RESEARCH ARTICLE

Key Points:
- Fluvial export from the North Slope of Alaska is quantified
- River-supplied nitrogen is important for productivity of arctic coastal waters
- Regional estimates of fluvial export support pan-arctic modeling efforts

Supporting Information:
- Readme
- ts01-06

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River export of nutrients and organic matter from the North Slope of Alaska to the Beaufort Sea

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Abstract While river-borne materials are recognized as important resources supporting coastal ecosystems around the world, estimates of river export from the North Slope of Alaska have been limited by a scarcity of water chemistry and river discharge data. This paper quantifies water, nutrient, and organic matter export from the three largest rivers (Sagavanirktok, Kuparuk, and Colville) that drain Alaska's North Slope and discusses the potential importance of river inputs for biological production in coastal waters of the Alaskan Beaufort Sea. Together these rivers export ~297,000 metric tons of organic carbon and ~18,000 metric tons of organic nitrogen each year. Annual fluxes of nitrate-N, ammonium-N, and soluble reactive phosphorus are approximately 1750, 200, and 140 metric tons per year, respectively. Constituent export from Alaska's North Slope is dominated by the Colville River. This is in part due to its larger size, but also because constituent yields are greater in the Colville watershed. River-supplied nitrogen may be more important to productivity along the Alaskan Beaufort Sea coast than previously thought. However, given the dominance of organic nitrogen export, the potential role of river-supplied nitrogen in support of primary production depends strongly on remineralization mechanisms. Although rivers draining the North Slope of Alaska make only a small contribution to overall river export from the pan-arctic watershed, comparisons with major arctic rivers reveal unique regional characteristics as well as remarkable similarities among different regions and scales. Such information is crucial for development of robust river export models that represent the arctic system as a whole.

1. Introduction

Fluxes of water and water-borne materials from land are defining features of estuarine ecosystems, yet estimates of fluvial export are poorly constrained in many regions of the world. In the Arctic, we have a solid understanding of seasonal and annual water discharge from rivers as a consequence of long-term monitoring at key locations as well as broader modeling efforts [*Lammers et al.*, 2001; *Rawlins et al.*, 2003; *Syed et al.*, 2007]. However, our understanding of constituent export from arctic rivers has lagged well behind our understanding of water export due to a relative lack of spatial and temporal information on water chemistry [*Holmes et al.*, 2000; *Bring and Destouni*, 2009]. While some arctic rivers, such as the Yukon [*Striegl et al.*, 2005; *Dornblaser and Striegl*, 2007; *Spencer et al.*, 2008, 2009] and the Kolyma [*Welp et al.*, 2005; *Finlay et al.*, 2006; *Neff et al.*, 2006; *Mann et al.*, 2012] have been given focused attention in recent years, logistical challenges associated with field campaigns have generally limited studies of river water chemistry in the Arctic.

Growing evidence of climate change impacts in the Arctic [*Arctic Climate Impact Assessment* (*ACIA*), 2005; *Anisimov et al.*, 2007], including widespread changes in arctic hydrology [*White et al.*, 2007; *Rawlins et al.*, 2010], has highlighted an urgent need to improve understanding of constituent fluxes from arctic rivers. Increasing water discharge to the Arctic Ocean and surrounding seas, first documented for rivers in Russia [*Peterson et al.*, 2002; *McClelland et al.*, 2006] and more recently documented for rivers in Canada [*Déry et al.*, 2009], is likely to be accompanied by changing water chemistry [*Frey and McClelland*, 2009; *Holmes et al.*, 2013]. However, we cannot thoroughly assess potential changes in constituent fluxes until we have established a contemporary baseline.
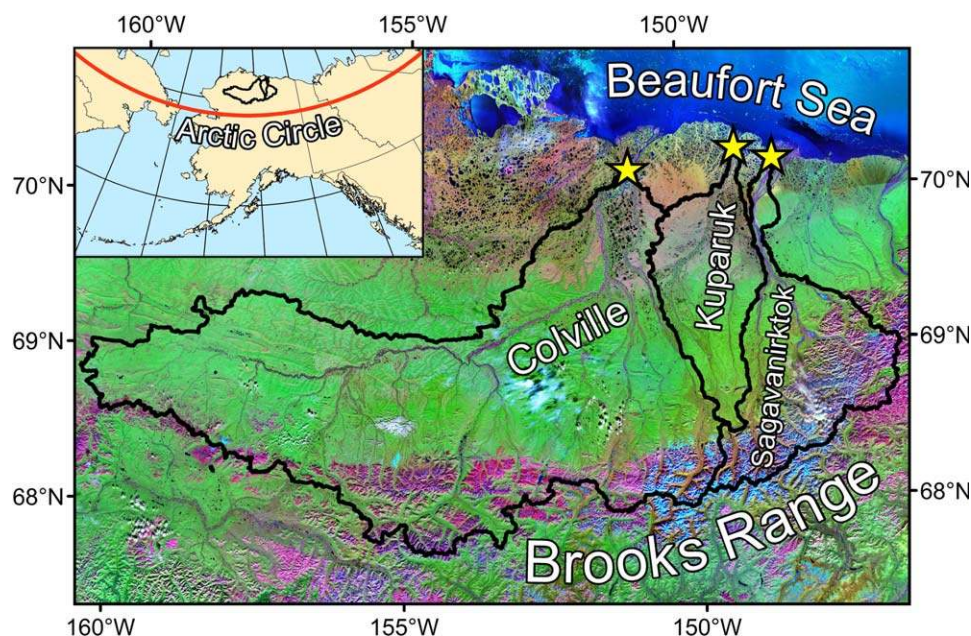
Figure 1. Boundaries of the Sagavanirktok, Kuparuk, and Colville river watersheds superimposed on a false color composite image of the North Slope of Alaska that displays bare soil and rock as pink/magenta and vegetation as bright green. Data for the false-color image were acquired from https://zulu.ssc.nasa.gov/mrsid/mrsid.pl. Elevation data used for watershed delineation came from the National Elevation Dataset (NED) and was obtained through the USGS at a 2 arc sec resolution and projected using the Alaskan Albers Equal Area NAD 1983 projection resulting in a resolution of approximately 40 m (http://seamless.usgs.gov/). Watershed delineation was performed using ESRI ArcGIS software, version 9.3.

Among the many constituents exported from land to sea in the Arctic, inorganic nutrients and organic matter are of particular interest as potential resources supporting biological production in coastal waters. River inputs have historically been considered a minor resource to coastal ecosystems of the Arctic, but increasing knowledge of how nutrients and organic matter in arctic rivers vary seasonally is stimulating new thought about their potential role in arctic coastal waters [*Holmes et al.*, 2008, 2012; *Tank et al.*, 2012]. For example, estimates of dissolved organic matter export have been revised upward [*Raymond et al.*, 2007; *Holmes et al.*, 2012], and experimental evidence suggests that dissolved organic matter exported during the spring freshet is more labile than dissolved organic matter exported during the summer [*Holmes et al.*, 2008].

This paper quantifies water, nutrient, and organic matter export from the Sagavanirktok, Kuparuk, and Colville river watersheds (Figure 1) and discusses the potential importance of river inputs as a resource supporting productivity in coastal waters of the Alaskan Beaufort Sea. The work presented here complements a broader effort during recent years to quantify export from the six largest rivers of the Arctic, including the Mackenzie and Yukon in North America and the Yenisey, Ob', Lena, and Kolyma in Eurasia [*McClelland et al.*, 2008; *Holmes et al.*, 2012]. In both cases (i.e., this paper and the recent work on major arctic rivers) characterizing seasonality has been a major goal, with particular emphasis on capturing the spring freshet. While the Sagavanirktok, Kuparuk, and Colville rivers make only a small contribution with respect to overall river export from the pan-arctic watershed, they are the three largest rivers draining the North Slope of Alaska. As such, they are of major regional importance when considering how terrestrial inputs may influence productivity in the coastal ocean. Data from the North Slope rivers also give us an opportunity to compare and contrast export characteristics, such as nutrient and organic matter yields, with the major arctic rivers. These comparisons are helpful not only for highlighting unique characteristics of individual rivers or regions, but also identifying general characteristics that are consistent despite large differences in geographic locations and scales among drainage basins. Such information is crucial for the development of robust river export models that represent the arctic system as a whole.

2. Watershed Characteristics

The Sagavanirktok, Kuparuk, and Colville rivers drain a combined area of 80,433 km^2 and are underlain by continuous permafrost. There are, however, a variety of notable differences among the drainage basins. The

Table 1. Drainage Basin Characteristic for the Sagavanirktok, Kuparuk, and Colville Rivers[a]

	Sagavanirktok	Kuparuk	Colville
Area (km^2)	12,580	8107	59,756
Mean elevation (m)	841	249	569
Max elevation (m)	2442	1214	2343
Mean slope (%)	28.9	2.5	11.5
Annual precipitation (cm)	29.4	31.1	48.4
Annual discharge (km^3)	1.6	1.3	19.7

[a]Annual discharge values are measured (Kuparuk) and modeled (Sagavanirktok and Colville) averages for 2000–2007. Discharge data for the Kuparuk were acquired from USGS gauging station 15896000.

Colville River basin is larger (∼6×) and receives greater annual precipitation (∼1.6×) than the other two basins (Table 1). As a consequence, mean annual water discharge from the Colville is much higher than from the other two rivers. While size, annual precipitation, and annual discharge are fairly similar for the Sagavanirktok and Kuparuk basins, their elevation and slope characteristics are very different. The Sagavanirktok has the highest mean elevation and slope values of the three river basins, whereas the Kuparuk has the lowest mean elevation and slope values. Maximum elevation is also much higher for the Sagavanirktok as compared to the Kuparuk basin. In contrast, maximum elevations in the Sagavanirktok and Colville basins are similar. A major consequence of the differences in elevation and slope among drainage basins is that the proportion of foothill and coastal plain tundra versus high mountain terrain with less vegetation cover (and more exposed rock) differs substantially among the three basins. This is represented visually in Figure 1, where lower elevation green areas account for much larger proportions of the Colville and Kuparuk basins as compared to the Sagavanirktok basin. Glacier coverage also differs among the three river basins; the Kuparuk basin has none whereas there are multiple small glaciers in the other two basins. This is unlikely to be a significant factor with respect to differences in annual watershed export to the Beaufort Sea. Even in the Sagavanirktok, where glaciers are most prevalent, they only account for a small percentage of the total drainage area. However, glacier contributions may be relevant with respect to export of water and water-borne constituents during low flow conditions in the late summer and fall.

While proportions of mountain, foothill, and coastal plain area differ among the three watersheds, their general hydrology is similar. Mean annual surface air temperature is approximately −10°C [*Zhang et al.*, 1996], and snow covers the land surface for about two-thirds of the year. Snowmelt begins during the mid-May to mid-June timeframe, and accounts for a large percentage of annual runoff. For example, previous work focusing on the Kuparuk River has shown that spring snowmelt accounts for up to 80% of the annual runoff in that system [*McNamara et al.*, 1998]. Little to no water flows in the rivers during the winter months. Frozen ground during the spring freshet constrains runoff to the soil surface [*Woo*, 1986; *Kane et al.*, 1989; *MacLean et al.*, 1999; *Petrone et al.*, 2006]. The snow matrix initially restricts water flow across the landscape, but flow rapidly increases as water tracks to major stream channels are established [*Kane et al.*, 1989, 1991]. Snowmelt generally occurs from south to north across the watersheds. This thaw pattern, in combination with ice dams that form in the river channels, results in episodic lowland flooding as river water flows toward the coast in the spring. As the summer progresses and the ground thaws, water flow paths are no longer restricted to the soil surface. However, maximum summer thaw depths range from 0.25 to 1.0 m [*Hinzman et al.*, 1991; *Zhang et al.*, 1997]. As such, infiltration remains strongly restricted to the near surface zone.

3. Methods

3.1. River Discharge Estimation

The US Geological Survey (USGS) continuously monitors river stage from thaw to freeze-up near the mouth of the Kuparuk River (station 15896000). Daily discharge values calculated from measured stage-discharge relationships for this site are available at http://waterdata.usgs.gov/nwis/uv?15896000. The USGS does not measure discharge at downstream locations on the Sagavanirktok and Colville rivers. Consequently, water discharge from these two rivers was simulated using a version of the NASA Seasonal to Interannual Prediction Project (NSIPP) Catchment Based Land Surface Model (CLSM). This catchment-based approach to modeling land surface processes is described in *Koster et al.* [2000] and *Ducharne et al.* [2000]. The CLSM version used here includes processes such as permafrost dynamics, snow dynamics, and stormflow, and accounts

for snow heterogeneity [*Stieglitz et al.*, 2001; *Shamen et al.*, 2002, *Déry et al.*, 2004]. This model has been successfully applied in the Kuparuk River watershed in past studies [*Stieglitz et al.*, 1999; *Déry et al.*, 2005; *McClelland et al.*, 2007]. Before applying the model to the Sagavanirktok and Colville river watersheds, however, it was tested on the Kuparuk River watershed for the specific timeframe of the present study. Model performance was also assessed using data from private consulting firms who measured peak discharge near the mouths of the Sagavanirktok and Colville rivers during spring 2006–2007. PND Engineers Inc. provided data for the Sagavanirktok, and Michael Baker Jr. Corporation provided data for the Colville.

For the present modeling effort, a 90 m resolution digital elevation model (DEM) of the North Slope of Alaska was downloaded from National Elevation Dataset (http://seamless.usgs.gov/). Thereafter, the Sagavanirktok, Kuparuk, and Colville watersheds were delineated and divided into 9, 13, and 25 subbasins, respectively. The DEM was also used to compute topographic index statistics for each subbasin using the multiple flow direction (MFD) method [*Pan et al.*, 2004]. The topographic index distribution of each subbasin was applied for computing saturation area and surface runoff in the CLSM [*Koster et al.*, 2000]. Hydrometeorological data including near surface air temperature, precipitation, relative humidity, wind speed, surface atmospheric pressure, incoming solar radiation, and downward longwave radiation are used to drive the model. To this end, we used the European Center for Medium-Range Weather Forecasts (ECMWF) ERA-Interim [*Dee et al.*, 2011] 6 hourly reanalysis product for the period 2000–2007 on a 1.5° × 1.5° cell. Atmospheric forcing via the ERA-Interim grid cells was area-weighted according to the proportional coverage of each grid cell within a given subbasin [e.g., *Wang et al.*, 2007]. A simple linear interpolation method was then used to estimate hourly atmospheric forcing variables from the 6 hourly reanalysis data. The CLSM was applied to each subbasin after a 50 year spin-up for each model run. Daily simulated discharges at the mouths of the Sagavanirktok, Kuparuk, and Colville rivers were calculated using a simple linear river routing method based on the travel time of each subbasin to the river mouth. The travel time was computed as the distance from the center of each subbasin to the river mouth divided by a constant flow velocity. In this study, a 0.5 m/s flow velocity was used.

3.2. Sample Collection and Analyses

Water samples were collected at downstream locations (Figure 1) on the Sagavanirktok, Kuparuk, and Colville rivers between May and August in 2006 and 2007. Sampling sites on the Sagavanirktok (70°14.924′N, 148°18.180′W) and Kuparuk (70°19.722′N, 148°56.964′W) were relatively close together and could be visited from a central base of operations in Deadhorse. The Colville site (70°13.502′N, 150°59.653′W) was more remote, requiring air travel from Deadhorse to the village of Nuiqsut. Colville water was primarily collected from the Nechelik channel, a branch of the river that runs through the western side of the river delta near Nuiqsut. In 2006, we sampled the Nechelik channel and the Colville main stem simultaneously several times and found no significant difference in in situ water quality parameters (temperature, conductivity, alkalinity, and pH) or constituent concentrations. Overall, values measured in the Nechelik channel were 98 ± 33% (mean ± standard error) of values measured in the main stem. Sampling frequency was highest during May/June at all three rivers. With negative days indicating sampling before peak discharge and positive days indicating sampling after peak discharge, samples were collected as follows during the May/June timeframe. Sagavanirktok, 2006: samples were collected twice per day on days −2, −1, 0, 4, 5, 6, and 7; samples were collected once per day on days 1, 2, 3, 8, 9, 10, 11, 12, 16, 17, 25, and 30. Sagavanirktok, 2007: samples were collected twice per day on days −15, −14, −11, −10, −9, −8, −7, −6, −5, −4, −3, and −2; samples were collected once per day on days −13, −12, −1, and 0. Kuparuk, 2006: samples were collected three times on day −4; samples were collected twice per day on days −3, −2, 2, 3, 4, and 5; samples were collected once per day on days 0, 1, 6, 7, 8, 9, 10, 14, 15, 23, and 28. Kuparuk, 2007: samples were collected three times per day on days −7, and −6; samples were collected twice per day on days −5 and −3; samples were collected once on day −4. Colville, 2006: samples were collected twice on day 0; samples were collected once per day on days −1, 1, 6, 7, 8, 9, 16, and 29. Colville, 2007: samples were collected twice per day on days −8, −7, and −2; samples were collected once per day on days −6, and −1. After the spring freshet in 2006, sampling at all three rivers continued at 1–2 week intervals until late July. During 2007, sampling did not continue throughout the summer, but all three rivers were sampled in late August. Together the sampling efforts during 2006 and 2007 captured conditions before, during, and following the spring freshet. However, due to interannual variability in the timing of the spring freshet, samples from the 2 years bracketed different portions of hydrograph. During 2006, sampling covered the descending limb of the

spring peak particularly well, whereas during 2007 sampling was most concentrated during the ascending limb of the spring peak.

Water was collected from the subsurface, as near as possible to the centroid of flow, using an extendable pole sampler equipped with a 1 L polycarbonate bottle. Water depth varied from less than $1/2$ m during low flow to 2–4 m during high flow at the sampling sites. Vertical and cross-sectional variability within the river channels was not quantified in this study. While high flow rates during the spring freshet certainly facilitated mixing, quantification of this variability would be desirable in future studies. Water from the sampler was used to fill three 1 L transport bottles (also polycarbonate). Transport bottles were kept on ice in the dark and processed in the laboratory within 2 h of sampling. The sampler and transport bottles were rinsed 3 times with river water before each collection. In the laboratory, water was filtered through precombusted Whatman GF/F disks (0.7 μm nominal pore size). Filters were saved for analysis of particulate organic matter concentrations and stable C and N isotope ratios (separate filters for C and N). Filtrate was saved for dissolved organic matter and nutrient analyses. Individual filters were frozen in small plastic Petri dishes and then dried in batches at 60°C. Filtrate for dissolved organic matter analysis was frozen in 60 mL polycarbonate bottles. Filtrate for all other dissolved constituent analyses was frozen in 60 mL HDPE bottles. All storage bottles were rinsed three times with filtered sample before filling.

Nutrient and organic matter analyses were distributed between Toolik Field Station, the University of Texas Marine Science Institute, the Marine Biological Laboratory, and the Woods Hole Research Center. Specifically, nitrate + nitrite and total dissolved nitrogen (following in-line oxidation to nitrate using alkaline persulfate/UV digestion) were measured on a Lachat QUICKCHEM FIA+ 8000 autoanalyzer at the Woods Hole Research Center. Nitrate + nitrite, is referred to as "nitrate" throughout this paper because the sum of nitrate + nitrite is strongly dominated by nitrate. Ammonium and soluble reactive phosphorus (SRP) were measured at the Toolik Field Station laboratory (2006 only). Ammonium was determined following the *Holmes et al.* [1999] fluorescence method. SRP was measured on a UV/Vis Spectrophotometer using standard wet chemistry as described in *Strickland and Parsons* [1972]. Samples were also collected for ammonium and SRP analysis during 2007, but it was not possible to analyze these samples at Toolik Field Station and later analyses at Woods Hole Research Center suggested that extended storage may have compromised the samples. Thus, no ammonium or SRP data are included for 2007. DON concentrations were estimated by subtracting nitrate and ammonium values from TDN values during 2006. DON concentrations for 2007 were estimated from TDN minus nitrate alone. Comparison of DON estimates with and without subtraction of ammonium using data from 2006 demonstrates that the error introduced by not accounting for ammonium in these rivers is small. For the Sagavanirktok, Kuparuk, and Colville, average differences between DON estimates with and without accounting for ammonium are 2%, 2%, and 6%, respectively, and maximum differences are 5%, 9%, and 12%, respectively. Dissolved organic carbon concentrations were measured on a Shimadzu TOC analyzer at the Marine Biological Laboratory in 2006 and at the University of Texas Marine Science Institute in 2007. Particulate organic nitrogen (PON) and carbon (POC) concentrations and stable isotope ratios were measured on a Finnigan MAT Delta Plus continuous flow mass spectrometer coupled to a Carlo Erba 1500 elemental analyzer at the University of Texas Marine Science Institute. POC samples were triple acidified with sulfurous acid (H_2SO_3, ACS 6% SO_2 minimum) to remove inorganic carbon prior to analysis. This procedure involves wetting the POC filters three times with sulfurous acid, with 20 min rest periods in a 60°C oven between acid applications. After the third acid application, the POC filters are dried for 24 h at 60°C. While this paper focuses on POC, PON, DOC, DON, SRP, ammonium, and nitrate, a variety of other data (including alkalinity, suspended sediment, major ion, and a limited amount of total dissolved phosphorus data) that were also collected as part of the 2 year field effort are publicly available from the Arctic System Science Data Archive at the National Center for Atmospheric Research Earth Observing Laboratory (http://www.eol.ucar.edu/projects/arcss/).

3.3. Constituent Export Estimation

Constituent fluxes were estimated using a binned approach that accounted for differences in concentration values during four distinct parts of the hydrologic year. More specifically, average concentrations ± one standard error for each river were calculated for (1) prepeak discharge in the spring, (2) peak discharge ± 2 days, (3) postpeak discharge through the end of June, and (4) the remainder of the hydrologic year. These values were then used in combination with daily discharge to calculate constituent fluxes. A binned approach was used in favor of a regression-based approach to estimate fluxes because date-specific
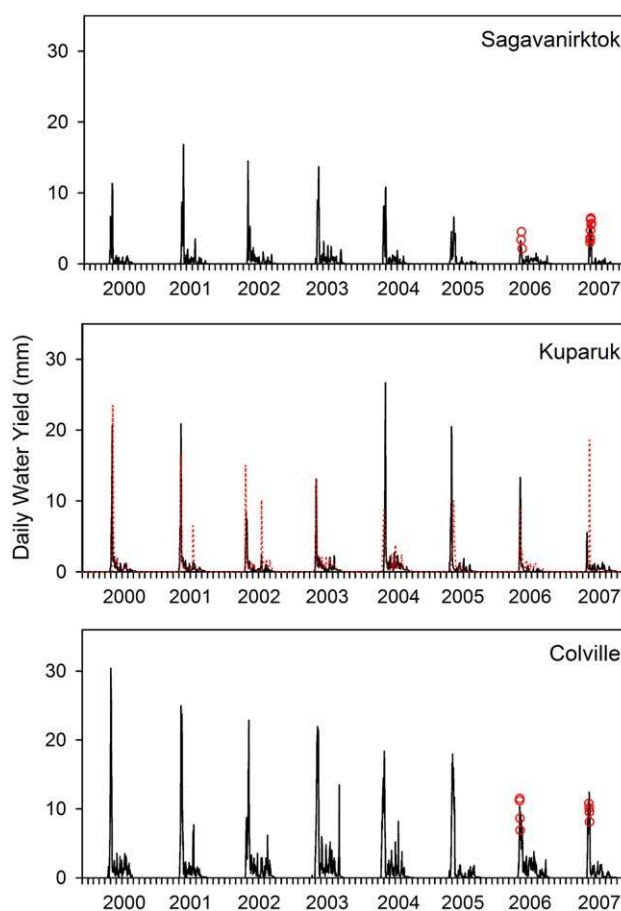
Figure 2. Daily water yield (mm) from the Sagavanirktok, Kuparuk, and Colville river watersheds over the 2000–2007 timeframe. Model results are shown in black. Measured values are shown in red (dashed line for Kuparuk and open circles for Sagavanirktok and Colville).

concentration measurements could not be confidently matched with daily model estimates of discharge for regression development. A previous application of the CLSM on the upper Kuparuk River showed that discharge was well represented over 1–2 week time intervals [*McClelland et al.*, 2007]. While a lack of year-round chemistry measurements makes it difficult to constrain estimates of concentration between late summer and early spring, low water discharge (including no flow for much of the winter) strongly limits the potential for significant constituent export during this period. On average, water discharge from September to April contributes 7%, 11%, and 9% of annual discharge from the Sagavanirktok, Kuparuk, and Colville, respectively. This does not include potential contributions from springs that are not accounted for in model estimates for the Sagavanirktok and Colville, but we expect that such contributions are small. Flux estimates were calculated not only for the 2 years that field work was con-ducted, but also for the broader 2000–2007 timeframe to acquire 8 year averages that more completely capture interannual variability in river discharge.

4. Results and Discussion

4.1. Model Performance

Comparison of daily simulated and measured water yield for the Kuparuk drainage basin over the 2000–2007 timeframe (Figure 2) shows that the CLSM captures the seasonal dynamic well, but can substantially overestimate or under-estimate the peak magnitude of individual events from year to year. Simulated discharge was $114 \pm 9\%$ (mean $\pm$ standard error) of measured discharge when compared over 1 week intervals and $96 \pm 8\%$ when compared annually (Figure 3). Annual constituent flux estimates calculated using simulated and measured discharge data were also similar (Figure 3).

Although far less data are available for the Sagavanirktok and Colville basins, the model results agree reasonably well with discharge measurements taken during peak runoff periods in 2006 and 2007 (Figure 2). In the Sagavanirktok basin, simulated discharge was 94% of measured discharge in 2006 and 72% of measured discharge in 2007 during the peak runoff period. In the Colville basin, simulated discharge was 88% of measured discharge in 2006 and 103% of measured discharge in 2007 during the peak runoff period.

4.2. Seasonal and Interannual Variability in River Discharge

Annual river discharge to the Alaskan Beaufort Sea is strongly dominated by runoff during the spring freshet, which typically occurs during late May and/or early June (Figure 2). On average, 58%, 52%, and 53%
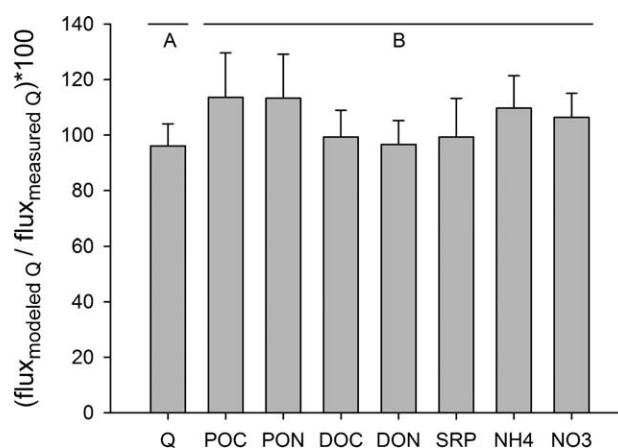
Figure 3. (a) Modeled water discharge expressed as a percentage of measured water discharge and (b) constituent flux estimates calculated using modeled discharge expressed as a percentage of constituent flux estimates calculated using measured discharge. All are mean annual values ± 1 standard error for the Kuparuk River over the 8 year analysis period. Q = water discharge.

of the annual water discharge occurred during 2 weeks of high spring flow each year in the Sagavanirktok, Kuparuk, and Colville rivers respectively over the 2000–2007 analysis period. While the seasonal distribution of river discharge in the three rivers is similar, there is also substantial variability with respect to hydrograph shape and total discharge among years (Figure 2). Annual water yield ranged from 7.0 to 19.5 cm in the Sagavanirktok, 7.9 to 20.2 cm in the Kuparuk, and 20.4 to 46.3 cm in the Colville over the 8 year period of analysis. Corresponding ranges in annual water discharge were 0.9–2.5, 0.6–1.6, and 12.2–27.7 km^3/yr for the three rivers, respectively. These variations correlate with annual precipitation that ranged from 19.7 to 38.2, 22.0 to 40.0, and 34.3 to 62.6 cm for the Sagavanirktok, Kuparuk, and Colville watersheds, respectively.

The discharge range reported here for the Kuparuk River spans ∼80% of the range measured by the USGS (0.6–2.1 km^3/yr) from 1972 through 2009. Previous estimates of annual water discharge to the Beaufort Sea from the other two rivers are scarce. However, our estimate of average annual water discharge from the Colville River (Table 1) is similar to an estimate of 16 km^3/yr reported by *Arnborg et al.* [1966] based on field measurements conducted during 1962. In contrast, our estimate of average water discharge from the Sagavanirktok River (1.6 km^3/yr; Table 1) is much lower than the ∼6.5 km^3/yr estimated by *Rember and Trefry* [2004] using scaled-up USGS data (1971–2001) from ∼20% of the total watershed area. This discrepancy is not surprising given that the USGS gauge is located far upstream, and captures a greater proportion of runoff from high mountain terrain (including orographic precipitation and glacier contributions) as compared with the overall river basin.

4.3. Nutrient and Organic Matter Dynamics

Seasonality of river chemistry has been documented at a variety of locations around the pan-arctic domain [*Holmes et al.*, 2012], including several studies at different scales within the Sagavanirktok, Kuparuk, and Colville river watersheds [e.g., *Townsend-Small et al.*, 2011; *Holmes et al.*, 2008; *Rember and Trefry*, 2004; *McNamara et al.*, 2008]. However, the combination of river discharge modeling and water chemistry results reported in this paper has enabled the most comprehensive estimates of nutrient and organic matter export from the North Slope of Alaska to the Beaufort Sea to date. Nutrient and organic matter concentrations as well as organic matter composition (inferred from C:N and stable isotope ratios) varied widely over time and among rivers during the 2 year study period, but variations were most pronounced during the spring freshet. This general pattern is evident when constituent values are plotted as a function of days from peak discharge (Figures 4–7). It is also evident in the binned averages and standard errors that were used to calculate fluxes (supporting information Table S1). Results of pair-wise comparisons (Tukey-Kramer HSD test) among binned averages are provided in supporting information Tables S2 and S3.

Dissolved inorganic nutrient (nitrate, ammonium, and SRP) concentrations reached maximum values during the spring at all three rivers, but each nutrient exhibited different behavior with respect to peak discharge (Figure 4). Nitrate concentrations decreased, while SRP concentrations increased in the days approaching peak discharge. Ammonium concentrations were less tightly linked to discharge, with relatively high values before and during peak flow. Nitrate values were also higher in late summer as compared to mid summer (particularly in the Sagavanirktok and Kuparuk), although more data are needed to confirm this pattern. In any case, nitrate strongly dominated the dissolved inorganic nitrogen pool in all three rivers. Overall, inorganic nutrient concentrations were not remarkably different among rivers.
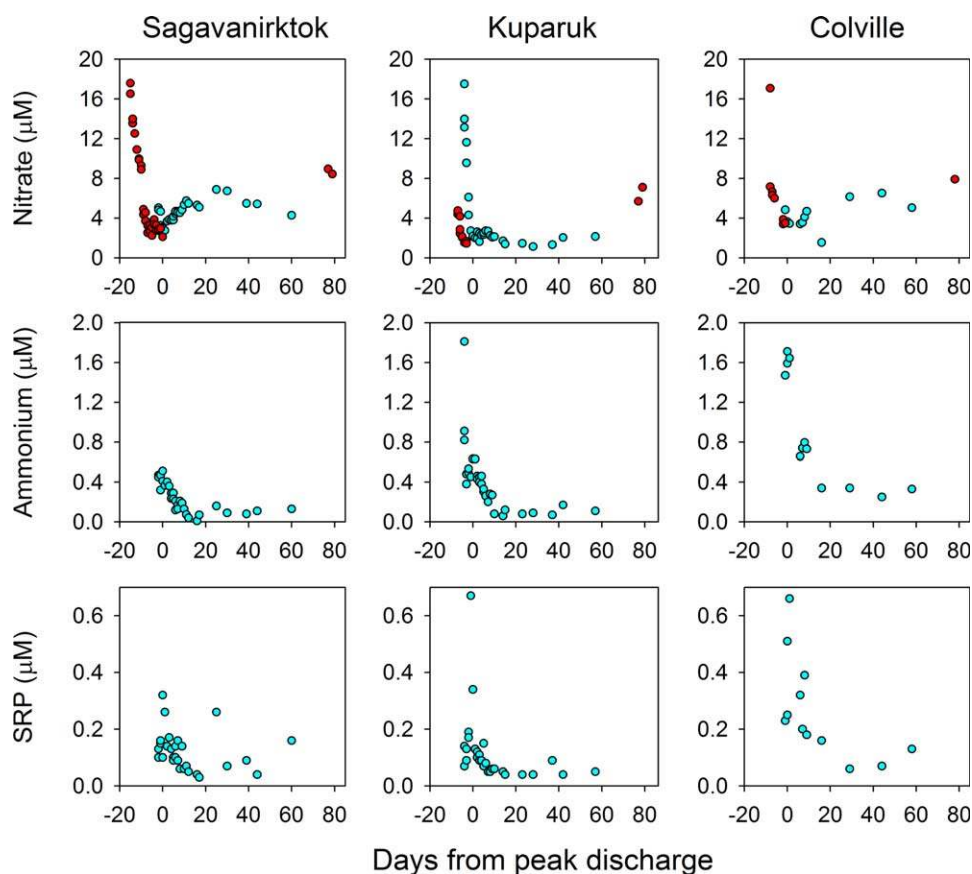
Figure 4. Temporal variations in nitrate, ammonium, and SRP concentrations in the Sagavanirktok, Kuparuk, and Colville rivers. Data from 2006 (blue) and 2007 (red) are plotted relative to the timing of peak discharge (day 0) for each year.

As observed for SRP, dissolved and particulate organic matter concentrations peaked during high river discharge in the spring at all three rivers (Figures 5 and 6). Dissolved organic nitrogen was also notably higher during late summer as compared to mid summer. The Kuparuk River was richest with respect to dissolved organic matter, exhibiting higher maximum concentrations in the spring as well as higher concentrations during mid summer (Figure 5). The Sagavanirktok had the lowest dissolved organic matter concentrations. While the Colville River was intermediate with respect to dissolved organic matter concentrations, it had much higher concentrations of particulate organic matter than the other two rivers (Figure 6). Indeed the relative importance of dissolved versus particulate carbon shifted from strong dominance of the dissolved pool in the Kuparuk to strong dominance of the particulate pool in the Colville. In the case of the Sagavanirktok, the dissolved and particulate carbon pools were relatively balanced.

Variations in organic matter concentrations were accompanied by changes in organic matter composition. More specifically, C to N ratios of dissolved and particulate organic matter increased during the spring freshet at all rivers (Figures 5 and 6). In contrast, the C:N of dissolved organic matter shifted to conspicuously low values during late summer while the C:N of particulate organic matter remained relatively constant. Changes in stable C and N isotope ratios (δ^{13}C and δ^{15}N) of particulate organic matter provided further evidence of compositional changes (Figure 7). With the exception of a few outliers, carbon isotope values peaked with maximum river discharge in the spring. Nitrogen isotope values also showed a general increase during the spring, but variations with respect to the timing of the spring freshet were more complex. In two of the rivers (Colville and Kuparuk), minimum values were recorded on the day of peak discharge. Nitrogen isotope values were also relatively low on the day of peak discharge in the Sagavanirktok. For ~1 week following peak discharge, nitrogen isotope values increased in all three rivers. Stable carbon and nitrogen isotope values remained relatively constant during the remainder of the sampling period, with the following exceptions: (1) Carbon isotope values in the Kuparuk River showed a general decrease
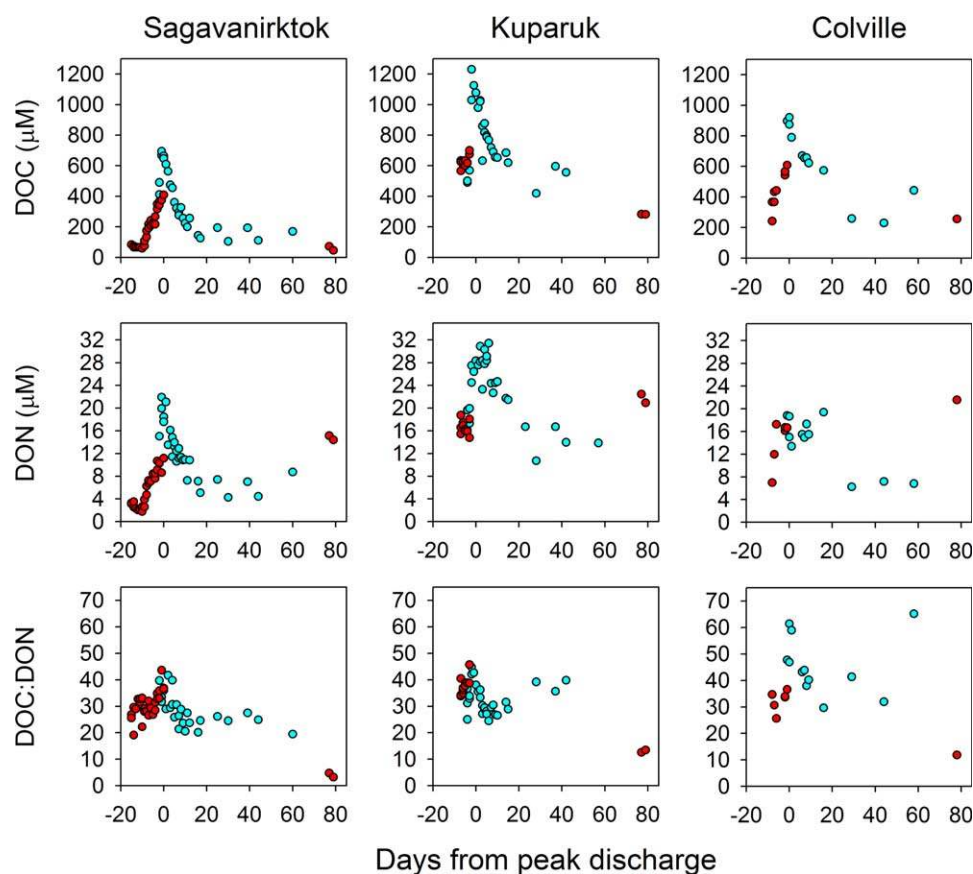
Figure 5. Temporal variations in DOC and DON concentrations and DOC:DON ratios in the Sagavanirktok, Kuparuk, and Colville rivers. Data from 2006 (blue) and 2007 (red) are plotted relative to the timing of peak discharge (day 0) for each year.

over the mid through late summer period. (2) Nitrogen isotope values in the Colville River were more variable during mid summer than in the other rivers. (3) Nitrogen isotope values in the Colville and Sagavanirktok were markedly lower during late summer as compared to mid summer. Although some unique seasonal patterns were evident among the three rivers, overall ranges in C:N and stable isotope ratios of dissolved and particulate organic matter were not remarkably different. While C:N and stable isotope ratios revealed seasonal changes in organic matter composition, dark bottle incubations conducted with water that was collected on a subset of dates during the 2006 field campaign demonstrated that microbial decomposition of DOC also varied widely among seasons in all three rivers [*Holmes et al.*, 2008]. In particular, DOC collected during the spring freshet was far more labile than DOC collected during mid summer [*Holmes et al.*, 2008]. The combination of relatively high C:N and lability of DOC during the spring freshet contradicts the general assumption that high C:N material is more recalcitrant. *Spencer et al.* [2008] suggest that labile dissolved organic matter exported from arctic rivers during the spring has a higher proportion of fresh vegetation leachates versus processed soil leachates in comparison to dissolved organic matter exported later in the summer.

In addition to the seasonal variability discussed above, there were also notable differences in inorganic nutrients and organic matter between the two study years. These differences are most evident where the data sets for 2006 and 2007 overlap in Figures 4–7. For example, nitrate in the Kuparuk River was much greater in the days leading up to peak discharge during 2006 than 2007 (Figure 4). Dissolved organic matter in the Sagavanirktok River provides another striking example, where concentrations at peak flow were much higher in 2006 than 2007 (Figure 5). These interannual variations in water chemistry track differences in discharge characteristics (peak magnitude and shape) between the 2 years (Figure 2). Specific mechanisms behind variability in water chemistry are discussed below.

When snow melts in the spring, frozen ground constrains runoff to the soil surface [*Woo*, 1986; *Kane et al.*, 1989; *MacLean et al.*, 1999; *Petrone et al.*, 2006]. This facilitates leaching of dissolved organic matter from
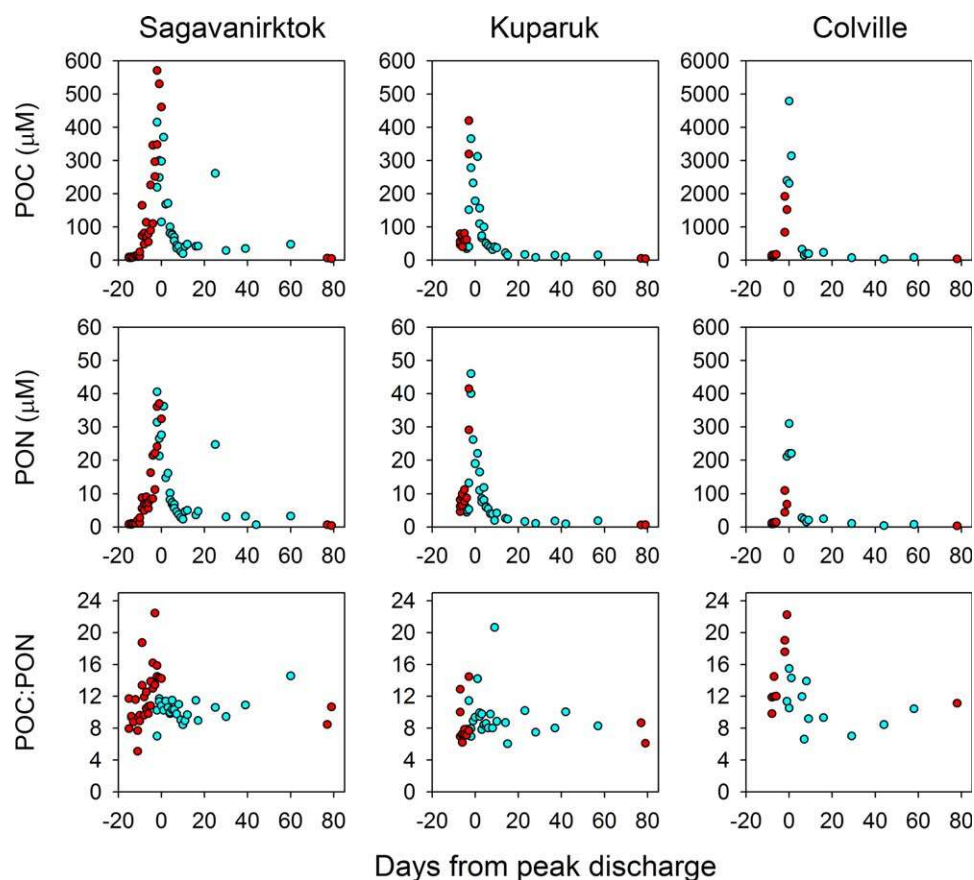
Figure 6. Temporal variations in POC and PON concentrations and POC:PON ratios in the Sagavanirktok, Kuparuk, and Colville rivers. Data from 2006 (blue) and 2007 (red) are plotted relative to the timing of peak discharge (day 0) for each year.

Figure 7. Temporal variations in $\delta^{13}C$ and $\delta^{15}N$ values particulate organic matter in the Sagavanirktok, Kuparuk, and Colville rivers. Data from 2006 (blue) and 2007 (red) are plotted relative to the timing of peak discharge (day 0) for each year.
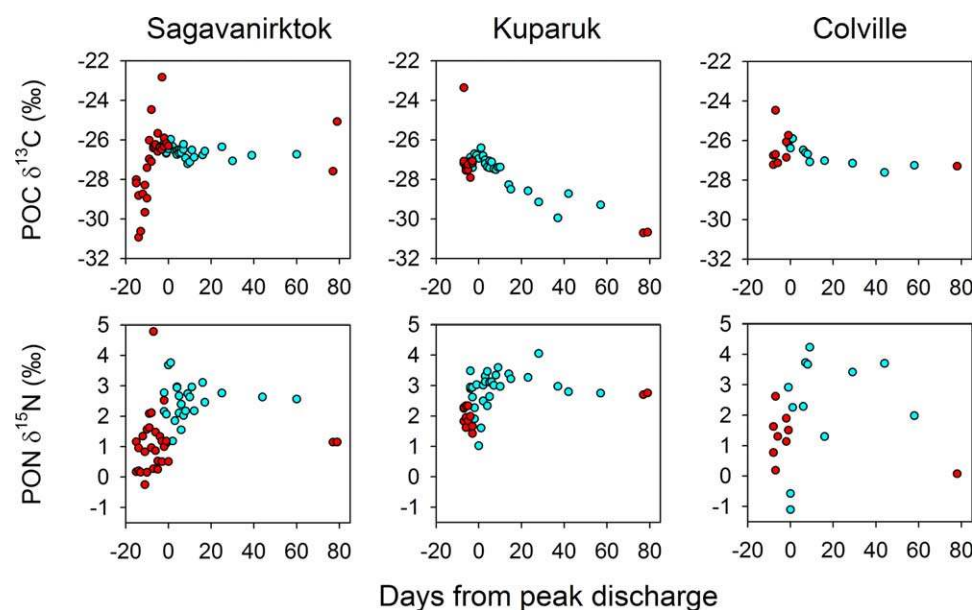
detritus as well as senescent above-ground plant biomass that is soaked while liquid water builds up near the snow-soil interface. Movement of snowmelt across the landscape is initially restricted by the snow itself, but flow rapidly increases once pathways are established and running water consolidates in major stream channels [*Kane et al.*, 1989, 1991]. The energy associated with increased flow supports increased particle transport. Thus, a large pulse of water that is rich in dissolved and particulate organic matter is exported during the spring freshet.

The explanation for relatively high inorganic nutrient concentrations in the spring is less clear, but may be linked to microbial activity in arctic soils during the winter [*Giblin et al.*, 1991; *Hobbie and Chapin*, 1996; *Schimel et al.*, 2004]. While factors such as snowpack and soil/vegetation type influence the amounts and temporal patterns of microbial activity, net mineralization leads to a buildup of inorganic nitrogen in soils over the winter [*Schimel et al.*, 2004]. It is likely that some of this nitrogen is flushed from surface soils in the spring. However, *Schimel et al.* [2004] points out that much of the mineralized nitrogen is immobilized by microbial and plant uptake during the spring thaw. Thus, interactions between flushing and uptake processes may account for different patterns of nitrate and ammonium concentrations in river water over the spring freshet. The snow itself is also a potential source of relatively high nitrate concentrations in the spring. *Jaffe and Zukowski* [1993] measured concentrations of ∼11 μM nitrate in snowpack averaged over a large area of the North Slope of Alaska. However, given that nitrate concentrations decrease strongly at peak flow, an immobilization mechanism during the spring thaw would still be required. In contrast, peak concentrations of SRP during peak discharge suggest tighter coupling with organic matter export and less immobilization of SRP than dissolved inorganic nitrogen in the spring.

Over the summer, increased biological activity and changes in water flow interact to control nutrient and organic matter concentrations in arctic rivers. Warmer temperatures support net immobilization of nitrogen in arctic soils as microbial and plant demands increase [*Giblin et al.*, 1991; *Nadelhoffer et al.*, 1991; *Schimel et al.*, 2004]. At the same time, thawing of the active layer facilitates movement of water through deeper soil layers [*Woo*, 1986; *Kane et al.*, 1989]. Where deeper flow paths equate with longer soil water residence times, greater nutrient, and organic matter cycling is possible. However, there is less potential for leaching of dissolved organic matter and greater potential for trapping of dissolved organic matter as a consequence of adsorption when flow paths drop below organic-rich surface layers into mineral soils [*MacLean et al.*, 1999; *Petrone et al.*, 2006]. Processing of nutrients and organic matter within the rivers also becomes important in the summer as flow decreases and water travel times through river networks increase [*Peterson et al.*, 1997; *Wollheim et al.*, 2001]. The net effect of these temperature and flow-mediated processes is that nutrient and organic matter concentrations in the Sagavanirktok, Kuparuk, and Colville rivers remain low throughout much of the summer.

Although conditions later in the year were not well covered by this study, the observed increases in nitrate at the end of August suggest that seasonal nitrogen demand was at least beginning to subside. Furthermore, the marked drop in C:N of dissolved organic matter in all three rivers at the end of August suggests that autochthonous production, for example, by benthic microalgae with molar C:N ratios of ∼7 under optimal growth conditions [*Hillebrand and Sommer*, 1999], was a dominant source of dissolved organic matter at that time (i.e., proportionally more important than typical allochthonous inputs of dissolved organic matter with C:N ratios >20). Corresponding low stable carbon isotope values of particulate organic matter in the Kuparuk River are consistent with this conclusion: δ^{13}C values of terrestrial organic matter typically range between −26 and −29, whereas δ^{13}C values below 30 are indicative of contributions by epilithic algae in lotic systems [*Finlay*, 2001]. One might expect an increase in the relative importance of autochthonous production to be accompanied by a drawdown of nitrate. However, given the low amounts of dissolved and particulate organic matter in the rivers during late August, it is likely that overall nitrogen demand was small. The absence of low stable carbon isotope values of particulate organic matter at the end of August in the Sagavanirktok and Colville rivers may reflect higher background concentrations of terrestrial POC that would obscure the autochthonous signal.

Differences in dissolved and particulate organic matter concentrations among the three rivers are linked to drainage basin characteristics. More specifically, differences in dissolved organic matter concentrations (Kuparuk > Colville > Sagavanirktok) are consistent with differences in relative runoff contributions from lower (organic-rich) versus higher (organic-poor) elevation terrain among the three drainage basins (Figure 1 and Table 1). In contrast, differences in particulate organic matter concentrations (Colville ≫ Kuparuk ≈ Sagavanirktok) are best explained by greater water yield in the Colville as compared to the other two basins

Table 2. Constituent Flux (Metric Tons/yr) and Yield (mg/m²/yr) Estimates for the Sagavanirktok, Kuparuk, and Colville Rivers During the 2 Years That Sampling Was Conducted[a]

	Sagavanirktok		Kuparuk		Colville	
	2006	2007	2006	2007	2006	2007
POC						
tons/yr	1108 ± 219	1452 ± 254	1178 ± 205	1420 ± 246	90,099 ± 16,650	102,477 ± 18,244
mg/m²/yr	88 ± 17	115 ± 22	145 ± 25	175 ± 30	1508 ± 279	1715 ± 305
PON						
tons/yr	110 ± 17	139 ± 20	146 ± 30	175 ± 37	8081 ± 1753	8745 ± 1948
mg/m²/yr	8.7 ± 1.3	11 ± 2	18 ± 4	22 ± 5	135 ± 29	146 ± 33
DOC						
tons/yr	2764 ± 394	2560 ± 332	9775 ± 724	7208 ± 246	101,401 ± 10,090	73,891 ± 7478
mg/m²/yr	220 ± 31	204 ± 26	1206 ± 89	889 ± 30	1697 ± 169	1237 ± 125
DON						
tons/yr	153 ± 25	104 ± 16	362 ± 21	228 ± 7	3329 ± 650	2158 ± 404
mg/m²/yr	12 ± 2	8 ± 1	45 ± 3	28 ± 1	56 ± 11	36 ± 7
SRP						
tons/yr	3.5 ± 0.9	3.2 ± 0.9	4.5 ± 1.3	4.5 ± 1.5	100 ± 27	78 ± 22
mg/m²/yr	0.3 ± 0.1	0.3 ± 0.1	0.6 ± 0.2	0.6 ± 0.2	1.7 ± 0.5	1.3 ± 0.4
Ammonium-N						
tons/yr	2.5 ± 0.3	2.3 ± 0.2	4.6 ± 0.7	4.5 ± 0.7	141 ± 14	116 ± 9
mg/m²/yr	0.2 ± 0.0	0.2 ± 0.0	0.6 ± 0.1	0.6 ± 0.1	2.4 ± 0.2	1.9 ± 0.2
Nitrate-N						
tons/yr	83 ± 10	75 ± 12	49 ± 11	28 ± 6	1313 ± 166	1001 ± 160
mg/m²/yr	6.6 ± 0.8	5.9 ± 0.9	6.0 ± 1.4	3.4 ± 0.8	22 ± 2.8	17 ± 2.3

[a]The error estimates shown here reflect variability in constituent concentrations. Flux and yield values were calculated using mean concentrations ± 1 standard error for four distinctive parts of the annual hydrograph. Computational details are provided in section 2.

(Table 1). Differences in topographic features (i.e., slope and elevation), which are often correlated with overall particle loads in rivers [*Milliman and Syvitski*, 1992], were not clearly linked to differences in particulate organic matter concentrations among the three rivers.

Averages of chemistry data collected during (1) prepeak discharge in the spring, (2) peak discharge ±2 days, (3) postpeak discharge through the end of June, and (4) the remainder of the year (supporting information Table S1) mask some important temporal variations within hydrologic periods, but the binned data do capture major differences in chemistry among hydrologic periods (supporting information Table S2) and among rivers (supporting information Table S3). In particular, averages during the peak discharge period are significantly different than averages during one or more of the other periods in 76% of comparisons, and significantly different than all other periods in 30% of comparisons. When comparing binned chemistry data among rivers, differences are most pronounced between the Colville and Kuparuk (50% of comparisons are significantly different), and least pronounced between the Sagavanirktok and Kuparuk (31% of comparisons are significantly different).

4.4. Annual Export of Nutrients and Organic Matter

Constituent export estimates for the 2 year field study period (2006 and 2007) are shown in Table 2, and 8 year averages calculated for the 2000–2007 timeframe are shown in Table 3. Constituent export estimates for individual years between 2000 and 2005 are provided in supporting information Tables S4–S6. Export estimates for 2006 and 2007 are lower than the 8 year averages for all three rivers. Given the interannual variability in constituent export exhibited by these rivers, it would be difficult to generalize using estimates from individual years. However the 8 year averages presented in Table 3 provide a broad basis for generalized discussion of constituent export from the North Slope of Alaska to the Beaufort Sea.

Together the Sagavanirktok, Kuparuk, and Colville rivers export an average of ~297,000 metric tons of organic carbon and ~18,000 metric tons of organic nitrogen to the Alaskan Beaufort Sea each year (Table 3). A strong majority of this export (>90%) comes from the Colville River, but the disparity among rivers is greater for particulate organic matter than dissolved organic matter. For example, the Colville accounts for 97% of POC export but only 88% of DOC export from the three rivers. While much of the difference in organic matter export among rivers is a reflection of the Colville's larger drainage basin, particulate organic matter yields are also an order of magnitude higher in the Colville as compared to the other two rivers (Table 3). Dissolved organic matter yields are also higher in the Colville, but the differences among rivers are not as pronounced.

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Table 3. Mean Annual Constituent Flux (Metric Tons/yr) and Yield (mg/m^2/yr) Estimates ±1 Standard Error for the Sagavanirktok, Kuparuk, and Colville Rivers Over the 2000–2007 Timeframe[a]

	Sagavanirktok	Kuparuk	Colville
POC			
tons/yr	2657 ± 367	1505 ± 114	157,448 ± 16,510
mg/m^2/yr	211 ± 29	186 ± 14	2635 ± 276
PON			
tons/yr	260 ± 36	187 ± 14	13,512 ± 1367
mg/m^2/yr	21 ± 3	23 ± 2	226 ± 65
DOC			
tons/yr	5010 ± 614	10,882 ± 748	119,629 ± 25,334
mg/m^2/yr	398 ± 49	1342 ± 92	2002 ± 150
DON			
tons/yr	216 ± 26	391 ± 30	3611 ± 285
mg/m^2/yr	17 ± 6	48 ± 4	60 ± 5
SRP			
tons/yr	5.8 ± 0.7	5.5 ± 0.4	126 ± 10
mg/m^2/yr	0.5 ± 0.1	0.7 ± 0.0	2.1 ± 0.2
Ammonium-N			
tons/yr	4.5 ± 0.6	5.9 ± 0.5	186 ± 16
mg/m^2/yr	0.4 ± 0.1	0.7 ± 0.1	3.1 ± 0.3
Nitrate-N			
tons/yr	123 ± 15	57 ± 6	1568 ± 138
mg/m^2/yr	9.8 ± 1.2	7.0 ± 0.7	26 ± 2

[a]Here the standard error values reflect interannual variability in river discharge. Values for individual years contributing to the 8 year mean are provided in Table 2 (2006–2007) and supporting information Table S4–S6 (2000–2005).

Average annual fluxes of nitrate-N, ammonium-N, and SRP from the three rivers combined are approximately 1750, 200, and 140 metric tons per year, respectively (Table 3). As discussed for organic matter, contributions from the Colville River dominate due to the combined effects of a much larger drainage area and higher constituent yields. Dissolved inorganic nitrogen (nitrate + ammonium) accounts for ~33% of total nitrogen export (organic + inorganic) from the Colville River, whereas inorganic nitrogen fluxes account for approximately 37% and 14% of the total nitrogen exported from the Sagavanirktok and Kuparuk, respectively.

In comparison with the six largest rivers draining the pan-arctic watershed (Yenisey > Lena > Ob' > Mackenzie > Yukon > Kolyma by discharge), total fluxes of dissolved nutrients and organic matter from rivers on the North Slope of Alaska are small. When normalized by watershed area, however, values for the North Slope rivers (Table 3) are similar to those reported for the major arctic rivers [*Holmes et al.*, 2012]. For example, annual DOC yields range from 820 to 2338 mg/m^2/yr and annual nitrate yields range from 10 to 29 mg/m^2/yr among the major arctic rivers, with no clear distinction between those flowing from North America and those flowing from Eurasia [*Holmes et al.*, 2012].

Contrary to the dissolved constituents discussed above, particulate organic matter yields differ substantially between the major North American and Eurasian arctic rivers. For example, POC yields are ~900 and 1175 mg/m^2/yr for the Yukon and Mackenzie respectively [*Striegl et al.*, 2007; *Rachold et al.*, 2004], whereas POC yields range from ~66 to 490 mg/m^2/yr among the Yenisey, Ob', Lena, and Kolyma [*Rachold et al.*, 2004]. In this context, the Sagavanirktok and Kuparuk cluster with the Eurasian rivers while the Colville is more similar to the Yukon and Mackenzie. Indeed the Colville POC yield is ~40 times higher than that of the Yenisey River. As a result, the average annual flux of POC from the Colville River (Table 3) is very similar to the average annual flux of POC from the Yenisey (~170,000 metric tons/yr) [*Rachold et al.*, 2004] despite the Yenisey's vastly larger size.

4.5. Significance of River Export to Productivity in the Coastal Ocean

Overall, export of inorganic nitrogen from the Sagavanirktok, Kuparuk, and Colville rivers has the potential to support ~12.9 kilotons (10^9 g) of new organic carbon production in the coastal ocean each year [assuming a molar C:N ratio of 6.625, *Redfield et al.*, 1963]. This value is small relative to an estimated 200 kilotons of carbon fixed by primary producers annually within ~10 km of shore along the Alaskan Beaufort Sea coast [*Schell et al.*, 1984]. River-supplied organic matter contributions, on the other hand, could support ~120 kilotons of new production if all of the organic nitrogen were remineralized. Thus, the importance of terrestrial inputs with respect to productivity in coastal waters of the Alaskan Beaufort Sea depends strongly on the fate of river-supplied organic matter. While we know that dissolved organic matter exported from the Sagavanirktok, Kuparuk, and Colville rivers during the spring freshet is more labile than dissolved organic matter exported later in the summer [*Holmes et al.*, 2008], we do not know how much terrigenous organic matter is respired during its residence time in arctic coastal waters or how much nitrogen is conserved within the microbial community.

Based on a range of C:N ratios and bacterial growth efficiencies, *Tank et al.* [2012] concluded that bacteria in the Arctic Ocean must retain nitrogen during decomposition of river-supplied DON under most circumstances, but processing of bacterial biomass within the microbial food web ultimately results in a net release of ammonium that amounts to ~20–40% of the riverine DON input. An additional 5% of the river-supplied DON is estimated to be remineralized as a result of photoammonification [*Tank et al.*, 2012]. While these estimates are for the Arctic Ocean as a whole, gradients from the land margin to offshore locations are also

an important consideration. Transformation rates are expected to be highest in nearshore waters, yet very little work on nutrient and organic matter cycling has focused on this environment in the Arctic, particularly with respect to the seasonal dynamics of river inputs [*McClelland et al.*, 2012].

The fate of river-supplied dissolved organic matter in the Arctic Ocean has been given more attention than that of particulate organic matter in recent years. This difference in treatment is, in part, because total organic matter export is dominated by the dissolved pool in many arctic rivers. However, because C:N ratios of particulate organic matter are much lower than C:N ratios of dissolved organic matter [*Lobbes et al.*, 2000; *Guo and Macdonald*, 2006], the proportions of export accounted for by the dissolved versus particulate pools differ markedly for carbon and nitrogen. This is clearly exemplified in the North Slope rivers, where C:N ratios of particulate organic matter average ∼10 and C:N ratios of dissolved organic matter average ∼30 (compare Figures 5 and 6). In the Sagavanirktok, differences in C:N of dissolved and particulate organic matter result in DOC export that is roughly twice as large as POC export while DON and PON export are approximately equal. Similarly, DOC export in the Kuparuk is ∼7.2 times higher than POC export, but DON export is only ∼2.1 times higher than PON export. Thus, river-supplied particulate organic matter may serve as an important nitrogen source in arctic coastal waters, even though total organic matter export is often dominated by the dissolved fraction.

The Colville River is unusual in having much greater particulate than dissolved organic matter export. Nonetheless, large differences in the C:N ratios of particulate and dissolved organic matter again result in large differences in the relative amount of export accounted for by the two pools depending on whether carbon or nitrogen is considered. DOC export is ∼3/4 of POC export, while DON export is ∼1/4 of PON export. In this case, although total organic matter export is dominated by the particulate fraction to begin with, explicit consideration of nitrogen reveals an even greater imbalance between dissolved and particulate export.

Another reason that dissolved organic matter has been given more attention than particulate organic matter in recent years is that dissolved organic matter is, on aggregate, much younger than the particulate organic matter exported by arctic rivers, and the older material is assumed to be less labile than the younger material [*Guo and Macdonald*, 2006; *Raymond et al.*, 2007]. Nonetheless, some fraction of the particulate organic matter pool is likely to be important with respect to inorganic nitrogen release. If 10% of the Colville River PON flux is remineralized, then ∼1351 metric tons of inorganic nitrogen becomes available to support primary production each year. This is comparable to the 722–1444 metric tons per year of remineralized nitrogen expected from Colville River DON (assuming 20–40% lability as reported in *Holmes et al.* [2008]). Differences in residence times of particulate versus dissolved organic matter in the coastal environment may also be an important consideration. While river-supplied DON is transported/mixed away over a relatively short time period, sedimentation leaves behind a more localized pool of particulate organic matter that may contribute N (through mineralization) over a much longer time period.

While the discussion above has emphasized the potential importance of river-supplied organic matter as a nitrogen source supporting primary production in arctic coastal waters, river inputs may also provide an import carbon source for heterotrophic production. An early study by *Schell* [1983] using ^{14}C as a tracer of ancient carbon from soils along the Alaskan Beaufort Sea coast suggested that terrestrial organic matter was not a significant resource to metazoan consumers in the estuarine/marine environment. However, that study did not consider the potential importance of modern carbon from DOC inputs, nor the potential for carbon contributions from a younger fraction of terrestrial POC [*Guo and Macdonald*, 2006]. More recently, *Dunton et al.* [2006] used stable isotope data to argue that arctic cod living in lagoons along the Alaskan Beaufort Sea coast may derive as much as 70% of their carbon from terrestrial sources. Additional evidence is clearly needed before broad generalizations about the role of terrestrial carbon in arctic coastal food webs can be made. Nonetheless, this new evidence suggesting that terrestrial inputs could be the dominant source of carbon to an upper trophic level organism such as the arctic cod is intriguing. We assume that bacteria are the primary processors of terrestrial organic matter in arctic coastal waters. Is there substantial carbon transfer between the microbial and metazoan food webs? Alternatively, are there metazoan consumers in arctic coastal waters that assimilate significant amounts of terrestrial organic matter directly and provide a shorter path to higher trophic levels?

As we work to develop a fundamental understanding of land-sea coupling in northern Alaska, we recognize that changes in vegetation, microbial activity, and surface/subsurface hydrology as a consequence of changes in temperature and precipitation patterns on the North Slope are likely to alter constituent export to the Beaufort Sea. Indeed long-term data from the upper Kuparuk River suggest that constituent export

may already be changing [*McClelland et al.*, 2007]. *McClelland et al.* [2007] examined patterns in nitrate and DOC export from the late 1970s to the early 2000s. Nitrate export increased by ∼5 fold beginning in the 1990s. At the same time, DOC export decreased by about one half. The change in nitrate export was primarily attributed to an increase in discharge-normalized nitrate concentrations, while the change in DOC export was primarily attributed to a decrease in river discharge during the 1990s. It is impossible to say whether similar changes in constituent export are happening at a larger scale across the North Slope. However, if broadly manifest, such changes would significantly alter the relative importance of river-supplied organic matter and inorganic nitrogen as resources supporting productivity in coastal waters of the Alaskan Beaufort Sea. The timing of constituent export is also likely to change. For example, there are many reports of earlier spring thaw in the Arctic [*White et al.*, 2007]. In the case of snowmelt, this translates into an earlier spring freshet. The consequences of an earlier spring freshet for the coastal ocean ecosystem are currently unclear, but changes in the relative timing of peak discharge and sea-ice breakup may lead to a change in the distribution of productivity between nearshore and offshore waters [*McClelland et al.*, 2012].

5. Summary

Robust estimates of watershed export are essential for evaluating the importance of land-derived nutrients and organic matter as a resource to coastal ocean ecosystems in the Arctic. In this study, we have used a combination of river discharge modeling and water chemistry measurements to provide comprehensive estimates of water, nutrient, and organic matter export from the three largest rivers draining the North Slope of Alaska. While the USGS maintains a discharge gauge near the mouth of the Kuparuk River, modeling was necessary to estimate discharge from the Sagavanirktok and Colville rivers. Water sampling during the spring and summer captured wide variations in nutrient and organic matter concentrations as well as the composition of the organic matter being exported. Given that a large proportion of annual water discharge from the Sagavanirktok, Kuparuk, and Colville rivers occurs during a brief period in late May and/or early June, information collected during the spring freshet was particularly helpful for constraining estimates of nutrient and organic matter export. Most notably, concentrations of organic matter and SRP peaked during the spring freshet whereas concentrations of nitrate were highest preceding the spring freshet and dropped sharply as discharge increased. Overall, nutrient and organic matter fluxes from the North Slope of Alaska are dominated by the Colville River. This is in part due to the larger size of the Colville River, but also because constituent yields are greater in the Colville watershed as compared to the other two watersheds. In addition, the Colville River is unique in having higher particulate than dissolved organic matter export. Nitrogen from the rivers may be an important resource supporting primary production in coastal waters. However, organic nitrogen export is much greater than inorganic nitrogen export, and knowledge of remineralization pathways and rates in arctic coastal waters remains very limited. Knowledge of the role that terrestrial carbon plays in arctic coastal food webs is also limited. While we are focused on fundamental aspects of land-sea coupling in the Arctic, climate change adds urgency to the work. Changes in hydrology and biogeochemical cycling under warmer conditions are expected to alter (and to some extent already are altering) watershed export, and our ability to anticipate how the coastal ocean ecosystem will respond depends strongly on how well we define the system under current conditions.

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