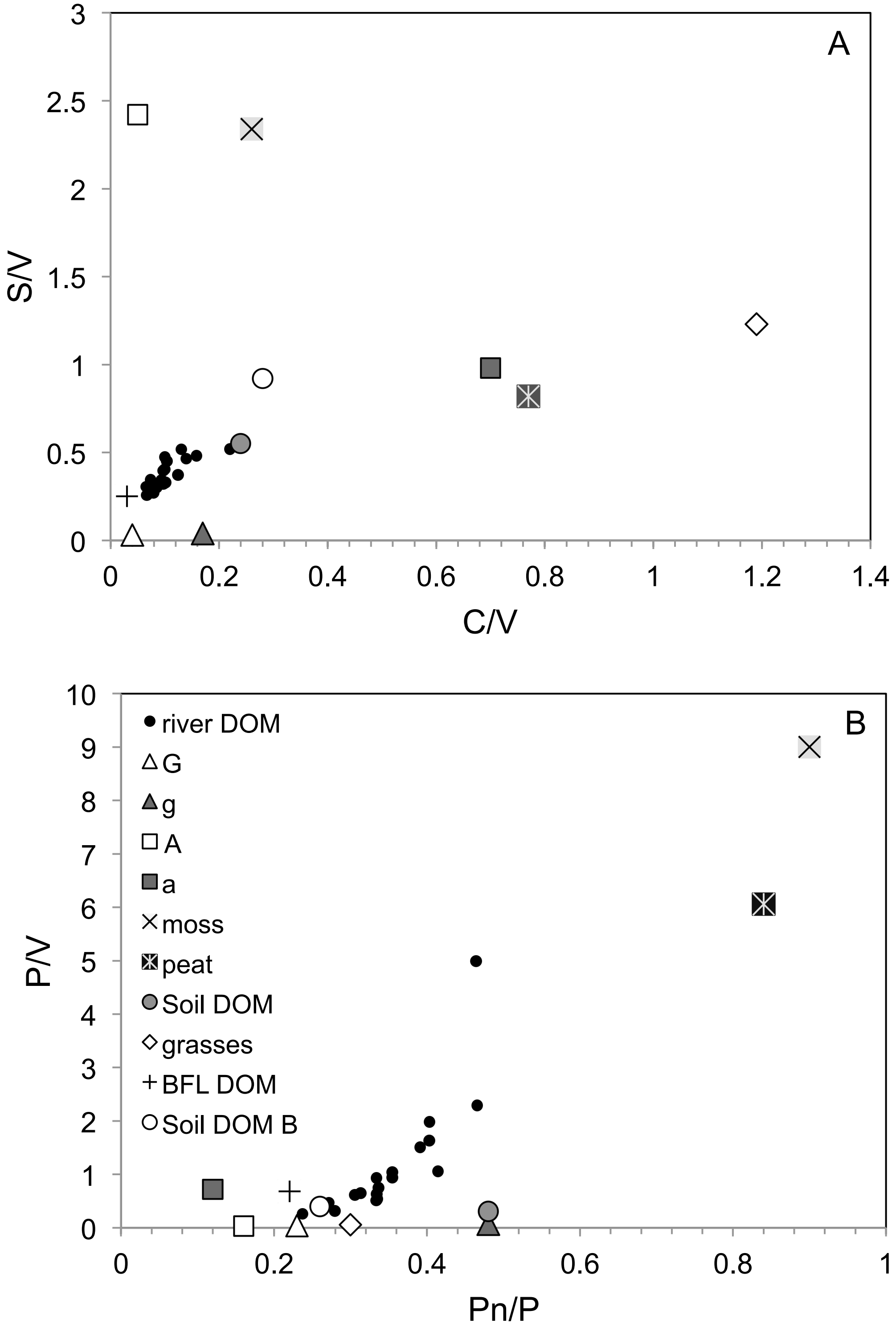
A
S/V
C/V
3
2.5
2
1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
B
P/V
Pn/P
10
9
8
7
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
● river DOM
△ G
▲ g
□ A
■ a
× moss
⊠ peat
● Soil DOM
◇ grasses
+ BFL DOM
○ Soil DOM B

Figure 6

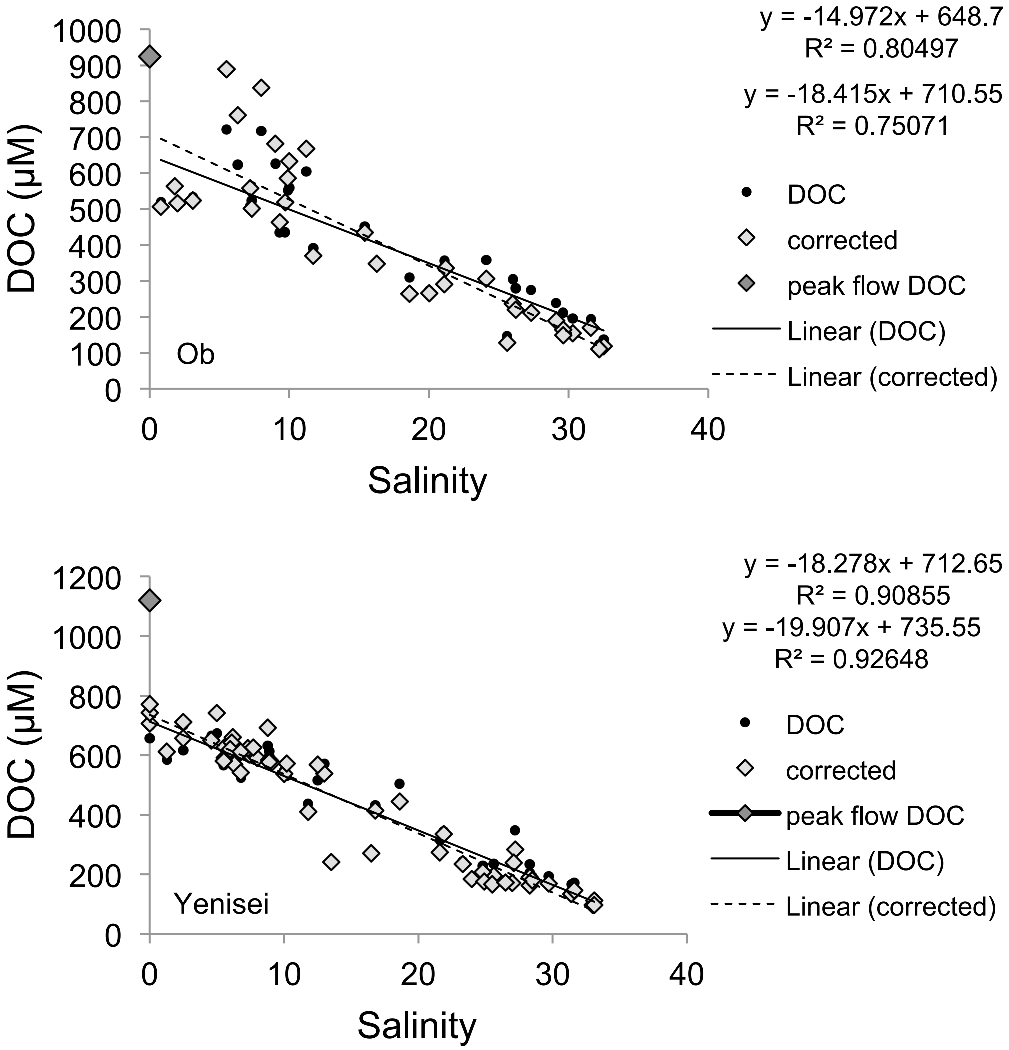
y = -14.972x + 648.7
R² = 0.80497
y = -18.415x + 710.55
R² = 0.75071
DOC
corrected
peak flow DOC
Linear (DOC)
Linear (corrected)
DOC (µM)
1000
900
800
700
600
500
400
300
200
100
0
Ob
0
10
20
30
40
Salinity
y = -18.278x + 712.65
R² = 0.90855
y = -19.907x + 735.55
R² = 0.92648
DOC
corrected
peak flow DOC
Linear (DOC)
Linear (corrected)
DOC (µM)
1200
1000
800
600
400
200
0
Yenisei
0
10
20
30
40
Salinity

Figure 7

Table 1. Geographical, climatic and geochemical characteristics of the different river/watershed systems

| *River and Watershed characteristics* | Yukon | Mackenzie | Ob | Yenisey | Lena | Kolyma |
|---|---|---|---|---|---|---|
| Discharge ($km^3$ $yr^{-1}$)[1] | 208 | 298 | 427 | 636 | 581 | 111 |
| Length (km)[1] | 2716 | 3679 | 3977 | 4803 | 4387 | 2091 |
| Catchment ($10^6$ $km^2$)[1] | 0.83 | 1.78 | 2.99 | 2.54 | 2.46 | 0.65 |
| MAAT (°C) | -0.4 | 0.7 | 1.4 | -1.0 | -6.5 | -10.1 |
| Mean slope (m $km^{-1}$) | 2.93 | 2.23 | 1.28 | 1.94 | 1.83 | 2.16 |
| SPM ($10^6$ t/y)[2] | 60 | 124 | 15.5 | 4.7 | 20.7 | 10.1 |
| Southernmost Lat. (°N) | 58.8 | 52.2 | 45.3 | 45.7 | 52.2 | 60.6 |
| Cont. permafrost (%)[3] | 19 | 13 | 1 | 31 | 77 | 99 |
| Deciduous BL forest (%)[3] | 0.4 | 1.4 | 10.2 | 3.4 | 1.1 | 0.4 |
| Evergreen NL forest (%)[3] | 17.5 | 23.7 | 14.9 | 20.6 | 7.4 | 0.2 |
| Deciduous NL forest (%)[3] | 0 | 0 | 1.5 | 32.7 | 58.8 | 49.1 |
| Mixed forest (%)[3] | 1.9 | 9.2 | 12.0 | 10.6 | 4.9 | 0.2 |
| Total forest (%)[3] | 19.7 | 34.4 | 38.6 | 67.3 | 72.1 | 49.9 |
| Forest – MODIS (%)[3] | 26 | 35 | 25 | 35 | 32 | 10 |
| Shrubland (%)[3] | 19.2 | 10.5 | 2.6 | 9.0 | 12.5 | 32.1 |
| Grassland (%)[3] | 42.9 | 30.0 | 15.9 | 7.2 | 0.8 | 0.1 |
| Cropland (%)[3] | 0.3 | 2.4 | 22.9 | 6.2 | 0.6 | 0 |
| Wetlands (%)[3] | 0.4 | 0.1 | 8.5 | 2.6 | 3.3 | 3.8 |
| Water bodies (%)[3] | 7.0 | 10.3 | 2.4 | 2.1 | 1.7 | 1.6 |

[1] Holmes et al. 2011, [2] Holmes et al. 2002, [3] We used both Modis vegetation continuous fields (VCF) data and Global Land Cover (GLC) data to generate the vegetation statistics. For reference see: Modis VCF - http://glcf.umiacs.umd.edu/data/vcf/ and GLC - http://ies.jrc.ec.europa.eu/global-land-cover-2000 and http://bioval.jrc.ec.europa.eu/products/glc2000/products.php; MAAT = mean annual air temperature, BL = broad leaf, NL = needle leaf

Table 2. Mean and discharge-weighted average values for dissolved organic carbon and lignin phenol parameters in the six rivers

| | Yukon | Mackenzie | Ob | Yenisey | Lena | Kolyma |
|---|---|---|---|---|---|---|
| DOC (mg/l) | 7.64 (7.93) | 4.35 (4.20) | 10.48 (8.58) | 8.80 (8.03) | 11.37 (11.94) | 6.56 (7.25) |
| $\sum_8$ (μg/l) | 52.94 (66.64) | 12.59 (12.70) | 66.02 (60.94) | 108.45 (86.17) | 134.76 (101.87) | 49.55 (64.17) |
| $\Lambda_8$ | 0.52 (0.55) | 0.28 (0.20) | 0.61 (0.53) | 1.03 (0.77) | 0.98 (2.14) | 0.65 (0.77) |
| $\sum_6$ (μg/l) | 49.42 (63.00) | 12.07 (11.70) | 60.67 (55.50) | 103.08 (82.45) | 127.67 (113.1) | 46.30 (38.14) |
| $\Lambda_6$ | 0.49 (0.53) | 0.27 (0.20) | 0.56 (0.51) | 0.97 (0.89) | 0.93 (2.10) | 0.6 (0.85) |
| S/V | 0.47 (0.48) | 0.33 (0.3) | 0.48 (0.58) | 0.31 (0.31) | 0.28 (0.28) | 0.41 (0.38) |
| C/V | 0.14 (0.13) | 0.10 (0.10) | 0.14 (0.15) | 0.07 (0.08) | 0.08 (0.08) | 0.10 (0.10) |
| P/V | 1.81 (1.41) | 1.02 (1.0) | 1.49 (1.47) | 0.58 (0.59) | 0.46 (0.47) | 0.63 (0.55) |
| Pn/P | 0.37 (0.36) | 0.35 (0.35) | 0.39 (0.39) | 0.33 (0.33) | 0.31 (0.31) | 0.30 (0.29) |
| Ad/Al$_v$ | 0.87 (0.78) | 0.84 (0.8) | 1.13 (1.07) | 1.03 (0.97) | 1.16 (1.07) | 1.03 (1.10) |
| Ad/Al$_s$ | 0.65 (0.38) | 0.60 (0.60) | 0.82 (0.79) | 0.72 (0.69) | 0.79 (0.77) | 0.71 (0.56) |
| CAD/FAD | 1.39 (1.24) | 0.85 (0.9) | 1.36 (1.35) | 0.80 (0.82) | 0.72 (0.73) | 0.77 (0.75) |
| 3,5Bd/V | 0.87 (1.03) | 0.75 (0.8) | 0.7 (0.83) | 0.36 (0.36) | 0.36 (0.37) | 0.53 (0.45) |
| $\Lambda_{Pn}$ | 0.14 (0.13) | 0.07 (0.12) | 0.18 (0.18) | 0.1 (0.08) | 0.08 (0.08) | 0.08 (0.07) |
| $\Lambda_V$ | 0.33 (0.31) | 0.2 (0.2) | 0.37 (0.34) | 0.74 (0.64) | 0.73 (0.50) | 0.43 (0.58) |

Concentration of lignin is given as the sum of 8 lignin phenols ($\sum_8$; V, S, C) and the sum of 6 lignin phenols ($\sum_6$; V and S). Yields (Λ-values) are given in mg100mg$^{-1}$DOC and reflect the concentration of the 8 or 6 lignin phenols normalized to DOC concentrations.

Table 3. Total annual discharge of dissolved organic carbon and lignin phenols from the six rivers along with their relative contributions.

| | Yukon | Mackenzie | Ob | Yenisei | Lena | Kolyma | Annual load |
|---|---|---|---|---|---|---|---|
| DOC (Tg $yr^{-1}$) | 1.75 | 1.20 | 3.04 | 5.08 | 6.47 | 0.71 | 18.25 |
| % total DOC | 9.60 | 6.60 | 16.70 | 27.80 | 35.50 | 3.90 | 100.00 |
| Lignin (Gg $yr^{-1}$) | 14.70 | 3.60 | 21.50 | 54.30 | 91.60 | 6.16 | 192.00 |
| % total Lignin | 7.70 | 1.90 | 11.20 | 28.30 | 47.70 | 3.20 | 100.00 |
| % freshet lignin* | 64 | 49 | 66 | 78 | 78 | 78 | |

*freshet lignin was calculated for the months May and June by multiplying the average daily discharge of these months with the average lignin concentrations measured during May and June and upscaling to 61 days. Discharge volumes were not necessarily highest in May, but the concentration of lignin phenols was always highest in the very early phase of freshet.

Table 4. Lignin phenol parameters in different source material and aquatic environments

| | Ad/Al$_v$ | S/V | C/V | P/V | Pn/P | $\Lambda_{Pn}$ | CAD/FAD | $\Lambda_v$ |
|---|---|---|---|---|---|---|---|---|
| Gym. Wood [1,2,3] | 0.19 | 0.03 | 0.04 | 0.04 | 0.23 | 0.05 | 0.11 | 10 |
| Gym. Needles [1,2,3,5] | 0.32 | 0.04 | 0.17 | 0.07 | 0.47 | 0.29 | 3.18 | 7.2 |
| Ang. Wood [1, 2,3] | 0.15 | 2.42 | 0.05 | 0.03 | 0.16 | 0.01 | 0.19 | 3.34 |
| Ang. Leaves [1,2,3] | 0.24 | 0.98 | 0.7 | 0.72 | 0.12 | 0.04 | 8.7 | 1.06 |
| Grasses [3] | 0.19 | 1.23 | 1.19 | 0.06 | 0.3 | 0.05 | 0.43 | 2.7 |
| Moss [3] | 0.82 | 2.34 | 0.26 | 9.0 | 0.9 | 2.38 | 2.83 | 0.23 |
| Wetland plants [5] | 0.22 | 1.9 | 3.05 | 0.5 | 0.22 | - | 5.53 | - |
| Peat (sphagnum sp.) [3] | 0.27 | 0.82 | 0.77 | 6.06 | 0.84 | 1.41 | 0.66 | 0.3 |
| Peat[5] | 0.34 | 0.82 | 0.88 | 1.49 | 0.44 | 0.36 | 0.74 | 1.13 |
| Boreal forest soil-org. h.[4] | 0.42 | 0.24 | 0.42 | 0.22 | 0.30 | - | 0.63 | 1.05 |
| Boreal forest soil-inorg. h.[4] | 1.65 | 0.11 | 1.18 | 0.81 | 0.20 | - | 3.82 | 0.28 |
| Boreal forest soil [13] | 2.25 | 0.29 | 0.18 | - | - | - | 0.56 | 0.88 |
| Boreal forest soil [3] | 0.49 | 0.45 | 0.27 | - | - | - | - | - |
| Alpine Tundra soil [13] | 2.05 | 0.56 | 0.46 | - | - | - | 0.80 | 0.36 |
| DOM soil [3] | 1.15 | 0.55 | 0.24 | 0.31 | 0.48 | 0.04 | 0.79 | 0.78 |
| DOM-alpine bog [6] | 0.91 | 0.80 | 0.18 | 1.44 | - | - | 1.5 | - |
| DOM- needles leachate[7] (Picea sp.) | 0.49 | 0.02 | 0.23 | - | - | - | - | 0.95 |
| DOM- twigs leachate[7] (Picea sp.) | 1.31 | 0.16 | 0.14 | - | - | - | - | 0.90 |
| DOM- leaves leachate[7] (Betula sp.) | 0.52 | 0.73 | 0.42 | - | - | - | - | 0.66 |
| DOM-grass leachate [7] | 0.87 | 1.93 | 1.11 | - | - | - | - | 0.8 |
| DOM-sphagnum leachate [7] | 1.55 | 0.95 | 1.15 | - | - | - | - | 0.01 |
| DOM (tundra rivers) [8] | 1.32 | 0.70 | 0.46 | - | - | - | - | - |
| DOM (boreal lakes) [9] | 1.01 | 0.25 | 0.03 | 0.68 | 0.22 | 0.04 | - | 3.23 |
| DOM (Amazon river) [10] | 1.66 | 0.54 | 0.10 | 0.66 | - | - | - | 0.77 |
| DOM (Mississippi river) [11] | 0.88 | 0.80 | 0.15 | - | - | - | - | 0.14 |
| DOM (Broad river) [12] | 1.74 | 0.57 | 0.09 | 0.44 | 0.25 | 0.02 | 0.88 | 0.2 |

1-Hedges and Mann (1979); 2-Hedges and Parker, 3-Prokushkin et al, in prep, 4-Houel et al. (2006); 5-Williams et al (1998); 6-Ertel et al. (1993); 7-Spencer et al. (2008); 8-Lobbes et al. (2000); 9-Ouellet et al. (2009); 10-Ertel et al.(1986) and Hedges et al. (2000); 11-Opsahl and Benner (1998); 12-Benner and Kaiser (2010), 13-Ugolini et al 1981. Yields (Λ) are given in mg100mg$^{-1}$ DOC