Sources and the flux pattern of dissolved carbon in rivers of the Yenisey basin draining the Central Siberian Plateau

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Abstract
Frequent measurements of dissolved organic (DOC) and inorganic (DIC) carbon concentrations in rivers during snowmelt, the entire ice-free season, and winter were made in five large watersheds (15 000–174 000 km²) of the Central Siberian Plateau (Yenisey River basin). These differ in the degree of continuous permafrost coverage, mean annual air temperature, and the proportion of tundra and forest vegetation. With an annual DOC export from the catchment areas of 2.8–4.7 g C m⁻² as compared to an annual DIC export of 1.0–2.8 g C m⁻², DOC was the dominant component of terrigenous C released to rivers. There was strong temporal variation in the discharge of DOC and DIC. Like for other rivers of the pan-arctic and boreal zones, snowmelt dominated annual fluxes, being 55–71% for water runoff, 64–82% for DOC and 37–41% for DIC. Likewise, DOC and DIC exhibited also a strong spatial variation in C fluxes, with both dissolved C species decreasing from south to north. The rivers of the southern part of the plateau had the largest flow-weighted DOC concentrations among those previously reported for Siberian rivers, but the smallest flow-weighted DIC concentrations. In the study area, DOC and DIC fluxes were negatively correlated with the distribution of continuous permafrost and positively correlated with mean annual air temperature. A synthesis of literature data shows similar trends from west to east, with an eastward decrease of dissolved C concentrations and an increased proportion of DOC in the total dissolved C flux. It appears that there are two contemporary limitations for river export of terrigenous C across Siberia: (1) low productivity of ecosystems with respect to potentially mobilizable organic C, slow weathering rates with concomitant small formation of bicarbonate, and/or wildfire disturbance limit the pools of organic and inorganic C that can be mobilized for transport in rivers (source-limited), and (2) mobilization of available pools of C is constrained by low precipitation in the severe continental climate of interior Siberia (transport-limited). Climate warming may reduce the source limitation by enhancing primary production and weathering rates, while causes leading to surmounting the transport limitation remain debatable due to uncertainties in predictions of precipitation trends and other likely sources of reported increase of river discharges.

Keywords: dissolved carbon, riverine flux, permafrost, Central Siberian Plateau

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1. Introduction

Understanding the role of Siberian forested watersheds underlain by permafrost in global element cycling is becoming increasingly important as temperature increases and permafrost degrades at high latitudes (McGuire and Anderson 2009, Holmes et al. 2011). Much attention has been focused previously on land–atmosphere exchange of C in forests of Central and Eastern Siberia (Nakai et al. 2008, Dolman et al. 2004, Tchebakova et al. 2009) and hydrological trends linked to climate warming (Shiklomanov and Lammers 2009 and references therein), but considerably less is known about the transfer of C and other elements from terrestrial to aquatic systems in this region (Pokrovsky et al. 2005, Prokushkin et al. 2008).

Permafrost exerts strong controls on the hydrogeochemistry of subarctic rivers by constraining water flow to surface organic-rich soil layers with low residence times and little water–rock interaction (Rember and Trefry 2004, Pokrovsky et al. 2005, 2006, Striegl et al. 2007, Holmes et al. 2011, Bagard et al. 2011). A deeper soil active layer (the portion of soil that thaws and refreezes annually) and shrinkage of permafrost extent with warming (Frey and McClelland 2009, Romanovsky et al. 2010) may significantly increase soil infiltration and increase retention times in the soil profile (Frey and McClelland 2009) and adsorptive capacity of soils (Kawahigashi et al. 2004). These changes may also accelerate rates of biotic mineralization of DOC in soils (Striegl et al. 2007). Longer flow paths, therefore, decreases dissolved organic carbon (DOC) flux to rivers, while it increases the fluxes of inorganic carbon (DIC) and other major ions with enhancement of soil carbon mineralization (i.e., respiratory CO₂ production) and bedrock weathering at higher temperatures (Striegl et al. 2007, Cai et al. 2008). In particular, in carbonate-free soils, respiratory CO₂ will react with silicates (e.g., feldspars) to produce clay minerals and bicarbonate-ion (Amiotte-Suchet et al. 1999). Thus, riverine DIC in silicate watersheds, in opposite to calcareous soils, originates mainly from soil respiration (Striegl et al. 2007).

Other mechanisms, however, may result in an increase in fluvial export of DOC from terrestrial ecosystems under a changing climate. These include (i) an increase in primary productivity of vegetation that increases DOC production; (ii) increased precipitation, which increases microbial mobilization of DOC from organic-rich layers, and (iii) introduction of a new source of C from degrading C-rich permafrost in the western Siberia peatlands (Frey and Smith 2005, Gordeev and Kravchishina 2009) and the Yedoma complexes in eastern Siberia (Neff et al. 2006).

Among the apparent consequences of climate changes in high latitude basins are increased riverine discharge (Peterson et al. 2002, McClelland et al. 2006), northward shifts in vegetation (Sturm et al. 2001, Kharuk et al. 2005) and enhanced biogeochemical cycling of carbon, nutrients and major/trace elements (Frey and McClelland 2009). With approximately 50% of the world’s soil organic carbon (SOC) stored in the high latitude regions (Tarnocai et al. 2009) and the importance of high-carbon soils for driving riverine DOC fluxes (Aitkenhead and McDowell 2000), the arctic/subarctic river basins underlain by permafrost have an enormous potential to mobilize and transport terrestrial organic carbon (OC) to the Arctic Ocean (Guo and MacDonald 2006, Guo et al. 2007, McGuire and Anderson 2009). Contemporary riverine transport of dissolved carbon to the Arctic Ocean is estimated to be 18–33 Tg C as DOC, 6 Tg C as particulate organic carbon (POC) and another 43 Tg C as DIC annually (McGuire and Anderson 2009), representing a major component of the global carbon cycle (Spitz and Leenheer 1991, Hedges et al. 1997). Recent evidence from the northern hemisphere showing increased DOC and DIC concentrations in surface waters draining upland areas and wetlands (Freeman et al. 2001, Frey and Smith 2005, Striegl et al. 2007, Cai et al. 2008), highlights the importance of understanding the transfer of C between soil and freshwater systems (Hope et al. 1994, Billett et al. 2006).

In this study, we examine the seasonal and annual variations in concentrations and fluxes of two dissolved C species (DOC and DIC) in five rivers draining the Central Siberian plateau, which drain watersheds of similar lithology that span a range of continuous permafrost distribution, air temperatures and vegetation. Our objective was to use high-resolution measurements of river water C concentrations and discharge to understand how biological, edaphic and hydrological processes interact to control DOC and DIC fluxes. Specifically, we addressed the following questions: (1) What are the differences in DOC and DIC export among rivers draining similar lithology under different climatic contexts? (2) How do seasonal changes in flow paths (sources) control river dissolved C export? (3) How do climate parameters such as temperature and precipitation affect the export of different forms of dissolved C? and (4) How do permafrost distribution and vegetation types affect the net export of C species from river basins of the Central Siberian Plateau?

2. Study area

The study region is found in the central and southern part of the basaltic province located within the Central Siberian Plateau and includes a considerable part of the basins of the Nizhnyaya Tunguska and Podkammennaya Tunguska Rivers (figure 1), tributaries of the Yenisey River. Our five study rivers, Tembenchii (referred thereafter as TE), Kochechum (KO), Nidym (ND), Nizhnyaya Tunguska (NT) and Podkammennaya Tunguska (PT) drain basins that vary in watershed sizes, permafrost extent, climate and vegetation (table 1). Total watershed area of the rivers studied is about 500,000 km² or roughly one third of the Central Siberian Plateau. Permafrost extends throughout the studied area but ranges from continuous permafrost on the north to isolated patches in the southern part of the basins of the Nizhnyaya Tunguska and Podkammennaya Tunguska Rivers (Brown et al. 1998). The mean annual air temperatures (MAAT) range among basins from −10.9 to −6.3°C (2001–09, 0.5° × 0.5° grid data, CRU TS3.1 available at http://badc.nerc.ac.uk/, Mitchell and Jones 2005). A detailed description of each river basin is given in the electronic annex (available at stacks.iop.org/ERL/6/045212/mmedia).
Figure 1. Map of Central Siberian Plateau with inserts of watersheds of five analyzed rivers (Kochechum, Tembenchi, Nidym, Nizhnyaya Tunguska and Podkamennaya Tunguska) representing distribution of land cover classes (Bartholomé and Belward 2005) and permafrost (Brown et al 1998).

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

| River name (sampling station) | Coordinates of river mouths (sampling station) | MAP (mm) | MAAT (°C) | Basin area, 10³ km² | Mean annual discharge (km³ a⁻¹) | Permafrost distributionb | Vegetation coverc (%) |
|-------------------------------|-----------------------------------------------|----------|------------|---------------------|---------------------------------|------------------------|----------------------|
| Tembenchi (f. Tembenchi)      | 64°36’33” N 99°55’19” E                      | 465      | -10.92     | 22.4                | 7.9                             | 100 0                  | 0 53 45              |
| Kochechum (Tura)              | 64°17’10” N 100°11’37” E                      | 386      | -10.92     | 96.4                | 29.9                            | 100 0                  | 0 30 69              |
| Nidym                         | 64°07’12” N 99°57’52” E                       | 399      | -8.80      | 14.7                | 3.3                             | 100 0                  | 0 3 91               |
| Nizhnaya Tunguska (Tura)      | 64°16’14” N 100°15’16” E                      | 380      | -7.46      | 174.3               | 51.0                            | 62 34 5                | 2 95                 |
| Podkamennaya Tunguska (Baikit)| 61°39’00” N 96°24’01” E                       | 431      | -6.28      | 163.1               | 30.7                            | 15 46 39               | 1 94                 |

a 0.5° × 0.5° grid data for entire watershed (2001–09, CRU TS3.1, Mitchell and Jones 2005).
b C—continuous, D + S—discontinuous and sporadic, I—isolated patches permafrost (Brown et al 1998).
c Aggregated classes according to GLC2000 (Bartholomé and Belward 2005).

3. Methods

3.1. Analyses

Repeated river water sampling was used to examine seasonal and annual dynamics of concentrations of dissolved organic and inorganic C in rivers during several hydrologic years (2006–10) and to estimate annual carbon export. Sampling sites were located close to gauging stations of the Russian Federal Service of Hydrometeorology and Environment Monitoring (ROSHYDROMET) and/or river mouths if no gauging station on the river was established. Water samples were collected from just beneath the water surface at the mid-point of rivers at monthly intervals under ice conditions (October–April), at least once a week at snowmelt freshet (from mid May and beginning of June) and in summer and autumn (mid-June–September). Samples were immediately filtered (pre-rinsed 0.22 µm nitrocellulose filters, Millipore) and stored refrigerated prior to analysis. Dissolved organic carbon (DOC) concentrations were measured as non-purgeable organic carbon (NPOC) via high temperature combustion (Shimadzu TOCvp, Kyoto, Japan) with an uncertainty of 3% and a detection limit of 40 µM. Blanks of MilliQ water passed through the filters demonstrated negligible release of DOC from the filter material.

Dissolved inorganic carbon (DIC) concentrations were obtained from alkalinity determined following a standard HCl
titration procedure using an automatic Schott TitroLine alpha TA10plus titrator with an uncertainty of ±2% and a detection limit of 5 × 10⁻⁵ M. At the essentially neutral pH values of the river water (7.5–8.0), and 1–100 μg l⁻¹ of dissolved boron (Bagard et al 2011), the titrated alkalinity ([ALK] = [HCO₃⁻] + 2[CO₃²⁻] + [OH⁻] + [B(OH)₃]) represents, within 10% uncertainty, the total inorganic dissolved carbon. The contribution of weak organic acids to titratable alkalinity was evaluated via (i) titration of filtered river water subjected to UV and H₂O₂ degradation to remove (up to 80–90%) of dissolved organic matter without modifying the pH of solution and (ii) by adding organic-rich, bicarbonate-poor natural water to a standard bicarbonate solution and determining its alkalinity. In both cases, the contribution of natural DOM was found to be negligible (within ±10% of total titratable alkalinity).

Specific ultraviolet absorbance (SUVA), a measure of DOC aromatic carbon content (Weishaar et al 2003), was measured at 280 nm and normalized to DOC concentration (m l⁻¹ mg C⁻¹). The proportion of colloidal high molecular weight compounds in DOC (HMW DOC) was measured as the difference between OC concentrations in filtered water samples (0.22 μm, Millipore) and those that had passed through a dialysis membrane, representing low molecular weight substances (<1 kDa, LMW DOC). Dialysis was performed on-site using 20–50 ml precleaned dialysis bags placed in a large volume (10–20 l) of river water. The duration of this dialysis procedure was between 24 and 72 h, an exposure time based on experimental assessment of the time needed to attain equilibrium in DOC concentrations (Pokrovsky et al 2005, 2011). For dialysis experiments, EDTA-cleaned trace-metal pure SpectraPor 7Ò dialysis membranes made of regenerated cellulose (pore size of 1 kDa, or ~1 nm) were thoroughly washed in 0.1 M double-distilled HNO₃, ultrapure water, filled with ultrapure MilliQ deionized water and then placed into natural water. The efficiency of the dialysis procedure was evaluated by comparing concentration of major anion or neutral species (e.g., Cl⁻, H₂SiO₄) not associated with colloids between the dialysis bag and the external solution. These concentrations were always identical to within ±20%, suggesting an equilibrium distribution of dissolved compounds. To assess the mass balance during the dialysis procedure, concentrations of OC were measured in the external solution and internal compartments and compared with <0.22 μm filtrates. In all cases, better than 95% recovery for OC was achieved indicating that the adsorption of colloids onto and inside the thin Spectra Por 7 membrane was negligible.

Daily discharges for the TE (Point ID: 6629), NT (at Tura, Point ID: 6625) and monthly discharges for the PT (at Baikita, Point ID: 6614) were obtained from the ROSHYDROMET (Krasnoyarsk) for the period 2006–10. Long-term (1939–95) monthly discharges of these rivers including the PT (Point ID: 6614) were obtained from the R-ArcticNet Database (www.r-arcticnet.sr.unh.edu/v4.0/main.html). Since there is no gauging station at Kochechum River (KO), its daily and monthly discharges were estimated using data from the TE, assumed as river-analog with a basin with similar geomorphological characteristics (Gerasimov 1964) and long-term records of individual flow measurements. In this data set, the KO to TE long-term annual discharges (29.96 and 7.97 km³, respectively, Gerasimov 1964), yielded the ratio 3.76 which was used to estimate KO daily discharge from TE data. The ND discharge was acquired as long-term mean (Gerasimov 1964) and then monthly separation of discharge was estimated on the basis of the NT values, demonstrating similar annual runoff separation by seasons to Taimura River (Point ID: 6630), the analog of Nidym River. However, in the latter case, daily discharges were terminated in early 1990s.

Historic data for discharges, DIC and total organic carbon (TOC, the sum of dissolved and particulate organic carbon) concentrations in NT and TE were collected by the State Service of Hydrometeorology and Environment Monitoring (USSR) for the period 1966–75 (Hydrological Yearbooks of Russian Hydrological Survey, 1954–1975 1975).

3.2. Calculation of DOC and DIC fluxes

First, for comparative analysis of all five rivers, monthly, seasonal and annual concentrations of DOC and DIC were calculated as simple averages. Additionally, monthly, seasonal and annual concentrations of DOC and DIC have been calculated for the TE, KO (estimated using Tembenchi river discharge) and NT as flow-weighted means. The calculation of mean annual concentrations for ND and PT rivers is based on the contribution of each month to the annual runoff. Then, seasonal and yearly river C loads (mass C period⁻¹) were estimated using daily load (mass C day⁻¹) obtained from a time series of paired river flow and constituent concentration data used to construct a calibration curve. Finally, the area-normalized DOC and DIC exports with rivers have been expressed per watershed area (gC m⁻² a⁻¹) and additionally, due to significant differences in annual precipitation and specific runoff, the annual DOC and DIC mobilization in the catchment have also been normalized to annual runoff (gC m⁻² a⁻¹ mm⁻¹).

3.3. Statistics

Discharge and chemical data were analyzed by best fit function based on the method of least squares, Pearson correlation and one-way ANOVA with STATISTICA version 6 (StatSoft Inc., Tulsa, OK). Regressions and power functions were used to examine the relationships between discharge and river constituent concentrations or DOC parameters. Correlation coefficients were calculated to elucidate relationships between carbon concentrations in rivers and watershed attributes. ANOVA was used to test the differences in average concentrations and DOC parameters among rivers and regression slopes among watersheds.

4. Results

4.1. Hydrology

River discharge was extremely seasonal in all our study sites (figure 2), demonstrating up to three orders of magnitude variation between spring freshet (peak flow in first week of June) and late winter low flows (April). Smaller rivers in
the NT basin like Nidym River (ND) freeze completely in winter with zero discharge in early March. Annual hydrograph separation for the TE, NT and PT showed that 55–71% of annual discharge occurred during spring (May–June), the summer to autumn period (July–September) accounted for 18–42% of annual flow, and the winter season (October–April) contributed 3–11% (table 2). The proportion of summer flow decreased as latitude decreased, while the proportion of spring and winter flows increased. The mean seasonal distribution of discharge in our study period was similar to that from the long-term record (1939–95), but with elevated winter discharges of TE (up to 5% of annual discharge) and NT (5.0–8.6%). The contribution of snowmelt during the five years of our study varied from 46 to 67% in TE (KO), and from 53 to 79% in NT. The decreased proportion of snowmelt in the annual hydrograph corresponded to an elevated annual discharge in wet years when the summer–autumn period was characterized by higher precipitation and the proportion of summer discharge rose to almost 50%. In contrast, in dry years with low annual discharge (e.g. 2006), the proportion of spring freshet reached >80%, and summer constituted only 15–18% of the annual hydrograph.

Average annual discharge at both TE and NT during 2006–10 was ca. 30% higher than the 50 year record from 1939 to 1995 (10.3 versus 7.9 km³ and 65.2 versus 50.7 km³, respectively). On a seasonal basis, spring discharges increased 20% and summer discharges increased >40%. In general, there was a strong indication that annual discharge may be trending upward at these rivers at a rate of 0.333 km³ a⁻¹ a⁻¹ for the NT and 0.046 km³ a⁻¹ a⁻¹ for the TE (figure 3).

4.2. DOC and DIC: spatio-temporal variation

Concentrations of both dissolved C species in river waters showed high inter-seasonal and inter-annual variation depending on flow regimes of the rivers (figures 2 and 4). For each river, there was approximately an order of magnitude difference between the largest and smallest concentrations among seasons. Mean DOC concentrations were greatest during spring freshet in all rivers (table 3), although the northernmost basins (TE and KO) reached maximum DOC concentrations prior to the peak of discharges (figure 2(a)). Southernmost rivers (NT and PT) also showed an abrupt increase of DOC concentrations in the beginning of snowmelt and a gentle rise at higher discharges. As a result for all analyzed rivers, a power function (e.g., DOC = Qᵃ) provided the best fit to explain the relationships between discharge and river constituent concentrations or DOC parameters.

During the summer–autumn season, DOC concentrations gradually decreased, with peaks when discharges increased after rainfall events. The proportion of HMW DOC (>1 kDa) also declined after snowmelt (figure 5(a)). Aromaticity of riverine DOC (SUVA) demonstrated a similar trend which
followed the decrease of discharge (figure 5(b)). Interestingly, minimum DOC concentrations and SUVA index were observed in winter lowflow in April, and smallest concentrations of HMW DOC appeared at summer lowflow (July). Within the Central Siberian Plateau mean seasonal and annual DOC concentrations in rivers increased from north to south, positively correlating with MAAT ($r = 0.89$, $p = 0.045$) and forested area ($r = 0.86$, $p = 0.07$), but a negative trend found with an area of continuous permafrost distribution ($r = -0.66$, $p = 0.22$). Aromaticity of DOC (SUVA), in contrast, decreased from north to south (table 3).

In contrast to DOC, dissolved inorganic C concentrations were smallest during spring and steadily increased from summer to winter (figure 2). Summer–autumn stormflows resulted in short-term drops of DIC concentration in river waters. Similar to DOC, DIC concentrations increased from the northern to the southern part of the Central Siberian Plateau and correlated positively with MAAT ($r = 0.98$, $p = 0.004$), and negatively with permafrost distribution ($r = -0.93$, $p = 0.02$).

Flow-weighted and average concentrations were calculated separately for seasons (winter, spring and summer–autumn) and the entire year (table 3). Specifically, rivers demonstrated high concordance among seasonal flow-weighted and average concentrations, but annual average DIC values tended to be 1.3–2.2-fold larger than flow-weighted concentrations. DOC concentrations as seasonal averages were smaller in winter and spring (up to 10% for NT and 26% for KO) or similar in summer (1–2% difference) in comparison to flow-weighted means. Annual average concentrations were ca 20% smaller than annual flow-weighted DOC concentrations in the five rivers. Particularly, for the NT basin, average concentrations were 2.3-fold larger for DIC and 1.3-fold smaller for DOC compared to their respective flow-weighted means. Similarly, average annual concentrations in KO were 1.8-fold larger for DIC and 1.2-fold smaller for DOC.

### 4.3. Carbon export

Averages of 111, 552, 63, 1942 and 799 Gg C (as DOC and DIC) were transported annually by TE, KO, ND, NT and PT, respectively (table 2). Riverine carbon flux normalized to watershed area demonstrated an almost two-fold variation among basins (4.3–7.3 g C m$^{-2}$ a$^{-1}$), with southern catchment tending to show larger export rates. Dissolved organic carbon constituted the major proportion of the annual total dissolved C export, but decreased in importance in the southern rivers (62–65%) compared to northern rivers (74–82%). Export of DOC followed discharge, with the peak occurring during snowmelt. Annual DOC load was dominated by the snowmelt period (64–82% of annual total), due to both the larger discharges and a 3–4-fold elevation in DOC concentrations.
Figure 4. Effects of discharge on relationships between DOC and DIC concentrations ((a), (b)) and fluxes ((c), (d)) in the Kochechum ((a), (c)) and Nizhnyaya Tunguska ((b), (d)) rivers. Values shown in ovals are those observed in early spring in Kochechum river.

that occurred during the snowmelt period. The DIC load generally peaked during the summer–autumn season and in spring, despite low DIC concentrations in the latter period: 28–52% and 37–41% of annual values, respectively. However, in the southernmost river studied (PT) the seasonal load of DIC varied little, ranging from 28 to 37% in the three sampling seasons. As a result, the proportion of winter load in annual fluxes increased from 7 to 36% from our northernmost to southernmost site. To characterize inter-annual variation in discharges, linear regressions of C flux versus total water yield were calculated for each flow period in 2006–10 for the KO and NT basins. Despite a general positive correlation between DOC export and water yield (figures 6(a) and (b)), a limitation of DOC export during spring was observed on the NT. DOC export did not increase as water yields exceeded 150 mm, but instead reached a maximum of 3.7 g C m\(^{-2}\) period\(^{-1}\). Although DOC export during the summer–autumn season had a strong response to discharge, it did not reach spring values at the same discharge level. In contrast, DIC export demonstrated a weak relationship to discharge during the frost-free period with relatively stronger relationships for the NT than for the KO (figures 6(c) and (d)). Winter DIC export, however, was strongly related to discharge in both rivers.

Due to significant differences in annual precipitation and evapotranspiration among these watersheds, and corresponding differences in specific runoff (320 versus 188 mm in KO and NT), the efficiency of C mobilization from terrestrial ecosystems has also been evaluated by normalization of annual riverine DOC export to annual runoff. Figures 6(e) and (f) show that such normalized annual DOC and DIC export was 1.8 and 2.4-fold larger in NT basin relative to KO, indicating the higher efficacy of C release due to higher C stocks and/or more efficient mobilization/higher net DOC/DIC production in the southern watershed.

5. Discussion
5.1. Seasonal patterns of riverine C flux

There are several factors that distinguish runoff hydrology and hydrogeochemistry of high latitude basins from those of temperate regions: (1) snowmelt is the major hydrological event (Finlay et al. 2006), conveying to rivers about half of
throughout the region allows enrichment of solutes by DOC et al. (1999); (3) widespread occurrence of organic soils surface water flow in organic-rich soil layers (MacLean the annual precipitation inputs to the catchments in a 4–6 week period; (2) deep percolation of solutes is restricted due to the presence of permafrost, thus enhancing near-surface water flow in organic-rich soil layers (MacLean et al. 1999); (3) widespread occurrence of organic soils throughout the region allows enrichment of solutes by DOC and rapid translocation of water to the riverine system (Quinton et al. 2000, Carey and Woo 2001), and (4) matrix bypass mechanisms such as soil pipes (Gibson et al. 1993, Carey and Woo 2001) and inter-hummock flow (Quinton et al. 2000) may convey significant amounts of water during the melt period with wet antecedent conditions.

The snowmelt dominance of dissolved carbon flux in annual export is a combined result of elevated concentrations and/or high discharges during that period (Finlay et al. 2006, Holmes et al. 2011). Such phenomena occur widely across a large geographical range in the pan-arctic and boreal zones, and they reflect a large pool of C available for leaching and transport during freshet (McGuire and Anderson 2009). The strong positive relationship between C flux and discharge also suggests that hydrological flux may cause the most important limitation of C mobilization from the highly continental climate of interior Siberia with typical summer severe droughts. However, within a watershed, timing of snowmelt and local rainstorm events in areas with different stocks of mobile C may likely cause intra-seasonal variability of riverine C sources. In particular, we documented mismatch in the timing of maximum DOC concentrations and peak of discharge during spring freshet in northernmost rivers (i.e., Tembenchi and Kochechum). These findings suggest (1) higher DOC input in the earlier phase of spring freshet (May) originates from forested C-rich southern part of basins and (2) less DOC release at the peak of discharge (June) appears as snowmelt expands to headwater areas with high coverage of tundra vegetation and limited soil C available for transport. The lower concentrations of DOC also in summer season in headwaters of the Kochechum River reported by Pokrovsky et al. (2005) compared to Kochechum River downstream DOC levels corroborate this hypothesis. On the other hand, permafrost distribution on a watershed may also define basin-contributing areas, as lateral flow is confined to terrains with a shallow active layer due to their ability to restrict deep percolation. Our recent analysis of DOC chemical and isotopic tracers (Prokushkin et al. 2007) revealed a negligible signal of landscape elements characterized by deep active layers (i.e. south-facing slopes) in stream water due to an insufficient amount of precipitation to move solutes from the soil to surface waters.

The increasing retention time of solutes in deeper active layers caused by seasonal permafrost thaw leads to a net decrease of DOC export to rivers in summer due to DOC sorption and/or mineralization in the mineral soil (Strieglt et al. 2011).
Comparative analyses of watersheds with different permafrost coverage in Alaska have shown a reduction in DOC export and an increase in DIC and inorganic solute flux as a consequence of enhanced mineralization of soil organic matter and bedrock weathering (MacLean et al. 1999, Petrone et al. 2006). Similar conclusions have been drawn by Striegl et al. (2005) for the Yukon River by time series analysis for 1978–80 and 2001–03. Likewise, Kawahigashi et al. (2004) showed a significant decline in DOC concentrations in small tributaries to the Yenisey River along a gradient from continuous to discontinuous permafrost. This study also reported major alterations in biochemical composition of DOC in streams draining low-permafrost basins (e.g., an increase in lignocellulose compounds and an increase in the hydrophilic DOC fraction), which confirms the significant control that is exerted by the depth of soil active layer and distribution of permafrost on the flux, composition, and biodegradability of DOC in Siberian soils during the frost-free period. In this sense, seasonal changes of DOC flux, age and biochemical composition 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 younger topsoil DOC during freshet to more degraded DOC from subsoil during summer and winter low flows reflect the likely behavior of DOC with progressive warming and degradation of permafrost.

5.2. Riverine DOC composition

The relative proportion of HMW (colloidal, 1 kDa–0.22 μm) DOC exhibited both seasonal and spatial variations. The highest proportion of HMW DOC (60–70%) is observed during the spring flood period, in accord with recent data from another subarctic, but permafrost-free river Severnaya Dvina (Pokrovsky et al. 2010). During summer baseflow, the LMW (<1 kDa) fraction constitutes from 60 to 90% of DOC. These observations might be consistent with the presence of two pools of organic matter: allochthonous large size colloids formed by lixiviation from upper soil horizons and autochthonous (aquatic) small molecular-size substances, probably linked to bacterial and phytoplankton exudates. The relative proportions of both possible pools are highly variable seasonally. Allochthonous input of organic carbon strongly increases during the spring and summer-fall floods, whereas an autochthonous C typically peaks in open water season, though following changes in both light and temperature regimes that affect photosynthesis/respiration. Higher SUVA index in all rivers during spring freshet corroborates these findings, reflecting the input of fresh allochthonous (soil) organic matter from the watershed compared to autochthonous DOC with low SUVA appeared in summer and fall. Thus co-variation of colloidal material and aromaticity confirms the dominant role of soil humic substances in the riverine DOC flux in spring season and vice versa in river sources of DOC during summer–fall. Further, our study of aromaticity of DOC (SUVA index) in rivers of the Central Siberian Plateau showed a decreasing trend southward, indicating release of more processed DOC even during spring (table 3, figure 5(b)).

An alternative explanation for the seasonal changes in size distribution of DOC is based on the observation that the LMW fraction in Arctic rivers is more refractory than the colloidal fraction (Guo and MacDonald 2006). As such, summer-time LMW DOC in a large river may also originate from degradation of old OC buried in the permafrost, notably at the river banks. Note that such a distinction between colloidal and dissolved OC is rather conventional since it is known that fulvic acids, constituting an essential part of DOC in boreal waters, can be described as rigid oligoelectrolytes with molar mass of ~1000 Da and a radius (~1 nm) which is not much larger than that of hydrated metal ions (cf. Buffle 1988, Buffle et al. 2007).

On the other hand, increased productivity and northward shifts of vascular plants and specifically Larix spp. in headwater streams of northern rivers with warming may provide an important new source to the existing DOC pool. Indeed, the rivers we have analyzed demonstrate positive relationships between DOC concentrations and the forested area of their watersheds, which appears to serve as a useful proxy for the increased NEP and C stocks.
5.3. DIC production and transport

Weathering of basalts and associated transport of DIC is especially important in view of weathering control on CO$_2$ consumption from the atmosphere. Indeed, according to Dessert et al. (2001), the chemical weathering rate of volcanic rocks is 5–10 times higher than the chemical weathering of granite and gneiss. In such a case, the atmospheric CO$_2$
consumption derived from basalts weathering represents 30% of the global silicate weathering flux and acts as an important regulator of the Earth’s environment (Dessert et al. 2003).

This global estimate corresponds to the CO₂ consumption associated with the weathering of volcanic rocks occurring in soils, shallow groundwaters and rivers. It thus corresponds to the flux of CO₂ that is susceptible to be involved in a climatic feedback where higher surface temperature would lead to higher CO₂ consumption by chemical weathering (Dessert et al. 2003). Our study, providing the lowest values of DIC concentrations in basaltic monolithological river waters, is in full agreement with the temperature trend of atmospheric CO₂ consumption during volcanic rock weathering established in earlier studies. Indeed, there is a clear increase of DIC annual yield from 1.04 gC m⁻² yr⁻¹ for TE (MAAT = −10.9°C) to 2.77 gC m⁻² yr⁻¹ for NT (MAAT = −7.5°C). The other basaltic boreal rivers with similar runoff such as Kamchatka River and its tributaries (MAAT = −2.5°C, 522±87 mm yr⁻¹ runoff) exhibit significantly higher annual fluxes of DIC: 4.8 gC m⁻² a⁻¹ (Dessert et al. 2009).

5.4. Implications for climate change

Our observation that in the Central Siberian Plateau riverine DOC concentrations increase toward the south generally agrees with data obtained for streams in a latitudinal gradient from 55 to 68°N of Western Siberia (Frey and Smith 2005). It infers that climate warming (i.e. increase of MAAT and permafrost degradation) amplifies DOC flux. On the other hand, the negative effects of low MAAT and continuous permafrost distribution on annual and seasonal DOC and DIC concentrations in Siberian rivers oppose the patterns seen in earlier work conducted within discontinuous permafrost regions of Alaska (e.g. MacLean et al. 1999, Striegl et al. 2005, Petrone et al. 2006). It appears that the harsh climate and continuous permafrost of the Central Siberian Plateau may constrain C release in terrestrial environments through inhibition of the biotic and abiotic processes that produce mobile organic and inorganic C. In particular, low MAAT and continuous permafrost distribution in higher latitude and higher altitude rivers of the Central Siberian Plateau show especially decreased C concentrations.

To broaden our analysis of riverine dissolved C concentrations and export, we examined other high-resolution time series for watersheds within the Arctic Ocean basin. In total, this search yielded 12 estimates of annual DOC and DIC concentrations and fluxes in major Siberian and North America rivers (i.e. Ob’, Yenisey, Khantanga, Anabar, Olenek, Lena, Yana, Indigirka, Kolyma, Amguema, Yukon and Mackenzie) based on data reported in a number of papers (Gordeev et al. 1996, 2004, Striegl et al. 2007, Cai et al. 2008, McGuire and Anderson 2009, Holmes et al. 2011). We used these data to explore spatial changes in the proportion of organic and inorganic C in the overall export of terrigenous C to the Arctic Ocean across a strong climatic gradient from west to east, and also the lithological gradient associated with different proportions of sedimentary versus volcanic rocks. This compilation clearly shows a decrease of total dissolved C concentrations and exports in a northward direction for watersheds of the Central Siberian Plateau (figure 7), and a similar decline eastward for major Siberian rivers emptying into the Arctic Ocean. Despite low coverage by peatlands in the Central Siberian Plateau (0.7–2.1% of area, GLC2000, Bartholomé and Belward 2005), there are generally high DOC concentrations in all studied rivers as compared with rivers of large size watersheds of Western Siberia (Frey and Smith 2005) and Eastern Siberia (Gordeev and Kravchishina 2009, Gordeev et al. 2004) with greater peat soil distribution. In streams with small-size basins of Western Siberia, Frey and Smith (2005) reported elevated concentrations of DOC (up to 70 mg C L⁻¹) based on measurements in late summer.

Declining DIC concentrations in both northward and eastward directions were the main cause for the observed decrease in total dissolved C with latitude. In contrast, DOC concentrations declined northward in Central Siberia (this study), but did not demonstrate an obvious trend in eastward direction for other major Siberian rivers. Nevertheless, the proportion of DOC in total C grew from 40% at Ob River to 60% at Kolyma River and reached 80% in the easternmost Amguema River. Similarly, DOC proportion was ca 80% in the northernmost Tembenchii River and dropped to 60%...
in the southernmost Podkamennaya Tunguska River. North American rivers (i.e., Yukon and Mackenzie) generally showed the lowest DOC concentrations and export compared to rivers of the Siberian sector of the Arctic Ocean. In contrast, they both show an extremely high proportion of DIC in total dissolved C, causing an elevated C yield. The higher concentration of DIC in North American subarctic rivers stems from the extensive coverage of easily-weathered sedimentary rocks (Striegl et al. 2007), compared to the volcanic lithology of the Central Siberian rivers (Pokrovsky et al. 2006).

Thus, there are strong indications that ongoing changes in high latitude basins may result in an increased C flux to the Arctic Ocean, as both the transport (river flow) and carbon sources (e.g. terrestrial primary production) are increasing. The recently reported projections of increases of DOC and DIC concentrations in rivers in a north–south transect within the Ob basin (Western Siberia) due to projected near-doubling of area with −2°C MAAT isotherm (Frey and Smith 2005) corroborate our findings. Degradation of permafrost in Eastern Siberia, characterized by large C pools conserved in Pleistocene-age loess permafrost (yedoma) has been suggested to accelerate C turnover and increase terrestrial C release to the Kolyma River (Neff et al. 2006). Gordeev and Kravchishina (2009) reported recently up to 7-fold increase of C export to the Arctic ocean to 2100, as Arctic rivers demonstrate increasing runoff (Peterson et al. 2002, McClelland et al. 2006) and productivity of vegetation on their basins (Sturm et al. 2001, Kirdyanov et al. 2011). At our study sites the increase of riverine DOC concentrations and discharges for the period of 2006–10 as compared with period 1966–75 resulted in a 50% increase of DOC export in rivers of the Central Siberian Plateau. However, the source of water and consequently the longevity of increasing river discharges remain debatable (McClelland et al. 2006).

6. Conclusions

Forest ed basins of the Central Siberian Plateau, underlain by continuous and discontinuous permafrost, export disproportionately to net ecosystem productivity large amounts of terrigenous C to rivers. Similar to other rivers of the Arctic Ocean basin, snowmelt loads of dissolved C dominated its annual fluxes. Dissolved organic carbon was the dominant component of terrigenous C released to riverine systems. Dissolved carbon concentrations decrease from south to north, negatively correlated with the distribution of continuous permafrost and positively correlated with mean annual air temperature. Similar trends are found for 10 major Siberian rivers draining high latitude permafrost dominated areas Geochim. Cosmochim. Acta 75 3335–57.

Bartholomé E and Belward A S 2005 GLC2000: a new approach to global land cover mapping from Earth observation data Int. J. Remote Sens. 26 1959–77.

Billett M F, Deacon C M and Palmer S M 2006 Connecting organic carbon in stream water and soils in a peatland catchment J. Geophys. Res. 111 G02030.

Brown J, Ferrians O J Jr, Heginbottom J A and Melnikov E S 1998 Revised February 2001 Circum-Arctic Map of Permafrost and Ground Ice Conditions (Boulder, CO: National Snow and Ice Data Center/World Data Center for Glaciology, Digital Media).

Buffle J 1988 Complexation Reactions in Aquatic Systems. An Analytical Approach (Chichester: Ellis Horwood).

Buffle J, Zhang Z and Starcke V 2007 Metal flux and dynamic speciation at (bio)interfaces. Part I: critical evaluation and compilation of physicochemical parameters for complexes with simple ligand and fulvic/humic substances Environ. Sci. Technol. 41 7609–20.

Cai W J, Guo X H, Chen C T A, Dai M H, Zhang L J, Zhai W D, Lohrenz S E, Yin K, Harrison P J and Wang Y C 2008 A comparative review of weathering intensity and HCO3− flux in the world’s major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers Cont. Shelf Res. 28 1538–49.

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References

Aitkenhead J A and McDowell W H 2000 Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales Global Biogeochem. Cycles 14 127–38.

Amiotte-Suchet P, Aubert D, Probst J L, Cauhtier-Lafaye F, Probst A, Andreux F and Viville D 1999 δ13C pattern of dissolved inorganic carbon in a small granitic catchment: the Strengbach case study (Vosges Mountains, France) Chem. Geol. 159 129–45.

Bagard M-L, Chabaux F, Pokrovsky O S, Viers J, Prokushkin A S, Stille P, Rihs S, Schmitt A D and Dupre B 2011 Seasonal variability of element fluxes in two Central Siberian rivers draining high latitude permafrost dominated areas Geochim. Cosmochim. Acta 75 3335–57.

Buffle J, Zhang Z and Starcke V 2007 Metal flux and dynamic speciation at (bio)interfaces. Part I: critical evaluation and compilation of physicochemical parameters for complexes with simple ligand and fulvic/humic substances Environ. Sci. Technol. 41 7609–20.

Cai W J, Guo X H, Chen C T A, Dai M H, Zhang L J, Zhai W D, Lohrenz S E, Yin K, Harrison P J and Wang Y C 2008 A comparative review of weathering intensity and HCO3− flux in the world’s major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers Cont. Shelf Res. 28 1538–49.
Carey S K and Woo M K 2001 Slope runoff processes and flow generation in a subarctic, subalpine environment. *J. Hydrol.* 253 110–29

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

Dessert C, Dupré B, François L M, Schott J, Gaillardet J, Chakravani G and Bajpai S 2001 Erosion of Deccan Traps determined by river geochemistry: impact on the global climate and the $^{87}$Sr/$^{86}$Sr ratio of seawater. *Earth Planet. Sci. Lett.* 188 459–74

Dessert C, Dupré B, Gaillardet J, François L M and Allègre C J 2003 Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 203 257–73

Dessert C, Gaillardet J, Dupré B, Schott J and Pokrovsky O S 2009 Fluxes of high- versus low-temperature water–rock interactions in aerial volcanic areas: the example of the Kamchatka Peninsula. *Russia Geochim. Cosmochim. Acta* 73 148–69

Dolman A J, Maximov T C, Moors E J, Maximov A P, Elbers J A, Kononov A V, Waterloo M J and van der Molen M K 2004 Net ecosystem exchange of carbon dioxide and water of far eastern Siberian Larch (Larix cajanderii) on permafrost. *Biogeosciences* 1 133–144

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. *Geophys. Res. Lett.* 33 L10401

Frey K E, Evans C D, Monteith D T, Reynolds B and Fenner N 2001 Export of organic carbon from peat soils *Nature* 412 785

Frey K E and McClelland J W 2009 Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrol. Process.* 23 169–82

Frey K E and Smith L C 2005 Amplified carbon release from vast West Siberian peatlands by 2100. *Geophys. Res. Lett.* 32 L09401

Frey K E, Siegel D I and Smith L C 2007 Geochemistry of west Siberian streams and their potential response to permafrost degradation. *Water Resour. Res.* 43 W03406

Gerasimov I P 1964 Srednyaya Sibir. Moscow: Nauka p 480

Gibson J I, Edwards T W D and Prowse T D 1993 Runoff generation in a high boreal wetland in northern Canada. *Nordic Hydrol.* 24 213–24

Gordeev V V and Kravchishina M D 2009 River flux of dissolved organic carbon (DOC) and particulate organic carbon (POC) to the Arctic Ocean: what are the consequences of the global changes? *Influence of Climate Change on the Changing Arctic and Sub-Arctic Conditions* ed C J Nihoul and J C J Nihoul (Berlin: Springer) pp 145–60

Gordeev V V, Martin J M, Sidorov I S and Sidorova M V 1996 A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean. *Am. J. Sci.* 296 664–91

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. *Appl. Geochim.* 19 593–610

Guggenberger G, Rodionov A, Shibistova O, Grabe M, Kasansky O A, Fuchs H, Mitkeeva N, Zrazhevskaya G and Flessa H 2008 Storage and mobility of black carbon in permafrost soils of the forest tundra ecotone in northern Siberia. *Global Change Biol.* 14 1367–81

Guo L and MacDonald R W 2006 Source and transport of terrigenous organic matter in the upper Yukon River: evidence from isotope ($^{13}$C, $^{14}$C, and $^{15}$N) composition of dissolved, colloidal, and particulate phases. *Global Biogeochem. Cycles* 20 GB2011

Guo L, Ping C L and MacDonald R W 2007 Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. *Geophys. Res. Lett.* 34 L13603

Hedges J I, Keil R G and Benner R 1997 What happens to terrestrial organic matter in the ocean? *Org. Geochem.* 25 195–212

Holmes R M et al. 2011 Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. *Estuar. Coasts* at press (doi:10.1007/s12237-011-9386-6)

Hope D, Billett M F and Cresser M S 1994 A review of the export of carbon in river water: fluxes and processes. *Environ. Pollut.* 84 301–24

Hydrological Yearbooks of Russian Hydrological Survey, Yenisey Basin 1954–1975 (Krasnoyarsk: State Gidromet)

Kawagishi 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 Biol.* 10 1576–86

Kharkov V I, Divinskaya M L and Ranson K J 2005 Expansion of evergreen conifers to the larch-dominated zone and climatic trends. *Russ. J. Ecol.* 36 164–70

Kiryudin A V, Hagedorn F, Knorre A A, Fedotova E V, Vaganov E A, Naurzbaev M M, Moiseev P A and Rigling A 2011 20th century tree-line advance and vegetation changes along an altitudinal transect in Putorana Mountains, northern Siberia. *Boreas* at press (doi:10.1111/j.1502-3885.2011.00214.x)

MacLean R, Oswood M W, Irons J G III and McDowell W H 1999 The effect of permafrost on stream biogeochemistry: a case study of two streams in the Alaskan (USA) taiga. *Biogeochemistry* 47 239–67

McClelland J W, Déry S J, Peterson B J, Holmes R M and Wood E F 2006 A pan-Arctic evaluation of changes in river discharge during the latter half of the 20th century. *Geophys. Res. Lett.* 33 L06715

McGuire A D and Anderson L A 2009 Sensitivity of the carbon cycle in the Arctic to climate change. *Ecol. Monogr.* 79 523–55

Mitchell T D and Jones P D 2005 An improved method of constructing a database of monthly climate observations and associated high-resolution grids. *Int. J. Climatol.* 25 693–712

Nakai Y, Matsuura Y, Kajimoto T, Abaimov A P, Yamamoto S and Zyryanova O A 2008 Eddy covariance CO$_2$ flux above a Gmelin larch forest on continuous permafrost in Central Siberia during a growing season. *Theor. Appl. Climatol.* 93 133–47

Neff J C, Finlay J C, Zimov S A, Davydov S P, Carrasco J J, Schuer A E G and Davydova A I 2006 Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. *Geophys. Res. Lett.* 33 L23401

Peterson B J, Holmes R M, McClelland J W, Vorosmarty C J, Lammers R B, Shiikolomian I, Shiikolomian I A and Rahmstorf S 2002 Increasing river discharge to the Arctic Ocean. *Science* 298 2171–3

Petrone K C, Jones J B, Hinzman L D and Boone R D 2006 Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. *J. Geophys. Res.* 111 G02020

Pokrovsky O S, Schott J and Dupré B 2006 Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basic terrain in Central Siberia. *Geochim. Cosmochim. Acta* 70 3239–60

Pokrovsky O S, Schott J, Kudryavtsev D I and Dupré B 2005 Basalt weathering in Central Siberia under permafrost conditions. *Geochim. Cosmochim. Acta* 69 5659–80

Pokrovsky O S, Shirokova L S, Kirpotin S N, Audry S, Viers J and Dupré B 2011 Effect of permafrost thawing on the organic carbon and metal speciation in thermokarst lakes of western Siberia. *Biogeosciences* 8 565–83
Pokrovsky O S, Viers J, Shirokova L S, Shevchenko V P, Filipov A S and Dupré B 2010 Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in Severnaya Dvina River and its tributary Chem. Geol. 273 136–49

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 Biogeochem. Cycles 21 GB4003

Prokushkin A S, Tokareva I V, Prokushkin S G, Abaimov A P and Guggenberger G 2008 Fluxes of dissolved organic matter in larch forests of permafrost zone of Siberia Russ. J. Ecol. 39 153–61

Quinton W L, Gray D M and Marsh P 2000 Subsurface drainage from hummock-covered hillslopes in the arctic tundra J. Hydrol. 237 113–25

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

Rember R D and Trefry J H 2004 Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic Geochim. Cosmochim. Acta 68 477–89

Romanovsky V E et al 2010 Thermal state of permafrost in Russia Permafro. Periglac. Process. 21 136–55

Shiklomanov A I and Lammers R B 2009 Record Russian river discharge in 2007 and the limits of analysis Environ. Res. Lett. 4 045015

Spencer R G M, Aiken G R, Butler K D, Dornblaser M M, Striegl R G and 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

Spencer R G M, Aiken G R, Wickland K P, Striegl R G and 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

Spitz A and Leenheer J 1991 DOC in rivers Biogeochemistry of Major World Rivers SCOPE vol 42, ed E T Degens, S Kempe and J E Richey (Brisbane: Wiley) pp 213–32

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 Geophys. Res. Lett. 32 L21413

Striegl R G, Dornblaser M M, Aiken G R, Wickland K P and Raymond P A 2007 Carbon export cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005 Water Resour. Res. 43 W02411

Sturmi M, Racine C and Tape K 2001 Increasing shrub abundance in the Arctic Nature 411 546–47

Tarnocai C, Canedell J G, Schuur E A G, Kuhry P, Mazhitova G and Zimov S 2009 Soil organic carbon pools in the northern circumpolar permafrost region Global Change Biol. 23 GB20237

Tchebakova N M, Parfenova E and Soja A J 2009 The effects of climate, permafrost and fire on vegetation change in Siberia in a changing climate Environ. Res. Lett. 4 045013

Weishaar J L, Aiken G R, Bergamaschi B A, Fram M S and Fujii R 2003 Evaluation of specific ultravioletb absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon Environ. Sci. Technol. 37 4702–8