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Recent changes in nitrate and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska

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[1] Export of nitrate and dissolved organic carbon (DOC) from the upper Kuparuk River between the late 1970s and early 2000s was evaluated using long-term ecological research (LTER) data in combination with solute flux and catchment hydrology models. The USGS Load Estimator (LOADEST) was used to calculate June–August export from 1978 forward. LOADEST was then coupled with a catchment-based land surface model (CLSM) to estimate total annual export from 1991 to 2001. Simulations using the LOADEST/CLSM combination indicate that annual nitrate export from the upper Kuparuk River increased by ~5 fold and annual DOC export decreased by about one half from 1991 to 2001. The decrease in DOC export was focused in May and was primarily attributed to a decrease in river discharge. In contrast, increased nitrate export was evident from May to September and was primarily attributed to increased nitrate concentrations. Increased nitrate concentrations are evident across a wide range of discharge conditions, indicating that higher values do not simply reflect lower discharge in recent years but a significant shift to higher concentration per unit discharge. Nitrate concentrations remained elevated after 2001. However, extraordinarily low discharge during June 2004 and June–August 2005 outweighed the influence of higher concentrations in determining export during these years. The mechanism responsible for the recent increase in nitrate concentrations is uncertain but may relate to changes in soils and vegetation associated with regional warming. While changes in nitrate and DOC export from arctic rivers reflect changes in terrestrial ecosystems, they also have significant implications for Arctic Ocean ecosystems.

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1. Introduction

[2] Warming is expected to have a major impact on biogeochemical cycling in arctic watersheds through effects on hydrology, permafrost dynamics, and ecosystem metabolism [*Arctic Climate Impact Assessment* (*ACIA*), 2005]. Linkages between warming and greenhouse gas dynamics have been given particular attention in past studies [e.g., *McGuire et al.*, 2000; *Chapin et al.*, 2000]. However, changes in nutrient and organic matter export from arctic watersheds may also have important consequences. In particular, changes in nitrogen and organic carbon export from rivers would influence total production as well as the relative roles of autotrophy and heterotrophy in arctic coastal waters.

[3] There is considerable uncertainty about how warming will impact N export from rivers at high latitudes. Few long-term N flux data sets are available to directly examine trends. Moreover, where long-term data sets do exist, such as for several large rivers in the Russian Arctic, data quality issues have often limited their utility [*Holmes et al.*, 2000; *Zhulidov et al.*, 2000; *Holmes et al.*, 2001]. Therefore space-for-time substitutions are typically used to evaluate the potential consequences of warming on N export by high-latitude rivers. Recent studies in central Alaska find highest N export rates in watersheds with discontinuous permafrost as compared to watersheds with continuous or no permafrost [*Jones et al.*, 2005; *Petrone et al.*, 2006]. In fact, *Jones et al.* [2005] report N export rates that greatly exceed annual inputs for several watersheds in discontinuous permafrost regions, suggesting that warming may already be upsetting the balance between N inputs and outputs by exposing material previously preserved in permafrost to decomposition and export. In the West Siberian Lowlands of Russia, *Frey et al.* [2007] found highest fluvial N export rates in

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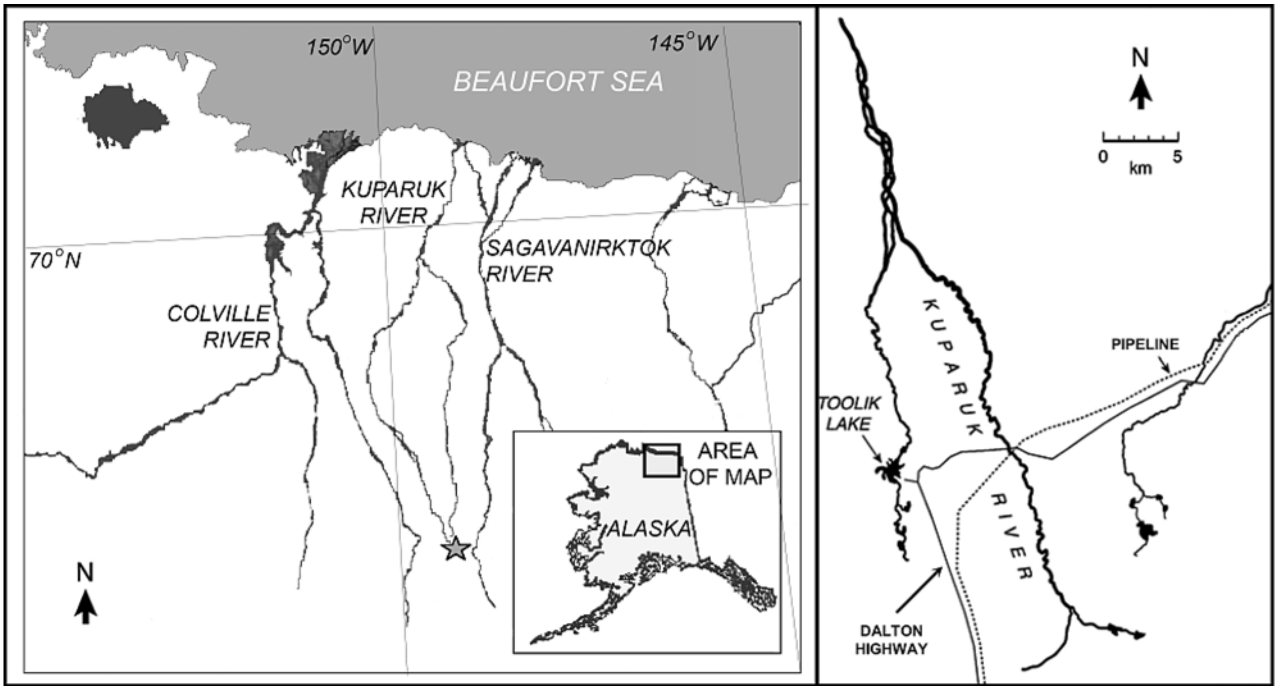

Figure 1. (left) Sampling location (star) on the North Slope of Alaska. (right) Detail of the upper Kuparuk River near Toolik Field Station. Nitrate and dissolved organic carbon (DOC) concentrations have been measured at this location since 1978.

watersheds free of permafrost. Differences in total dissolved N export were specifically attributed to differences in dissolved organic nitrogen (DON) in that study. *Frey et al.* [2007] speculate that N export will increase as warming leads to further permafrost loss, but note that their projections specifically apply to summer export, after the snowmelt period. At a much larger scale, *Dittmar and Kattner* [2003] speculate that nutrient inputs to the Arctic Ocean may have increased over the past several decades as a result of increases in river discharge.

[4] In contrast with the examples discussed above, it is also possible that warming could lead to reductions in N export from rivers at high latitudes. Increased N demand by vegetation (i.e., greater storage in biomass) and/or increased denitrification would produce this result. Furthermore, thickening active layers could deepen ground water flowpaths into previously frozen mineral soils and thereby facilitate greater adsorption of dissolved organic matter [*MacLean et al.*, 1999; *Petrone et al.*, 2006].

[5] There are also competing hypotheses about whether fluvial DOC export at high latitudes will increase or decrease with future warming. DOC concentrations have increased in some northern European [*Freeman et al.*, 2001; *Worrall and Burt*, 2004; *Tranvik and Jansson*, 2002] and North American [*Findlay*, 2005] rivers in recent decades. Furthermore, recently published data from the peat-rich West Siberian Lowland show a striking contrast in C export from warm, permafrost-free watersheds versus cold, permafrost-influenced watersheds, with the former exporting up to six times as much C as the latter [*Frey and Smith*, 2005]. Model simulations predict that warming of permafrost-influenced watersheds in the West Siberian Lowland will cause total C export for the region to more than triple by 2100 [*Frey and Smith*, 2005]. In contrast, *Striegl et al.* [2005] show a decrease in discharge-normalized DOC export by the Yukon River between the late 1970s and early 2000s. This decrease may be attributed to enhanced microbial mineralization of DOC in response to higher temperatures, longer flow paths, and longer residence times in soils with increasing active layer depths in watershed underlain by permafrost [*Striegl et al.*, 2005]. Changes in C storage are also strongly linked to N availability [*Rastetter and Shaver*, 1992; *McGuire et al.*, 1997; *Williams et al.*, 2000]. Thus the net effects of warming on fluvial DOC export will be determined by a balance between increased DOC production and mineralization along flow paths, which will in turn depend on soil characteristics, vegetation responses, permafrost dynamics, hydrology, and C quality.

[6] In this paper we specifically focus on export of nitrate and DOC in the upper Kuparuk River. Long-term data from the Arctic LTER were used in combination with hydrology and constituent flux modeling to evaluate patterns in nitrate and DOC export. This analysis revealed a major increase in nitrate export during recent years attributed to an increase in nitrate concentrations. There was a relatively small concomitant decrease in DOC export, but this export was primarily linked to a decrease in river discharge.

2. Site Description and Data Sets

[7] The Kuparuk River flows northward for approximately 250 km from the foothills of the Brooks Range to the Alaskan Beaufort Sea (Figure 1). The total watershed

area of the Kuparuk River is ~8400 km^2, and the upper Kuparuk River north of the Dalton Highway drains ~140 km^2 of this area. The upper Kuparuk River is typically frozen solid between October and the middle of May. Snowmelt provides about one-third of the annual discharge [*Kane et al.*, 2000]. This is much lower than for the Kuparuk watershed as a whole (~75% of discharge from the Kuparuk River to the Beaufort Sea occurs during the spring freshet) because the close proximity of the upper Kuparuk watershed to the Brooks Range makes it particularly susceptible to orographic rainstorms during the warm season. The difference in snowmelt contributions to annual discharge between the upper and lower portions of the Kuparuk River translates into differences in the seasonality of dissolved and particulate matter export. For example, DOC export from the Kuparuk River to the Beaufort Sea occurs predominantly during the spring melt period [*Rember and Trefry*, 2004], whereas DOC export from the upper Kuparuk is more evenly distributed between the spring and summer [*Peterson et al.*, 1986].

[8] The upper Kuparuk watershed is centered near 69.638°N, 149.408°W at an average altitude of 967 m [*McNamara et al.*, 1998]. There are no glaciers within this watershed, and lakes comprise only about 0.025% of the landscape area (A. Balser, personal communication, 2007). Its vegetation is dominated by tussock tundra, with shrubs, wet sedge, dry heath, and lichens also permeating its surface [*Walker and Walker*, 1996]. The predominant soils in the upper Kuparuk watershed are composed of an organic peat in the first 15–20 cm, underlain by silt and glacial till [*Hinzman et al.*, 1991]. Continuous permafrost with depths reaching 600 m controls the basin's subsurface hydrology to a large extent [*Osterkamp and Payne*, 1981; *McNamara et al.*, 1998], and flow from deep springs is not a major source of water [*Kriet et al.*, 1992]. Snowfall accumulation is relatively low, with a typical value of 130-mm snow water equivalent in any given year [*Zhang et al.*, 1996; *McNamara et al.*, 1998].

[9] The upper Kuparuk River has been the focus of intensive study for nearly 30 a. The river passes under the Dalton highway approximately 25 km downstream (channel length) from its headwaters (Figure 1). At this crossing the Kuparuk is a fourth-order stream, and discharge has been measured multiple times per day during the open water season since 1978. Data loggers have been employed since 1993. Early research efforts (1978–1980) focused on measuring concentrations of nutrients, organic matter, and sediments in the river, and downstream export of these constituents [*Peterson et al.*, 1986, 1992; *Kriet et al.*, 1992]. These efforts included sampling from May to August and demonstrated that dissolved organic matter (DOM) concentrations are positively correlated with discharge, whereas nitrate concentrations are negatively correlated with discharge in the upper Kuparuk River [*Peterson et al.*, 1986, 1992]. They also demonstrated that the total dissolved nitrogen (TDN) pool is dominated by DON, and nitrate is the dominant form of dissolved inorganic nitrogen (DIN).

[10] Subsequent work, supported by NSF-OPP and by the Arctic Tundra LTER (established 1987), has focused on understanding transport and processing mechanisms within the upper Kupark river [e.g., *Peterson et al.*, 1993, 1997; *Harvey et al.*, 1997; *Peterson et al.*, 2001; *Wollheim et al.*, 2001]. Concentrations of nutrients and organic matter have been measured as a routine part of these projects. Sampling frequency has varied from year to year, and indeed within years, depending on the particular studies underway. The baseline sampling effort for nutrients and organic matter has generally been 1–4 times per month during the June–August period, but sampling intervals have been as short as hourly during intensive studies.

[11] One recent finding that is particularly relevant to our work here is that nitrification in the river channel is very active, converting any ammonium entering the channel to nitrate within a few hundred meters of travel distance [*Wollheim et al.*, 2001]. Given this rapid conversion, any changes in soil organic N mineralization in the upper Kuparuk watershed that result in greater ammonium input are expected to be manifest as nitrate in the river water.

3. Data Analysis

[12] We used the USGS LOADEST program [*Runkel et al.*, 2004] to analyze variations in nitrate and DOC export in the upper Kuparuk River over the past 28 a. Provided with paired measurements of discharge and concentration for calibration, LOADEST uses a multiple regression approach to identify primary variables controlling constituent export. Discharge is the leading variable. In addition, the program considers seasonality and long-term change. A multiple regression model is then used to estimate daily export over the period of interest.

[13] LOADEST uses three different statistical approaches to estimate export and provides diagnostic output to help users determine which statistic is most appropriate for a particular application. Adjusted Maximum Likelihood Estimation (AMLE) and Maximum Likelihood Estimation (MLE) are most suitable when calibration model errors (residuals) are normally distributed, whereas Least Absolute Deviation (LAD) is more appropriate when calibration model errors are not normally distributed. AMLE accounts for bias introduced when calibration data sets are censored [*Cohn et al.*, 1992]. Output from AMLE and MLE converges when data sets are uncensored [*Cohn et al.*, 1992].

[14] The model that LOADEST identified as a bet fit for both the nitrate and the DOC data sets is

$$\begin{aligned}\mathrm{Ln(export)} = {} & \mathrm{a_0 + a_1\ LnQ + a_2\ LnQ^2 + a_3\ Sin(2\pi\ d_{time})} \\ & \mathrm{+ a_4\ Cos(2\pi\ d_{time}) + a_5\ d_{time} + a_6\ d_{time}^2}\end{aligned} \tag{1}$$

In this model, LnQ equals $\mathrm{Ln_{discharge}}$ minus center of $\mathrm{Ln_{discharge}}$, and $\mathrm{d_{time}}$ equals decimal time minus center of decimal time. This centering routine is applied to avoid multicolinearity [*Helsel and Hirsch*, 2002] associated with the use of linear and quadratic expressions of time and discharge. Coefficients $\mathrm{a_0}$ through $\mathrm{a_6}$ are listed in Table 1 along with core statistics. The model explains ~56% of the variation in daily nitrate export and ~95% of the variability in daily DOC export from the upper Kuparuk River.

[15] Equation (1) can be applied to concentration instead of export by substituting Ln(concentration) for Ln(export) and redefining coefficients $\mathrm{a_0}$ and $\mathrm{a_1}$ accordingly (Table 1).

Table 1. Model Coefficients for Export and Concentration of Nitrate and Dissolved Organic Carbon (DOC) in the Upper Kuparuk River[a]

	Coefficient Value	Std. Dev.	t Ratio	p Value
		Nitrate		
a_0	−0.38 (1.51)	0.90	−0.43 (1.68)	0.65 (0.09)
a_1	0.60 (−0.40)	0.06	10.24 (−6.88)	<0.001
a_2	0.12	0.05	2.61	0.008
a_3	−1.08	0.77	−1.40	0.16
a_4	0.15	0.56	0.26	0.79
a_5	0.03	0.007	3.82	<0.001
a_6	0.01	0.001	6.78	<0.001
		DOC		
a_0	8.09 (2.63)	0.32	25.50 (8.31)	<0.001
a_1	1.13 (0.13)	0.03	42.46 (4.92)	<0.001
a_2	0.04	0.02	1.76	0.07
a_3	1.18	0.32	3.63	<0.001
a_4	−0.18	0.09	−2.00	0.04
a_5	−0.02	0.003	−5.39	<0.001
a_6	0.001	0.001	2.00	0.04

[a] With the exception of a_0 and a_1, coefficients for export and concentration are the same. Values for concentration are given in parentheses for a_0 and a_1.

For nitrate in the upper Kuparuk River, a_1 is negative with respect to concentration and positive with respect to export. This change in sign reflects the fact that although nitrate concentrations decrease as discharge goes up, the concentration decrease is less influential than the discharge increase in determining nitrate export. In contrast, a positive correlation between discharge and concentration leads to an amplified a_1 coefficient for DOC export relative to what would be expect if DOC concentration was constant (or negatively correlated with discharge) in the upper Kuparuk River.

[16] Comparison of measured export of nitrate and DOC to LOADEST values for the upper Kuparuk River demonstrates good agreement over a wide range of conditions (Figures 2 and 3). The number of measurements vary year-to-year over the long-term data set. The years shown in Figure 2 were selected to demonstrate LOADEST performance because the number of measurements during these years was relatively high and because they reflect widely differing hydrologic conditions. A comprehensive comparison of measured versus LOADEST values from 1978 forward does, however, show that LOADEST tends to overestimate fluxes toward the lower end of the range (Figure 3). This effect is more evident in the nitrate than the DOC data, and is commensurate with greater variation in measured versus LOADEST values for nitrate overall. Given that the LTER concentration data used to calibrate

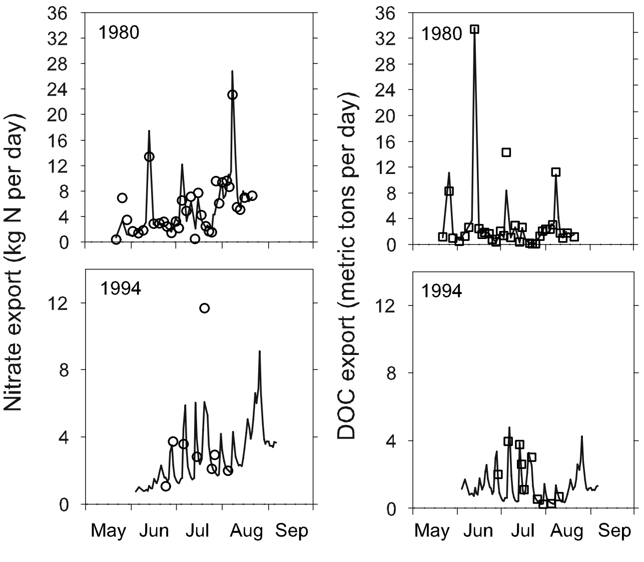

Figure 2. Comparison of (left) simulated and measured nitrate and (right) DOC export in the upper Kuparuk River for 2 selected years. Solid lines represent simulated export. Open symbols represent measured export. This comparison is provided as a demonstration of the USGS Load Estimator (LOADEST)'s ability to accurately simulate nitrate and DOC export under widely differing hydrologic conditions. See Figure 3 for a point-by-point comparison of measured and simulated export over the entire record.

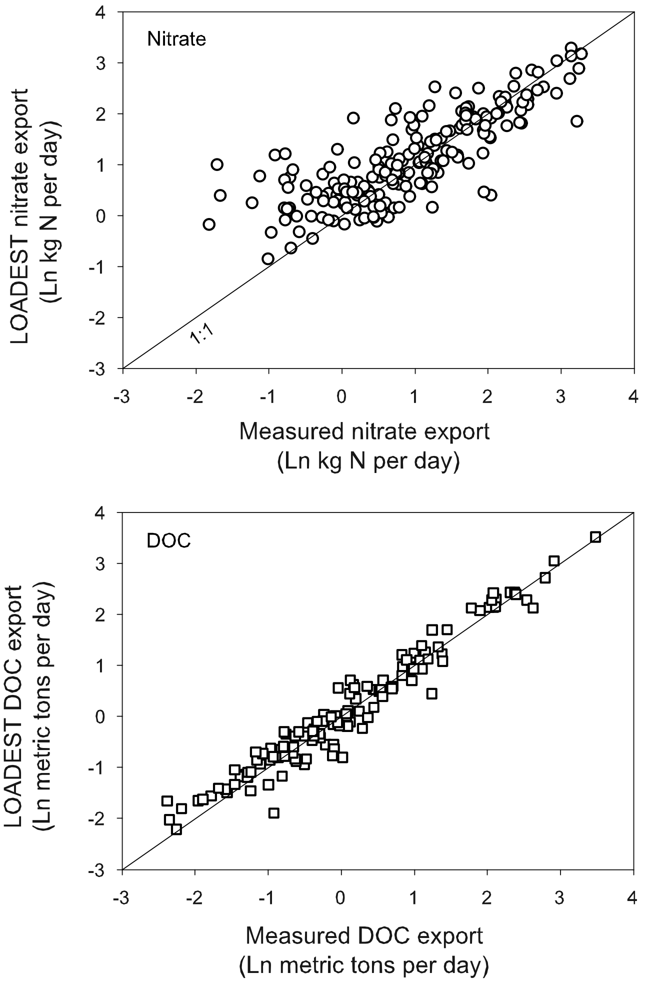

Figure 3. Comparison of all measured versus simulated nitrate (top) and DOC (bottom) export values. Data are plotted on a natural log scale to facilitate comparisons over several orders of magnitude.

LOADEST are predominantly from June, July, and August, one might also expect greater uncertainty in LOADEST output for May, September, and October than for June–August. This is not apparent on the basis of the data that we have from May: The difference between measured and modeled export is 0.28 ± 0.44 kg d^{-1} for DOC (n = 8) and −1.37 ± 0.91 kg d^{-1} for nitrate (n = 4). However, it is doubtful that this limited sampling effort captured the full dynamic of the early snowmelt period. We have no measured values from September to compare with LOADEST output, but we expect that this period is suitably represented by LOADEST because the range of hydrologic conditions during September is similar to August. We also have no measured values from October to compared with LOADEST output. DOC dynamics accompanying freeze-up introduce some uncertainty here, but October export is expected to be low in any case because of limited water flow (i.e., flow during only part of the month).

[17] The length and resolution of the model output matches that of the discharge data set driving it. As a consequence, annual flux estimates are most robust when discharge coverage over the hydrologic year is complete. The upper Kuparuk River typically begins flowing in the latter half of May and freezes solid by the end of October. Discharge records for the upper Kuparuk do not consistently cover this whole period. Thus to estimate annual export of nitrate and DOC (1991–2001), we coupled LOADEST with discharge output from a version of the NASA Seasonal to Interannual Prediction Project (NSIPP) Catchment Based Land Surface Model [*Koster et al.*, 2000; *Ducharne et al.*, 2000].

[18] In contrast to traditional land surface schemes, the CLSM employs the watershed as the fundamental hydrological unit instead of a rectangular grid cell. In each catchment unit, TOPMODEL [*Beven and Kirkby*, 1979] equations are applied to relate the soil moisture distribution to topography. Statistics of the topographic index (TPI), defined as $\ln(a/\tan\beta)$, where a is the upstream contributing area to a downslope point with a local slope $\tan\beta$, provide the means by which three different soil moisture regimes are identified in a catchment. The different zones are specified as a saturated area (high TPI values), an unsaturated area (intermediate TPI values), and a wilting area (low TPI values). Rainfall or snowmelt onto the saturated fraction contributes directly to surface runoff. Baseflow associated with lateral flow contributes additional runoff. Total simulated runoff is therefore the sum of these two components in the CLSM. The CLSM evapotranspiration scheme follows from the Mosaic land surface model [*Koster and Suarez*, 1996]. The scheme includes transpiration from the vegetation canopy and soil-based evaporation. Evapotranspiration rates are computed separately for the three soil moisture regimes considered by the CLSM [*Koster et al.*, 2000]. In the saturated zone, evapotranspiration rates meet the atmospheric demand, as soil moisture is readily available. In the unsaturated fraction of the catchment, potential evapotranspiration rates are reduced by a factor that depends on the soil moisture content. In the wilting zone, plant transpiration shuts off such that this component no longer contributes to the evaporative fluxes. In all instances, potential evapotranspiration or sublimation is computed using standard bulk formula that relies on vertical gradients of water vapor and wind speed [e.g., *Oke*, 1987]. The areal average of the evaporative fluxes from each soil moisture regime provides the total latent heat flux for a given watershed. Finally, by incorporating new processes including permafrost dynamics, stormflow, and snow heterogeneity into the model structure [*Stieglitz et al.*, 2001; *Shaman et al.*, 2002; *Déry et al.*, 2004], we have successfully scaled hydrologic processes from small arctic basins to the entirety of the Kuparuk basin (8140 km^2) [*Déry et al.*, 2005].

[19] A comprehensive meteorological data set is needed for application of the CLSM. Near-surface air temperature (T), precipitation (P), relative humidity (RH), wind speed (U), surface atmospheric pressure (Ps), incoming solar (K), and longwave (L) radiation constitute the main driving variables. For this study we used the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-40 reanalysis product [*Uppala et al.*, 2005], which provides 6-hourly fields over the period 1958 to August 2002 and at a horizontal grid resolution of 2 × 2 degrees. Specifically, we used ERA-40 data to drive the CLSM starting in 1991 and ending after 2001 (the last full year of ERA-40 data). The ERA-40 reanalysis product was chosen for its ability to reproduce high-latitude climate with a high degree of accuracy [*Cullather et al.*, 2000; *Serreze and Hurst*, 2000].

[20] The CLSM also requires information on several topographic parameters. To this end, a high-resolution digital elevation model (DEM) of the Kuparuk watershed has been acquired [*Nolan*, 2003]. Using the DEM, the Kuparuk River basin was divided into 13 subbasins to provide a better representation of the north-south gradient in topography. Statistics of the topographic index for each basin were generated on the basis of a 25-m resolution DEM. A three-parameter gamma distribution was then applied to the data and the first three moments of this function serve as input into the CLSM [*Sivapalan et al.*, 1987; *Ducharne et al.*, 2000]. The CLSM output does not always match the measured discharge in the upper Kuparuk on a daily basis, but the model does capture discharge dynamics over 1 to 2 week time intervals (Figure 4). Thus summation of daily CLSM discharge values to estimate monthly or annual fluxes in the upper Kuparuk basin is robust.

4. Results

[21] In the following two sections we first present time courses of nitrate and DOC export and then we evaluate the relative importance of variations in discharge versus concentration as proximate causes of recent changes in nitrate and DOC export. Potential mechanisms related to warming on the North Slope of Alaska are discussed in section 5.

4.1. Recent Changes in Nitrate and DOC Export

[22] Nitrate export from the upper Kuparuk River has increased substantially in recent years (Figures 5, 6, and 7). Figure 5 shows average daily nitrate export during June, July, and August calculated by LOADEST coupled with measured discharge over the complete period of record. Nitrate export values calculated by LOADEST coupled with CLSM simulated discharge (1991–2001) during June, July, and August are very similar to the LOADEST values driven by measured discharge (Figure 6). In addition, the LOADEST/

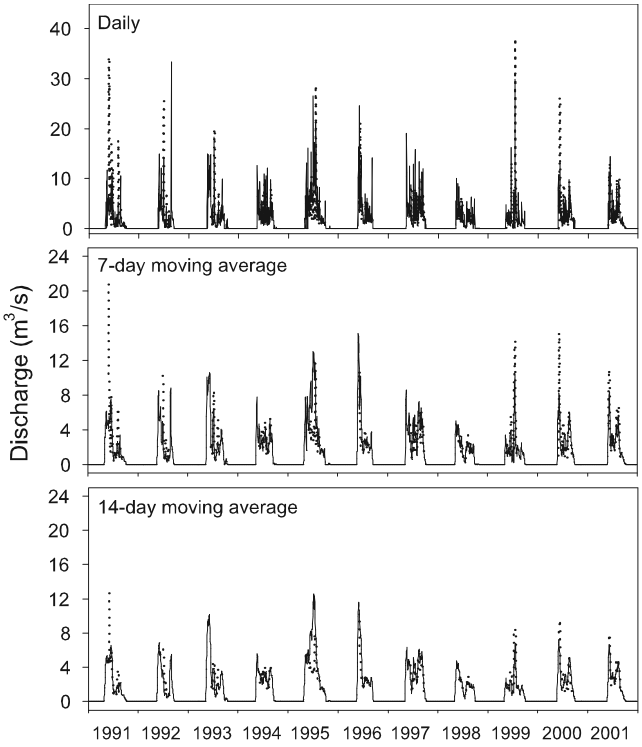

Figure 4. Comparison of simulated (solid lines) and measured (dotted lines) water discharge from the upper Kuparuk River, 1991–2001.

CLSM combination provides nitrate export estimates for May, September, and October when measurements of discharge are insufficient for calculating fluxes during most years (Figure 6). CLSM consistently captures the initial snowmelt period whereas measurements of discharge on the upper Kuparuk River typically start after snowmelt begins and have been delayed until early June in some years. Likewise, CLSM estimates of discharge extend to the end of the hydrologic year while the measurements do not. Together the LOADEST values driven by CLSM show that nitrate export has increased from May through September, with less pronounced changes toward the end of summer. These changes amount to a ~5 fold increase in annual nitrate export over the 1991–2001 period (Figure 7). After 2001, nitrate export decreased during June. In particular, values in 2004 and 2005 were only about one third of peak values (Figure 5). Nitrate export during July and August remained high through 2004 and then dropped substantially in 2005 (Figure 5).

[23] Trends in DOC export from the upper Kuparuk River are less clear than those identified for nitrate, although there is some indication of a decrease in DOC export during recent years (Figures 5, 7, and 8). Figure 5 shows average daily DOC export during June, July, and August calculated by LOADEST coupled with measured discharge over the complete period of record. As with the nitrate results, DOC export driven by measured versus CLSM discharge are similar during June, July, and August, and the LOADEST/CLSM combination allows export estimation in May, September, and October (Figure 8). However, unlike the nitrate results, major changes in DOC export during 1991–2001 are not evident throughout the summer but instead are limited to May. The change in DOC export during May had a strong influence on annual values, with average annual export during 1998–2001 amounting to only about 0.6 times the average annual export for 1991–1997 (Figure 7).

4.2. Proximate Causes: Are The Recent Changes in Nitrate and DOC Export Owing to Changes in Discharge, Concentration, or Both?

[24] While discharge is a primary determinate of all water-borne constituent fluxes in streams and rivers, interannual variability in constituent export may be attributed to changes in discharge, constituent concentration, or both. Variation in discharge accounts for about 80% of the interannual variation in DOC export during recent years, whereas the relationship between discharge and nitrate export is more complex (Figure 9). The increase in nitrate export during 1991–2001 is not matched by an equal percentage increase in discharge and indeed occurs despite decreases in discharge toward the end of the record in May and June. However, it is noteworthy that interannual variations in discharge and nitrate export become increasingly

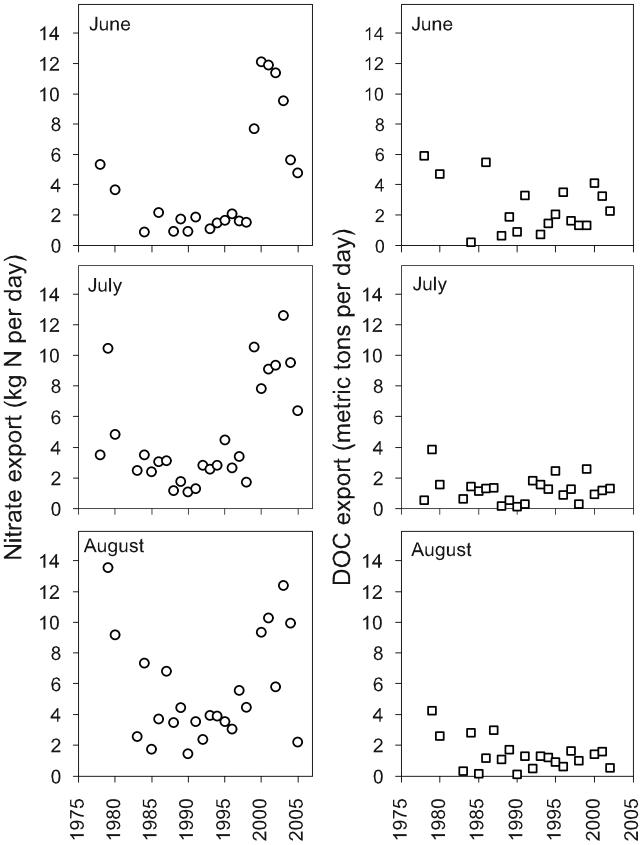

Figure 5. (left) Average daily nitrate and (right) DOC export during June, July, and August calculated from LOADEST values driven by measured discharge. Nitrate estimates cover 1978–2005. DOC estimates cover 1978–2002.

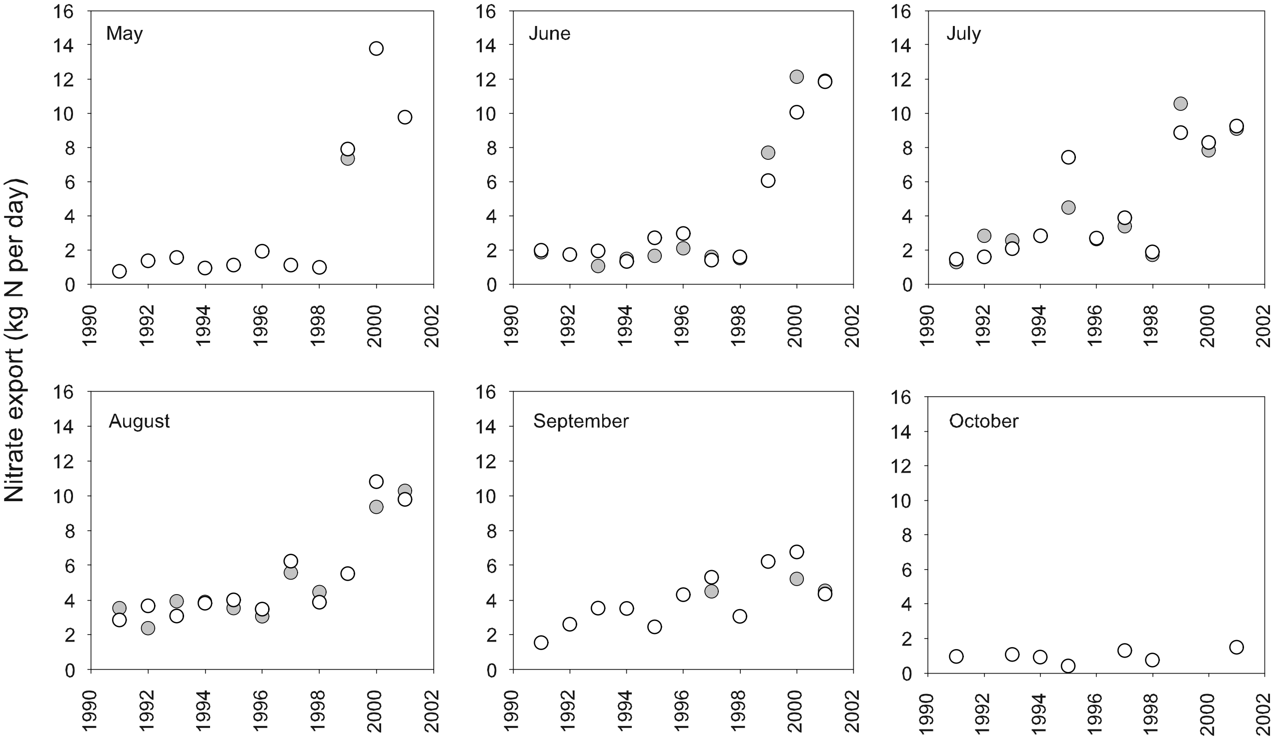

Figure 6. Nitrate export estimates in the upper Kuparuk River calculated using measured (open circles) and simulated (filled circles) river discharge to drive LOADEST from 1991 to 2001. Export estimates calculated using measured discharge are largely constrained to June, July, and August because of insufficient discharge data, whereas coupling of LOADEST with simulated discharge allows estimation of export over the complete river flow period.

similar later in the summer (Figure 9). This convergence reflects increasing dependence of interannual nitrate export variations on discharge (i.e., other factors contributing to nitrate export variations between 1991 and 2001 diminish from May through September).

[25] In contrast with discharge, nitrate concentrations clearly increase during recent years (Figure 10). These concentration increases are evident across a wide range of discharge conditions, indicating that the differences are not simply a reflection of lower discharge in recent years but a significant shift to higher concentration per unit discharge. Furthermore, the elevated values observed during the 2000–2005 period are unprecedented within the 28 a record. The increased concentrations are primarily responsible (proximate cause) for the increased nitrate export during 1991–2001. Although nitrate concentrations remained elevated after 2001, extraordinarily low discharge during June 2004 and June, July, and August 2005 outweighed the influence of higher concentrations in determining export during these years.

[26] DOC concentrations also change over the long-term record, but in contrast with nitrate it appears that the major change in DOC concentrations occurred before the 1990s (Figure 10). As discussed above, interannual variations in DOC export during 1991–2001 can largely be attributed to variations in discharge. More specifically, decreases in discharge during May are primarily responsible (proximate cause) for the modeled decrease in DOC export during recent years. It is important to keep in mind, however, that long-term changes in discharge-concentration relationships reflected in the model output are based on June–August data (recall that May data available for model calibration was limited to 1978–1980). Thus any unique changes in DOC concentrations during May that may have occurred are not accounted for in this analysis.

5. Discussion: Potential Linkage to Climate Change

[27] While nitrate concentrations remain negatively correlated with discharge and DOC concentrations remain positively correlated with discharge in the upper Kuparuk River as first identified by *Peterson et al.* [1986, 1992], the changes in concentrations, and indeed the contrasting magnitudes of the changes observed for nitrate and DOC, are indicative of recent changes in watershed processes that may be linked to warming. Greenhouse experiments in wet sedge tundra in the upper Kuparuk region showed that a 5.6°C warming of air temperature (average over an 8 a period) increased net N mineralization by 40–200% [*Shaver et al.*, 1998]. At the same time, the effect of warming on net ecosystem production (NEP) in the experimental plots was small [*Johnson et al.*, 2000]. DOC was not measured in the greenhouse experiments, but warming-induced increases in both production and decomposition of DOC are consistent with the overall C balance. Increases in DOC decomposition

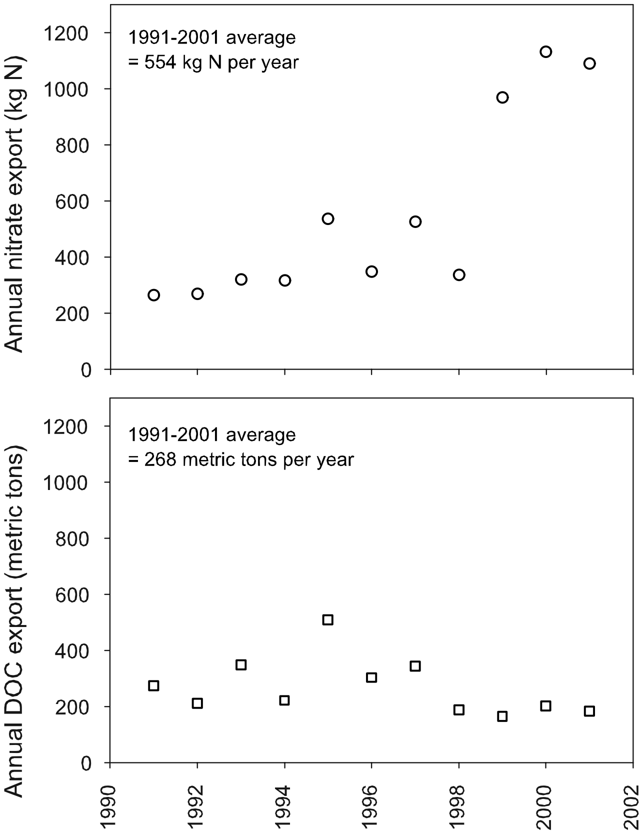

Figure 7. (top) Annual nitrate and (bottom) DOC export in the upper Kuparuk, 1991–2001, calculated from LOADEST values driven by modeled discharge.

would have to exceed increases in DOC production to account for a decrease in DOC concentrations in the upper Kuparuk River, but this differential would only be a small percentage of NEP. Likewise, changes in DON mineralization amount to a much larger percentage change with respect to the DIN pool than the DON pool.

[28] Increased surface air temperatures on the North Slope of Alaska over the past 30 a [*Chapman and Walsh*, 1993; *Overpeck et al.*, 1997; *Intergovernmental Panel on Climate Change*, 2001; *ACIA*, 2005] support the idea that warming may be a factor in the recent changes in nitrate and DOC in the upper Kuparuk River. More importantly, however, ground temperatures on the North Slope increased markedly over the 1990s [*Osterkamp and Romanovsky*, 1999; *Stieglitz et al.*, 2003]. We have no direct evidence of increasing ground temperature in the watershed of the upper Kuparuk River, but temperature records from boreholes in the lower portion of the Kuparuk watershed show 0.5–1.5°C increases at 20 m. While some of the observed subsurface temperature increase can be explained by an increase in air temperatures, model simulations suggest that variations in snow cover (insulation) were an equally important factor [*Stieglitz et al.*, 2003]. Trends in surface air temperature and snow depth were not discernable over the 1990s (i.e., changes in the 1990s contributed to increases over 30 a, but large year-to-year variations precluded detection of trends within the 1990s alone). However, variations in surface air temperature and snow depth combined to produce an amplified change in ground temperature [*Stieglitz et al.*, 2003]. It is also noteworthy that changes in ground temperatures at 20 m lagged surface air temperatures by about 4 a [*Stieglitz et al.*, 2003]. While lag times decrease at shallower soil depths, a delay in ground temperature changes relative to surface air temperature changes is nonetheless consistent with the major increase in Kuparuk River nitrate during 1999–2003: air temperature during the 1991–2001 period peaked in 1998.

[29] Deepening flow paths accompanying permafrost degradation may also contribute to changes in solute export with warming [*MacLean et al.*, 1999; *Petrone et al.*, 2006]. Extension of the active layer into previously frozen mineral soils may facilitate adsorption of dissolved organic matter. At the same time, deeper flow paths that convey a greater proportion of water through the mineral layers relative to the root zone and organic-rich surface layers promote increased nitrate export. However, we have no evidence to support deeper flow paths as a mechanism contributing to the observed changes in nitrate and DOC in the upper Kuparuk River. Like surface air temperature, active layer thickness on the North Slope peaked in 1998 but showed no overall trend during 1991–2001 (http://www.udel.edu/Geography/calm). Spatially integrated estimates of thawed soil volume in the Kuparuk region also showed no trend over the 1990s [*Shiklomanov and Nelson*, 2002]. We might have expected the active layer to deepen in parallel with increasing ground temperatures during the 1990s, but average permafrost temperatures that are well below 0°C limit this effect. Furthermore, increasing plant cover and litter accumulation associated with greater above ground production under warmer conditions can provide insulation that decreases active layer depth [*Johnson et al.*, 2000].

[30] In summary, it is the balance between increased production and mineralization of organic matter along flow paths, which in turn depends on vegetation responses, permafrost dynamics, hydrology, and organic matter quality that ultimately must determine whether nitrate and DOC export from watersheds increases or decreases with warming. Our findings are consistent with the tundra warming experiments in the upper Kuparuk region that show major increases in net N mineralization accompanied by only small changes in net ecosystem production [*Shaver et al.*, 1998; *Johnson et al.*, 2000]. We cannot say, however, whether or not the recent increase in nitrate export was balanced by a decrease in organic N export. It is possible that the standing stock of total soil N remained constant, implying only a change in the form of N export. It is also possible that the increase in nitrate export was linked to (1) an increase in new N contributions to the watershed or (2) a drawdown of the standing stock of N within the watershed. Of these two possible scenarios leading to greater total N export, the latter is more plausible because the stock of N stored in soil organic matter is several orders of magnitude greater than annual inputs of new N from precipitation and N fixation [*Shaver et al.*, 1992]. We also emphasize that changes in the upper Kuparuk River may not be representative of changes occurring in the Kuparuk River watershed as a whole. For example, the upper Kuparuk

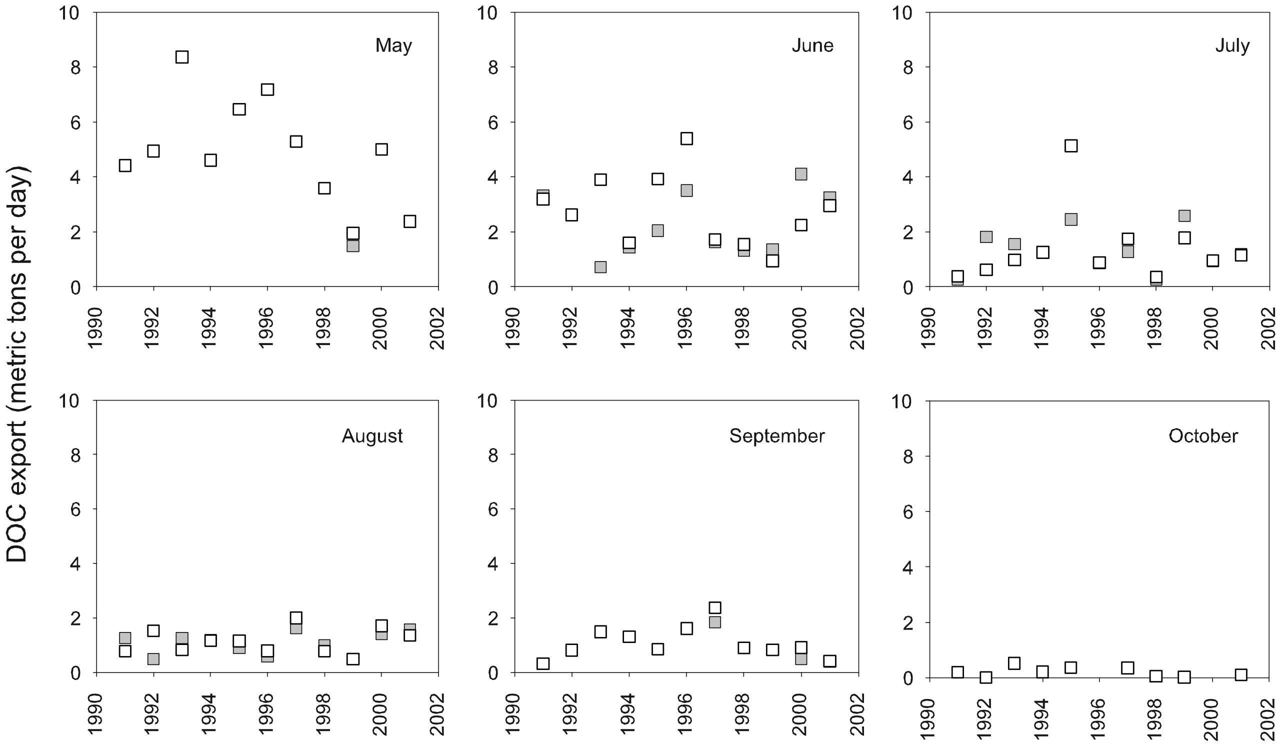

Figure 8. DOC export estimates in the upper Kuparuk River calculated using measured (open squares) and simulated (filled squares) river discharge to drive LOADEST from 1991 to 2001. Export estimates calculated using measured discharge are largely constrained to June, July, and August because of insufficient discharge data, whereas coupling of LOADEST with simulated discharge allows estimation of export over the complete river flow period.

catchment has steeper topography and fewer lakes than the coastal plain catchments feeding the Kuparuk River down stream. Thus while the long-term data from the upper Kuparuk River are extremely valuable, long-term studies of larger rivers that integrate changes in catchments with widely differing characteristics from headwaters to the sea are needed to facilitate generalizations about ongoing and future changes in N and C export in the Arctic.

6. Implications: How May Changes in Nitrate and DOC Export From Rivers Influence Productivity in the Arctic Ocean?

[31] As part of the *Journal of Geophysical Research: Biogeosciences* special issue on Change in the Arctic Freshwater System, we give particular attention here to land-sea coupling. Many of the contributions to this special issue were funded through the NSF-ARCSS “Arctic Freshwater Cycle: Land/Upper-Ocean Linkages” solicitation. While we have no intention of extrapolating observed changes in the upper Kuparuk River to arctic rivers in general, the current findings do provide a convenient framework for discussing potential impacts of changes in nitrate and DOC export from rivers to the Arctic Ocean.

[32] It is generally accepted that Pacific water inflows and mixing from the Atlantic layer provide the vast majority of N supporting primary production in the surface waters of the Arctic Ocean [*Codispoti et al.*, 1991; *Cooper et al.*, 1997; *Wheeler et al.*, 1997; *Luchetta et al.*, 2000; *Stein and Macdonald*, 2003]. Even in shelf regions, riverine contributions of inorganic N can account for only a small proportion of primary production annually. Within this broad context, a fivefold increase in nitrate export from arctic rivers (as observed in the upper Kuparuk River) would not represent a major perturbation. Within estuarine and nearshore ecosystems, on the other hand, such a change could have a significant effect on primary production. This is particularly true along the northern Alaska coastline, where primary production is relatively low and barrier islands impede mixing of nearshore waters with offshore waters [*Dunton et al.*, 2006].

[33] Relative to changes in nitrate export, changes in DOC export from rivers have a greater potential to influence productivity in the Arctic Ocean. The organic rich soils and peatlands at high latitudes result in disproportionate export of DOC via rivers to the Arctic Ocean as compared to other major ocean basins [*Opsahl et al.*, 1999; *Stein and Macdonald*, 2003; *Benner et al.*, 2005]. Until recently, the prevailing wisdom has been that terrigenous DOC from arctic rivers is too refractory to be important to the net metabolism of the Arctic Ocean [*Opsahl et al.*, 1999; *Dittmar and Kattner*, 2003; *Rachold et al.*, 2003; *Amon and Meon*, 2004]. However, two new studies suggest that 30–60% of the riverine DOC may actually be respired during a ~10 a residence time in the Beaufort Gyre [*Hansell et al.*, 2004; *Cooper et al.*, 2005]. These

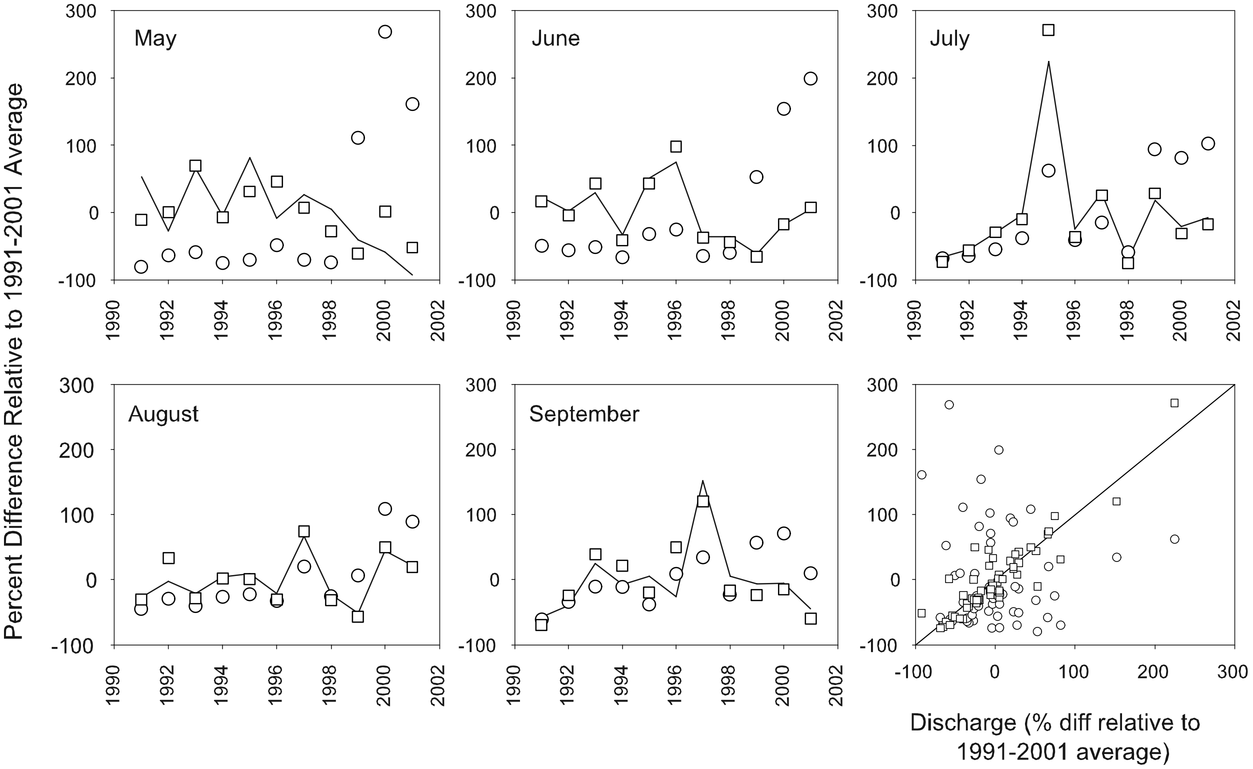

Figure 9. Comparison of nitrate (circles) and DOC (squares) export anomalies to discharge anomalies (lines) in the upper Kuparuk River, 1991–2001. Anomalies are calculated as percentage differences relative to 1991–2001 averages. Time courses for nitrate, DOC, and discharge are shown for May–September. The bottom right plots nitrate and DOC export anomalies versus discharge anomalies. The overall R^2 for DOC anomalies versus discharge anomalies is 0.81. The overall R^2 for nitrate anomalies versus discharge anomalies is <0.00. It should be noted, however, that variations in nitrate and discharge anomalies become increasingly similar later in the summer: Standard deviations of nitrate minus discharge anomalies are 165%, 107%, 77%, 42%, and 56% for May, June, July, August, and September, respectively.

results based on salinity and δ^{18}O versus DOC mixing relationships are supported by recent incubation experiments using river waters collected during the spring snowmelt period from the Kuparuk, Sagavanirktok, and Colville rivers that show 15–25% losses of DOC over a 1 month period [*Frazer et al.*, 2006].

[34] If DOC exported from arctic rivers is indeed more labile than previously thought, then associated N released during decomposition may be more important than river borne DIN for primary production in coastal waters. A compilation of data from Russian rivers draining into the Arctic Ocean shows that, on average, concentrations of DON are ~15 times greater than concentrations of DIN [*Lobbes et al.*, 2000]. DON:DIN ratios in the upper Kuparuk are similar to those of the Russian rivers, with the total dissolved N export most dominated by DON during the spring snowmelt period (DON:DIN averaging ~20 between late May and the end of June [*Peterson et al.*, 1992]).

[35] While the above discussion focuses on absolute changes in productivity, changes in the contributions of fluvial N and C to arctic coastal waters also have implications for net ecosystem metabolism. A relative increase in N availability might shift the net metabolism of arctic coastal waters in favor of autotrophy. At the same time, however, increased inorganic N availability could enhance organic matter decomposition by subsidizing bacterial N demand. Given that DOC and nitrate concentrations display opposing trends with variation in discharge, changes in the timing and magnitude of river discharge [*Peterson et al.*, 2002; *McClelland et al.*, 2004; *Wu et al.*, 2005] may lead to changes in the relative delivery of N and C to coastal waters beyond those related to longer/deeper flow paths and enhanced microbial activity.

[36] Like watershed responses to warming, effects of changing riverine inputs on ocean productivity must vary substantially around the Pan-Arctic domain depending on regional conditions (i.e., stratification and mixing regimes). Thus to better understand how changes in N and C export from rivers may influence productivity in the Arctic Ocean coupled watershed-ocean studies in different regions of the Arctic are needed. Furthermore, these studies should explicitly consider responses of nearshore, shelf, and open ocean ecosystems to changes in riverine contributions.

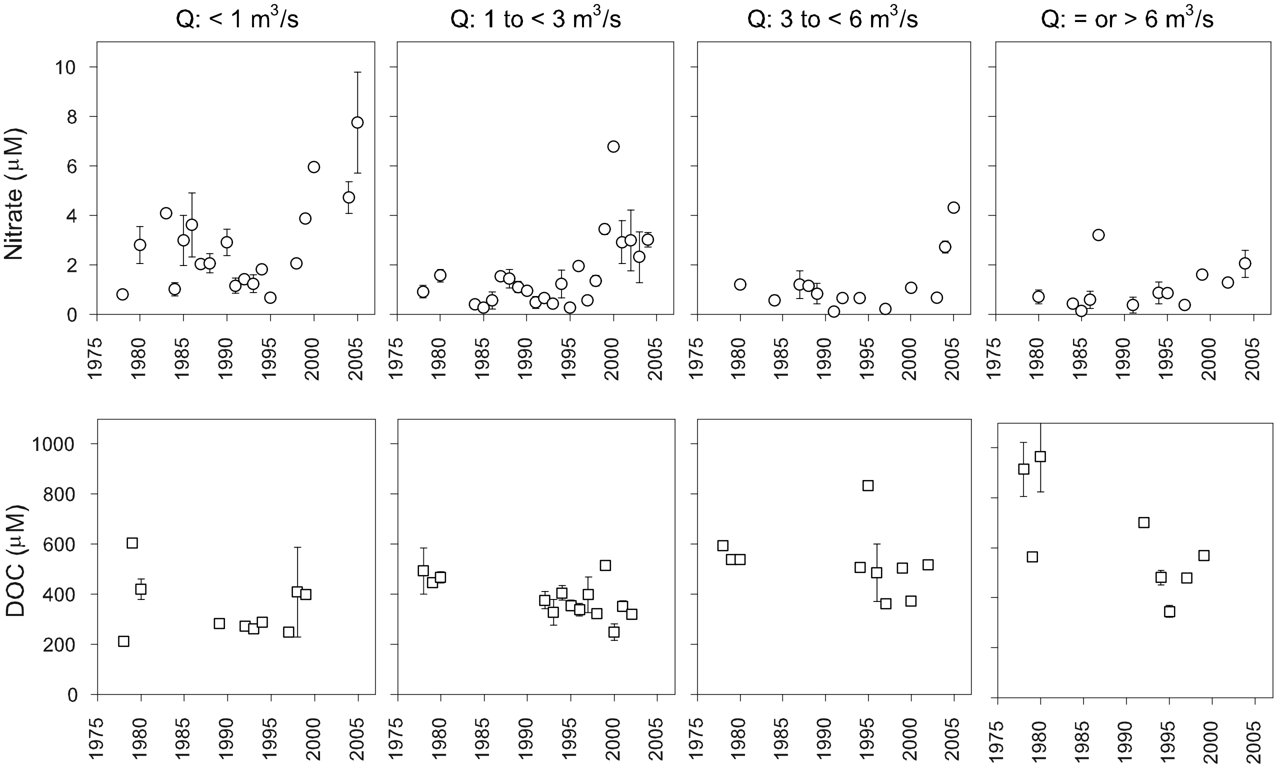

Figure 10. (top) Time courses of measured nitrate and (bottom) DOC concentrations from June–August separated into four discharge categories. Values are averages ±1 standard error.

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References

Amon, R. M. W., and B. Meon (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, *Mar. Chem.*, *92*, 311–330.

Arctic Climate Impact Assessment (ACIA) (2005), *Arctic Climate Impact Assessment*, 1042 pp., Cambridge Univ. Press, New York.

Benner, R., P. Louchouarn, and R. M. W. Amon (2005), Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic, *Global Biogeochem. Cycles*, *19*, GB2025, doi:10.1029/2004GB002398.

Beven, K. J., and M. J. Kirkby (1979), A physically based variable contributing area model of basin hydrology, *Hydrol. Sci. J.*, *24*, 43–69.

Chapin, F. S., III, et al. (2000), Feedbacks from arctic and boreal ecosystems to climate, *Global Change Biol.*, *6*, S211–S223.

Chapman, W. L., and J. E. Walsh (1993), Recent variations of sea ice and air-temperature in high-latitudes, *Bull. Am. Meteorol. Soc.*, *74*, 33–47.

Codispoti, L. A., G. E. Friederich, C. M. Sakamoto, and L. I. Gordon (1991), Nutrient cycling and primary production in the marine systems of the Arctic and Antarctic, *J. Mar. Syst.*, *2*, 359–384.

Cohn, T. A., E. J. Gilroy, and W. G. Baier (1992), Estimating fluvial transport of trace constituents using a regression model with data subject to censoring, American Statistical Association Section on Statistics and the Environment, Am. Stat. Assoc., pp. 142–151, Boston.

Cooper, L. W., T. E. Whitledge, J. M. Grebmeier, and T. Weingartner (1997), The nutrient, salinity, and stable oxygen isotope composition of Bering and Chukchi Seas waters in and near the Bering Strait, *J. Geophys. Res.*, *102*, 12,563–12,573.

Cooper, L. W., R. Benner, J. W. McClelland, B. J. Peterson, R. M. Holmes, P. A. Raymond, D. A. Hansell, J. M. Grebmeier, and L. A. Codispoti (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, doi:10.1029/2005JG000031.

Cullather, R. I., D. H. Bromwich, and M. C. Serreze (2000), The atmospheric hydrologic cycle over the Arctic Basin from reanalyses, part I: Comparison with observations and previous studies, *J. Clim.*, *13*, 923–937.

Déry, S. J., W. T. Crow, M. Stieglitz, and E. F. Wood (2004), Modeling snow cover heterogeneity over complex terrain for regional and global climate models, *J. Hydrometeorol.*, *5*, 33–48.

Déry, S. J., M. Stieglitz, A. K. Rennermalm, and E. F. Wood (2005), The water budget of the Kuparuk basin, Alaska, *J. Hydrometeorol.*, *6*, 633–655.

Dittmar, T., and G. Kattner (2003), The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: A review, *Mar. Chem.*, *83*, 103–120.

Ducharne, A., R. D. Koster, M. J. Suarez, M. Stieglitz, and P. Kumar (2000), A catchment-based approach to modeling land surface processes in a GCM. Part II: Parameter estimation and model demonstration, *J. Geophys. Res.*, *105*, 24,823–24,838.

Dunton, K. H., T. Weingartner, and E. C. Carmack (2006), The near shore western Beaufort Sea ecosystem: Circulation and importance of terrestrial carbon in arctic coastal food webs, *Progress Oceanogr.*, *71*, 362–378.

Findlay, S. E. G. (2005), Increased carbon transport in the Hudson River: Unexpected consequence of nitrogen deposition?, *Frontiers Ecol. Environ.*, *3*, 133–137.

Frazer, B. B., J. W. McClelland, R. M. Holmes, and P. Raymond (2006), The lability of dissolved organic carbon in arctic rivers on the North Slope of Alaska, *Eos Trans. AGU*, *87*(52), Fall Meet. Suppl., Abstract C51A-0403.

Freeman, C., C. D. Evans, D. T. Monteith, B. Renolds, and N. Fenner (2001), Export of organic carbon from peat soils, *Nature*, *412*, 785.

Frey, K. E., and L. C. Smith (2005), Amplified carbon release from vast West Siberian peatlands by 2100, *Geophys. Res. Lett.*, *32*, L09401, doi:10.1029/2004GL022025.

Frey, K. E., J. W. McClelland, R. M. Holmes, and L. C. Smith (2007), Impacts of climate warming and permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea, *J. Geophys. Res.*, *112*, G04S58, doi:10.1029/2006JG000369.

Hansell, D. A., D. Kadko, and N. R. Bates (2004), Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean, *Science*, *304*, 858–861.

Harvey, C. J., B. J. Peterson, W. B. Bowden, L. A. Deegan, J. C. Finlay, A. E. Hershey, and M. C. Miller (1997), Organic matter dynamics in the Kuparuk River in Alaska, USA, *J. N. Am. Benthological Soc.*, *16*, 18–23.

Helsel, D. R., and R. M. Hirsch (Eds.) (2002), Statistical methods in water resources, in *Techniques of Water Resources Research*, book 4, chap. A3, 510 pp., U.S. Geol. Surv., Washington, D. C.

Hinzman, L. D., D. L. Kane, R. E. Gieck, and K. R. Everett (1991), Hydrologic and thermal properties of the active layer in the Alaskan Arctic, *Cold Regions Sci. Technol.*, *19*, 95–110.

Holmes, R. M., B. J. Peterson, V. V. Gordeev, A. V. Zhulidov, M. Meybeck, R. B. Lammers, and C. J. Vörösmarty (2000), Flux of nutrients from Russian rivers to the Arctic Ocean: Can we establish a baseline against which to judge future changes?, *Water Resour. Res.*, *36*, 2309–2320.

Holmes, R. M., B. J. Peterson, A. V. Zhulidov, V. V. Gordeev, P. N. Makkaveev, P. A. Stunzas, L. S. Kosmenko, G. H. Kohler, and A. I. Shiklomanov (2001), Nutrient chemistry of the Ob' and Yenisey rivers, Siberia: Results from June 2000 expedition and evaluation of long-term data sets, *Mar. Chem.*, *75*, 219–227.

Intergovernmental Panel on Climate Change (IPCC) (2001), *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., 881 pp., Cambridge Univ. Press, New York.

Johnson, L. C., G. R. Shaver, D. H. Cades, E. Rastetter, K. Nadelhoffer, A. Giblin, J. Laundre, and A. Stanley (2000), Plant carbon-nutrient interactions control CO_2 exchange in Alaskan wet sedge tundra ecosystems, *Ecology*, *81*, 453–469.

Jones, J. B., Jr., K. C. Petrone, J. C. Finlay, L. D. Hinzman, and W. R. Bolton (2005), Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost, *Geophys. Res. Lett.*, *32*, L02401, doi:10.1029/2004GL021734.

Kane, D. L., L. D. Hinzman, J. P. McNamara, Z. Zhang, and C. S. Benson (2000), An overview of a nested watershed study in Arctic Alaska, *Nordic Hydrol.*, *31*, 245–266.

Koster, R. D. and M. J. Suarez (1996), Energy and water balance calculations in the Mosaic LSM, *NASA Tech. Memo. 04606*, *9*, 59 pp., Natl. Aeronaut. Space Admin., Silver Spring, Md.

Koster, R. D., M. J. Suarez, A. Ducharne, M. Stieglitz, and P. Kumar (2000), A catchment-based approach to modeling land surface processes in a GCM. Part I: Model structure, *J. Geophys. Res.*, *105*, 24,809–24,822.

Kriet, K., B. J. Peterson, and T. L. Corliss (1992), Water and sediment export of the upper Kuparuk River drainage of the North Slope of Alaska, *Hydrobiologia*, *240*, 71–81.

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

Luchetta, A., M. Lipizer, and G. Socal (2000), Temporal evolution of primary production in the central Barents Sea, *J. Mar. Syst.*, *27*, 177–193.

MacLean, R., M. W. Oswood, J. G. Irons III, and W. H. McDowell (1999), The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan (U.S.A) taiga, *Biogeochemistry*, *47*, 239–267.

McClelland, J. W., R. M. Holmes, B. J. Peterson, and M. Stieglitz (2004), Drivers of increasing river discharge in the Eurasian Arctic: Consideration of dams, permafrost thaw, and fires as potential agents of change, *J. Geophys. Res.*, *109*, D18102, doi:10.1029/2004JD004583.

McGuire, A. D., J. M. Melillo, D. W. Kicklighter, Y. Pan, X. Xiao, J. Helfrich, B. Moore III, C. J. Vorosmarty, and A. L. Schloss (1997), Equilibrium responses of global net primary production and carbon storage to doubled atmospheric carbon dioxide: Sensitivity to changes in vegetation nitrogen concentration, *Global Biogeochem. Cycles*, *11*, 173–189.

McGuire, A. D., J. Clein, J. M. Melillo, D. W. Kicklighter, R. A. Meier, C. J. Vorosmarty, and M. C. Serreze (2000), Modeling carbon responses of tundra ecosystems to historical and projected climate: The sensitivity of Pan-Arctic carbon storage to temporal and spatial variation in climate, *Global Change Biol.*, *6*, S141–S159.

McNamara, J. P., D. L. Kane, and L. D. Hinzman (1998), An analysis of streamflow hydrology in the Kuparuk River Basin, Arctic Alaska: A nested watershed approach, *J. Hydrol.*, *206*, 39–57.

Nolan, M. (2003), Distribution of a Star3i DEM of the Kuparuk River watershed, [CR-ROM], (*NSF OPP-0207220*), Joint Office of Scientific Support, Boulder, Colo.

Oke, T. R. (1987), *Boundary Layer Climates*, 2nd edition, 435 pp., Methuen, New York.

Opsahl, S., R. Benner, and R. W. Amon (1999), Major flux of terrigenous dissolved organic matter through the Artic Ocean, *Limnol. Oceanogr.*, *44*, 2017–2023.

Osterkamp, T. E., and M. W. Payne (1981), Estimates of permafrost thickness from well logs in northern Alaska, *Cold Regions Sci. Technol.*, *5*, 13–27.

Osterkamp, T. E., and V. E. Romanovsky (1999), Evidence for warming and thawing of discontinuous permafrost in Alaska, *Permafrost Periglacial Processes*, *10*, 17–37.

Overpeck, J., et al. (1997), Arctic environmental change of the last four centuries, *Science*, *278*, 1251–1256.

Peterson, B. J., J. E. Hobbie, and T. L. Corliss (1986), Carbon flow in a tundra stream ecosystem, *Can. J. Fish. Aquat. Sci.*, *43*, 1259–1270.

Peterson, B. J., T. Corliss, K. Kriet, and J. E. Hobbie (1992), Nitrogen and phosphorus concentrations and export for the upper Kuparuk River on the North Slope of Alaska, *Hydrobiologia*, *240*, 61–69.

Peterson, B. J., et al. (1993), Biological responses of a tundra river to fertilization, *Ecology*, *74*, 653–672.

Peterson, B. J., M. Bahr, and G. W. Kling (1997), A tracer investigation of nitrogen cycling in a pristine tundra river, *Can. J. Fish. Aquat. Sci.*, *54*, 2361–2367.

Peterson, B. J., et al. (2001), Control of nitrogen export from watersheds by headwater streams, *Science*, *292*, 86–90.

Peterson, B. J., R. M. Holmes, J. W. McClelland, C. J. Vörösmarty, R. B. Lammers, A. I. Shiklomanov, I. A. Shiklomanov, and S. Rahmstorf (2002), Increasing river discharge to the Arctic Ocean, *Science*, *289*, 2171–2173.

Petrone, K. C., J. B. Jones, L. D. Hinzman, and R. D. Boone (2006), Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost, *J. Geophys. Res.*, *111*, G02020, doi:10.1029/2005JG000055.

Rachold, V., H. Eiken, V. V. Gordeev, M. N. Grigoriev, H. W. Hubberten, A. P. Lisitzin, V. P. Shevchenko, and L. Schirrmeister (2003), Modern terrigenous organic carbon input to the Arctic Ocean, in *The Organic Carbon Cycle in the Arctic Ocean*, edited by R. Stein and R. W. Macdonald, pp. 33–55, Springer, New York.

Rastetter, E. B., and G. R. Shaver (1992), A model of multiple-element limitation for acclimating vegetation, *Ecology*, *73*, 1157–1174.

Rember, R. D., and J. H. Trefry (2004), Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic, *Geochim. Cosmochim. Acta*, *68*, 477–489.

Runkel, R. L., C. G. Crawford, and T. A. Cohn (2004), Load Estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers, *U.S. Geol. Surv. Tech. Meth.*, book 4, chap. A5, 69 pp., U. S. Geol. Surv., Denver, Colo.

Serreze, M. C., and C. M. Hurst (2000), Representation of mean Arctic precipitation from NCEP-NCAR and ERA reanalyses, *J. Clim.*, *13*, 182–201.

Shaman, J., M. Stieglitz, V. Engel, R. Koster, and C. Stark (2002), Representation of subsurface storm flow and a more responsive water table in a TOPMODEL-based hydrology model, *Water Resour. Res.*, *38*(8), 1156, doi:10.1029/2001WR000636.

Shaver, G. R., W. D. Billings, F. S. Chapin III, A. E. Giblin, K. J. Nadelhoffer, W. C. Oechel, and E. B. Rastetter (1992), Global change and the carbon balance of arctic ecosystems, *BioScience*, *42*, 433–441.

Shaver, G. R., L. C. Johnson, D. H. Cades, G. Murray, J. A. Laundre, E. B. Rastetter, K. J. Nadelhofer, and A. E. Giblin (1998), Biomass and CO_2 flux in wet sedge tundras: Response to nutrients, temperature, and light, *Ecol. Monogr.*, *68*, 75–97.

Shiklomanov, N. I., and F. E. Nelson (2002), Active-layer mapping at regional scales: A 13-year spatial time series for the Kuparuk Region, North Central Alaska, *Permafrost Periglacial Processes*, *13*, 219–230.

Sivapalan, M., K. Beven, and E. F. Wood (1987), On hydrologic similarity. 2: A scaled model of storm runoff production, *Water Resour. Res.*, *23*, 2266–2278.

Stein, R., and R. W. Macdonald (Eds.) (2003), *The Organic Carbon Cycle in the Arctic Ocean*, 363 pp., Springer, New York.

Stieglitz, M., A. Ducharne, R. D. Koster, and M. J. Suarez (2001), The impact of detailed snow physics on the simulation of snow cover and subsurface thermodynamics at continental scales, *J. Hydrometeorol.*, *2*, 228–242.

Stieglitz, M., S. J. Déry, V. E. Romanovsky, and T. E. Osterkamp (2003), The role of snow cover in the warming of arctic permafrost, *Geophys. Res. Lett.*, *30*(13), 1721, doi:10.1029/2003GL017337.

Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland (2005), A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn, *Geophys. Res. Lett.*, *32*, L21413, doi:10.1029/2005GL024413.

Tranvik, L. J., and M. Jansson (2002), Terrestrial export of organic carbon, *Nature*, *415*, 861–862.

Uppala, S. M., et al. (2005), The ERA-40 re-analysis, *Q. J. R. Meteorol. Soc.*, *131*, 2961–3012, doi:10.1256/qj.04.176.

Walker, D. A., and M. D. Walker (1996), Terrain and vegetation of the Imnavait Creek watershed, in *Landscape Function and Disturbance in Arctic Tundra*, edited by J. F. Reynolds and J. D. Tenhunen, *Ecol. Stud.*, vol. 120, pp. 73–108, Springer, New York.

Wheeler, P. A., J. M. Watkins, and R. L. Hansing (1997), Nutrients, organic carbon and organic nitrogen in the upper water column of the Arctic Ocean: Implications for the sources of dissolved organic carbon, *Deep Sea Res. II*, *44*, 1571–1592.

Williams, M., W. Eugster, E. B. Rastetter, J. P. McFadden, and F. S. Chapin (2000), The controls on net ecosystem productivity along an Arctic transect: A model comparison with flux measurements, *Global Change Biol.*, *6*, 116–126.

Wollheim, W. M., B. J. Peterson, L. A. Deegan, J. E. Hobbie, B. Hooker, W. B. Bowden, K. J. Edwardson, D. B. Arscott, A. E. Hershey, and J. Finlay (2001), Influence of stream size on ammonium and suspended particulate nitrogen processing, *Limnol. Oceanogr.*, *46*, 1–13.

Worrall, F., and T. Burt (2004), Time series analysis of long-term river dissolved organic carbon records, *Hydrol. Processes*, *18*, 893–912.

Wu, P., R. Wood, and P. Stott (2005), Human influence on increasing Arctic river discharges, *Geophys. Res. Lett.*, *32*, L02703, doi:10.1029/2004GL021570.

Zhang, T., T. E. Osterkamp, and K. Stamnes (1996), Some characteristics of the climate in Northern Alaska, U.S.A., *Arct. Alp. Res.*, *28*, 509–518.

Zhulidov, A. V., V. V. Khlobystov, R. D. Robarts, and D. F. Pavlov (2000), Critical analysis of water quality monitoring in the Russian Federation and former Soviet Union, *Can. J. Fish. Aquat. Sci.*, *57*, 1932–1939.

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