Estuaries and Coasts
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Seasonal and Annual Fluxes of Nutrients and Organic Matter from Large Rivers to the Arctic Ocean and Surrounding Seas

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Abstract River inputs of nutrients and organic matter impact the biogeochemistry of arctic estuaries and the Arctic Ocean as a whole, yet there is considerable uncertainty about the magnitude of fluvial fluxes at the pan-Arctic scale. Samples from the six largest arctic rivers, with a combined watershed area of 11.3×10^6 km^2, have revealed strong seasonal variations in constituent concentrations and fluxes within rivers as well as large differences among the rivers. Specifically, we investigate fluxes of dissolved organic carbon, dissolved organic nitrogen, total dissolved phosphorus, dissolved inorganic nitrogen, nitrate, and silica. This is the first time that seasonal and annual constituent fluxes have been determined using consistent sampling and analytical methods at the pan-Arctic scale and consequently provide the best available estimates for constituent flux from land to the Arctic Ocean and surrounding seas. Given the large inputs of river water to the relatively small Arctic Ocean and the dramatic impacts that climate change is having in the Arctic, it is particularly urgent that we establish the contemporary river fluxes so that we will be able to detect future changes and evaluate the impact of the changes on the biogeochemistry of the receiving coastal and ocean systems.

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Introduction

Massive inputs of river water make terrestrial influences particularly strong in the Arctic Ocean. Containing only ~1% of global ocean volume, the Arctic Ocean receives more than 10% of global river discharge. The three largest arctic rivers, the Yenisey, Lena, and Ob', are each comparable in watershed area and annual discharge to the Mississippi River, North America's largest river. The large river inputs to the Arctic Ocean strongly influence its salinity structure and impart estuarine characteristics throughout the basin (Aagaard and Carmack 1989; Serreze et al. 2003, 2006; McClelland et al. 2011).

Much of the current research in the Arctic investigates ongoing changes related to warming. Though most regions of Earth have warmed over recent decades, the observed warming in the Arctic is much greater than the global average, and consequently, observed changes are also more extreme (ACIA 2004; IPCC 2007). Changes in the hydrologic cycle have been the focus of much of the research (Serreze et al. 2003; White et al. 2007; Rawlins et al. 2010). The disproportionate influence of rivers on the Arctic Ocean means that changes in the discharge or chemistry of arctic rivers have potentially large implications for ocean physics, chemistry, and biology. Moreover, because river discharge and chemistry integrate processes occurring throughout their watersheds, they may be particularly sensitive indicators of terrestrial change (Holmes et al. 2000a; Bring and Destouni 2009). For example, Walvoord and Striegl (2007) quantify increases in groundwater contribution to river flows in the Yukon River basin in response to permafrost thaw and consider its effect on lateral export of inorganic and organic carbon and nitrogen to the Bering Sea. Similarly, Frey and McClelland (2009) consider how water chemistry is expected to change as permafrost thaws and speculate that increases in major ion concentrations associated with greater weathering of mineral soils as water flow paths deepen may be a particularly robust indicator.

Observational records extending back to the 1930s demonstrate that river discharge to the Arctic Ocean from the major rivers in Russia has increased almost 10% since the records began (Peterson et al. 2002). Patterns are less clear for rivers in the North American Arctic, in part due to much shorter discharge records. However, a recent analysis of rivers in northern Canada did detect a large increase over the 1989–2007 period (Déry et al. 2009), reversing the apparently declining discharge observed from 1964 to 2003 (Déry and Wood 2005). At the pan-Arctic scale, total river discharge to the Arctic Ocean and surrounding seas is estimated to have increased about 5.6 km^3/year/year during the 1964–2000 timeframe, with the rate of increase accelerating recently (McClelland et al. 2006). These river discharge increases are part of a suite of changes in the freshwater cycle of the Arctic that are impacting salinity in both the Arctic and North Atlantic oceans, with potential implications for ocean circulation and climate (Peterson et al. 2006). Changes in the seasonality of discharge have also been observed, which may impact coastal biogeochemistry and physics (McClelland et al. 2004; Adam et al. 2007).

In contrast to the rapidly evolving understanding of arctic river discharge, considerably less work has investigated the chemistry of arctic rivers. Although detailed studies have been undertaken on specific aspects of individual rivers including the Yukon (Striegl et al. 2005; Dornblaser and Striegl 2007; Spencer et al. 2008, 2009), Kolyma (Welp et al. 2005; Finlay et al. 2006; Neff et al. 2006), and Mackenzie (Emmerton et al. 2008a), relatively few studies have examined river fluxes to the Arctic Ocean at the continental or pan-Arctic scale (Gordeev et al. 1996; Holmes et al. 2000a, 2002; Lobbes et al. 2000; Dittmar and Kattner 2003). Those that have attempted large-scale syntheses have been hampered by a number of factors including inconsistent sampling and analytical methods across sites, lack of sufficient seasonal coverage, and data quality issues (Bring and Destouni 2009). For example, an analysis of historical nutrient data sets for 16 rivers across the Russian Arctic concluded that unusual patterns in the data (such as very high estimates of ammonium concentrations) were of sufficient concern that independent verification would be required (Holmes et al. 2000a). When these independent analyses were done as part of an expedition to the Ob' and Yenisey rivers during summer 2000, it became clear that at least some of the historical data for river chemistry in the Russian Arctic were grossly in error (Holmes et al. 2001). While much of the historical data for Russian arctic rivers may in fact be good, systematic quality control concerns have made it extremely difficult to separate the good from the bad (Zhulidov et al. 2000, 2001).

As a response to these challenges and to facilitate understanding of fluvial constituent fluxes to the Arctic Ocean at the pan-Arctic scale, we began the Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments (PARTNERS) project in 2002, an effort to obtain a coherent data set using identical sampling and analytical methods for the six largest arctic rivers in Russia, Canada, and Alaska (Fig. 1; McClelland et al. 2008). A related effort, the Student Partners Project, began in 2005. Recent papers have used data generated from these projects to investigate dissolved organic carbon (DOC), barium,

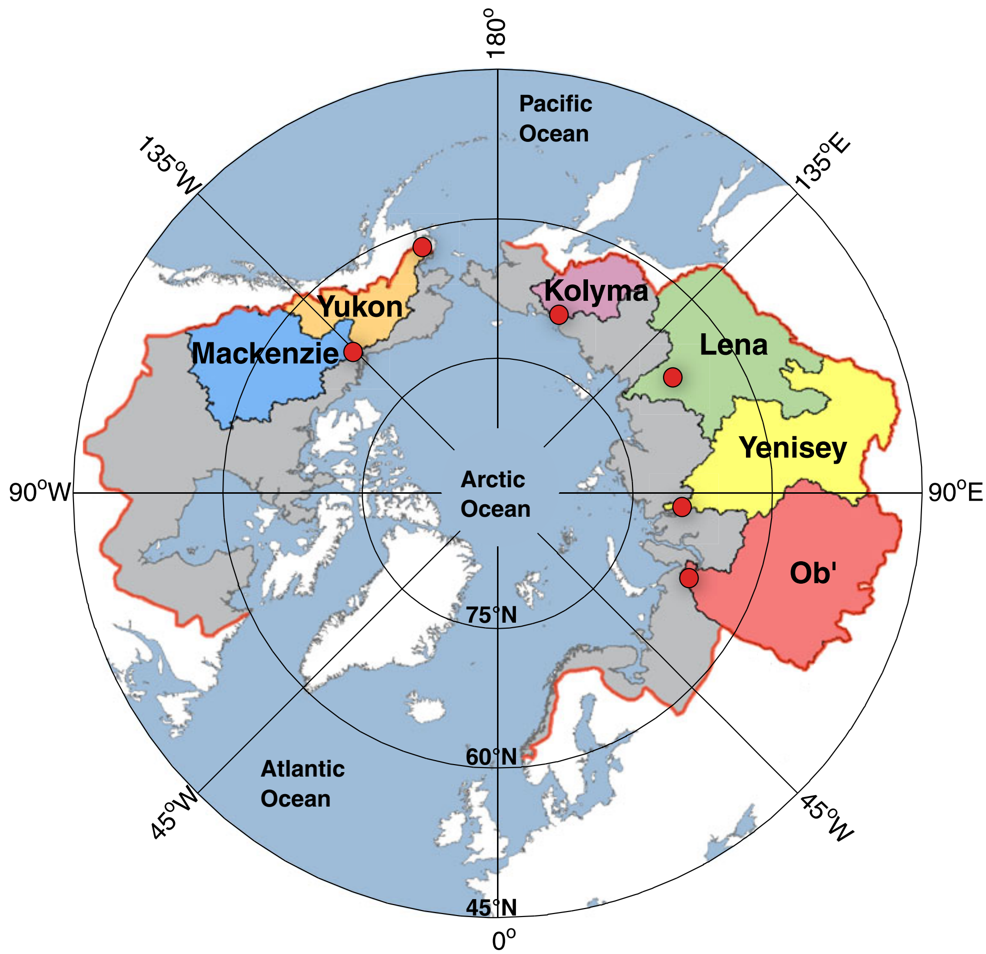

Fig. 1 Map showing the watersheds of the six rivers included in this study. *Red dots* show sampling locations (Ob' at Salekhard, Yenisey at Dudinka, Lena at Zhigansk, Kolyma at Cherskiy, Yukon at Pilot Station, Mackenzie at Tsiigehtchic or Inuvik), generally located close to the mouths of the rivers to facilitate estimation of constituent fluxes to the ocean. The *bold red line* shows the boundary of the 20.5×10^6-km^2 pan-Arctic watershed. Together the six rivers cover 53% of the pan-Arctic watershed

alkalinity, and $H_2{}^{18}O$ concentrations and fluxes over the 2–4-year period of data collection (Cooper et al. 2005, 2008; Raymond et al. 2007). Here we focus on seasonal and annual fluxes of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), nitrate (NO_3), total dissolved phosphorus (TDP), silica (Si), and DOC and extend the flux estimates to cover a 10-year period (1999–2008) using a statistical modeling approach. For constituents other than DOC, the estimates provided here represent the first time that seasonal and annual fluxes have been determined using consistent sampling and analytical methods at the pan-Arctic scale and as such provide the best available estimates for constituent flux from land to the Arctic Ocean and surrounding seas.

Methods

Field Sampling

In order to facilitate calculation of fluxes to the ocean, PARTNERS sampling sites were located as close to the mouths of the rivers as feasible (Table 1). The sites were Salekhard (Ob'), Dudinka (Yenisey), Zhigansk (Lena), Cherskiy (Kolyma), Pilot Station (Yukon), and Tsiigehtchic (Mackenzie). The sampling sites were the same for the Student Partners Project, except that some of the Mackenzie samples were collected further downstream, near Inuvik in the Mackenzie Delta. Calculation of constituent fluxes requires chemical concentration data as well as river discharge. Salekhard, Pilot Station, and Tsiigehtchic are also the downstream-most discharge monitoring stations on the Ob', Yukon, and Mackenzie rivers, respectively, which facilitated flux calculations (Table 1). For the Yenisey, Lena, and Kolyma rivers, we obtained discharge data from the closest monitoring stations (Igarka, Kyusyur, and Kolymskoye, respectively). As described in the modeling section, adjustments were made to account for the transit time of water between the discharge and chemistry stations when they differed.

Sampling for the PARTNERS Project began in 2003 and continued through 2006, with each of the six rivers being sampled a total of 17 times (Fig. 2). This effort was explicitly designed to capture low flow in late winter (through the ice), high flow in the spring, and intermediate flow during mid to

Table 1 Discharge gauging stations, PARTNERS sampling locations, and watershed characteristics

River/watershed	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie	Sum
Discharge gauging station	Salekhard	Igarka	Kyusyur	Kolymskoye	Pilot Station	Tsiigehtchic	–
Water quality station	Salekhard	Dudinka	Zhigansk	Cherskiy	Pilot Station	Tsiigehtchic	–
Watershed area (10^6 km^2)—at gauging station	2.99	2.40	2.43	0.53	0.83	1.68	10.9
Watershed area (10^6 km^2)—total	2.99	2.54	2.46	0.65	0.83	1.78	11.3
Discharge (km^3 year^{-1})—at gauging station	427	636	581	111	208	298	2,261
Discharge (km^3 year^{-1})—total	427	673	588	136	208	316	2,348
Runoff (mm year^{-1})	143	259	240	166	248	177	–
% Continuous permafrost	1	31	77	99	19	13	–
% Continuous + discontinuous permafrost	4	42	90	100	87	42	–
Human population density (people km^{-2})	8	3	0.4	0.1	0.2	0.2	–

Watershed areas are given for the region upstream of the discharge gauging station as well as for the entire watershed. Mean annual discharge (1999–2008, except 2001–2008 for the Yukon) is given at the gauging station and extrapolated to the entire watershed assuming that the unmonitored portion of the watershed has the same runoff as the monitored region of the watershed. Permafrost coverage is calculated using data from Brown et al. 1998, and human population density is calculated using data from Landscan (www.ornl.gov/sci/landscan)

late summer. Sampling frequency for the Student Partners Project varied greatly among rivers (Fig. 2).

PARTNERS field protocols were based on USGS sampling protocols. During open water periods, 60-kg D-96 samplers equipped with Teflon nozzles and Teflon sample collection bags were used to obtain depth-integrated and flow-weighted samples. These samples were collected at five roughly equal increments across the river channel and combined in a 14-L Teflon churn, resulting in a single composite sample intended to account for vertical or horizontal heterogeneity in constituent concentrations or properties. This is particularly important for particulate constituents where there is a strong vertical gradient; we found no evidence of vertical gradients for dissolved constituents (Raymond et al. 2007). Student Partners samples were collected from near the surface, either from a boat, through the ice, or from shore.

PARTNERS samples for all analyses except DOC were collected in Nalgene high-density polyethylene bottles after having been filtered through Pall Aquaprep 600 capsule filters (0.45 μm pore size). PARTNERS DOC samples were collected in acid-leached Nalgene polycarbonate bottles after filtration through precombusted Whatman QMA quartz filters (1 μm nominal pore size). Student Partners samples were collected in Nalgene high-density polyethylene bottles after filtration through Millipore Sterivex-HF capsule filters (0.45 μm pore size) or Whatman GFF filters (0.7 μm nominal pore size). All PARTNERS and Student Partners samples were frozen until analyzed.

Sample Analysis

All field samples from Russia, Canada, and Alaska were first shipped frozen to Woods Hole, Massachusetts, USA, but some were then distributed elsewhere for analysis. PARTNERS TDN samples were analyzed at the University of Texas using a Shimadzu high-temperature TOC/TN instrument. PARTNERS DIN (nitrate and ammonium) and Si samples were analyzed at the Woods Hole Research Center using a Lachat Quickchem FIA+ 8000 instrument. TDP samples were analyzed manually at the Woods Hole Research Center using the ascorbic acid method following persulfate oxidation (Clesceri et al. 1998). PARTNERS DOC samples were first UV-oxidized and cryogenically purified at Yale University, then analyzed for carbon content (and isotopic composition) at the National Ocean Sciences Atomic Mass Spectrometry (AMS) facility at the Woods Hole Oceanographic Institution or the University of Arizona's AMS facility. All Student Partners samples were analyzed at the Woods Hole Research Center using the methods described above, except that DOC was analyzed on a Shimadzu high-temperature TOC instrument.

PARTNERS and Student Partners constituent concentration data and modeled constituent fluxes are available without restriction at www.arcticgreatrivers.org and at the Arctic Observing Network's Cooperative Arctic Data and Information Center (AON-CADIS) as part of the Arctic Great Rivers Observatory (Arctic-GRO) data portal (McClelland et al. 2008). No systematic differences in constituent concentrations, attributable to either difference in sampling or analytical protocols, are apparent between the PARTNERS and Student Partners data sets.

Modeling

Constituent fluxes from each of the six rivers were estimated using the LoadRunner software package (Booth et al. 2007) to automate runs of the USGS LoadEstimator

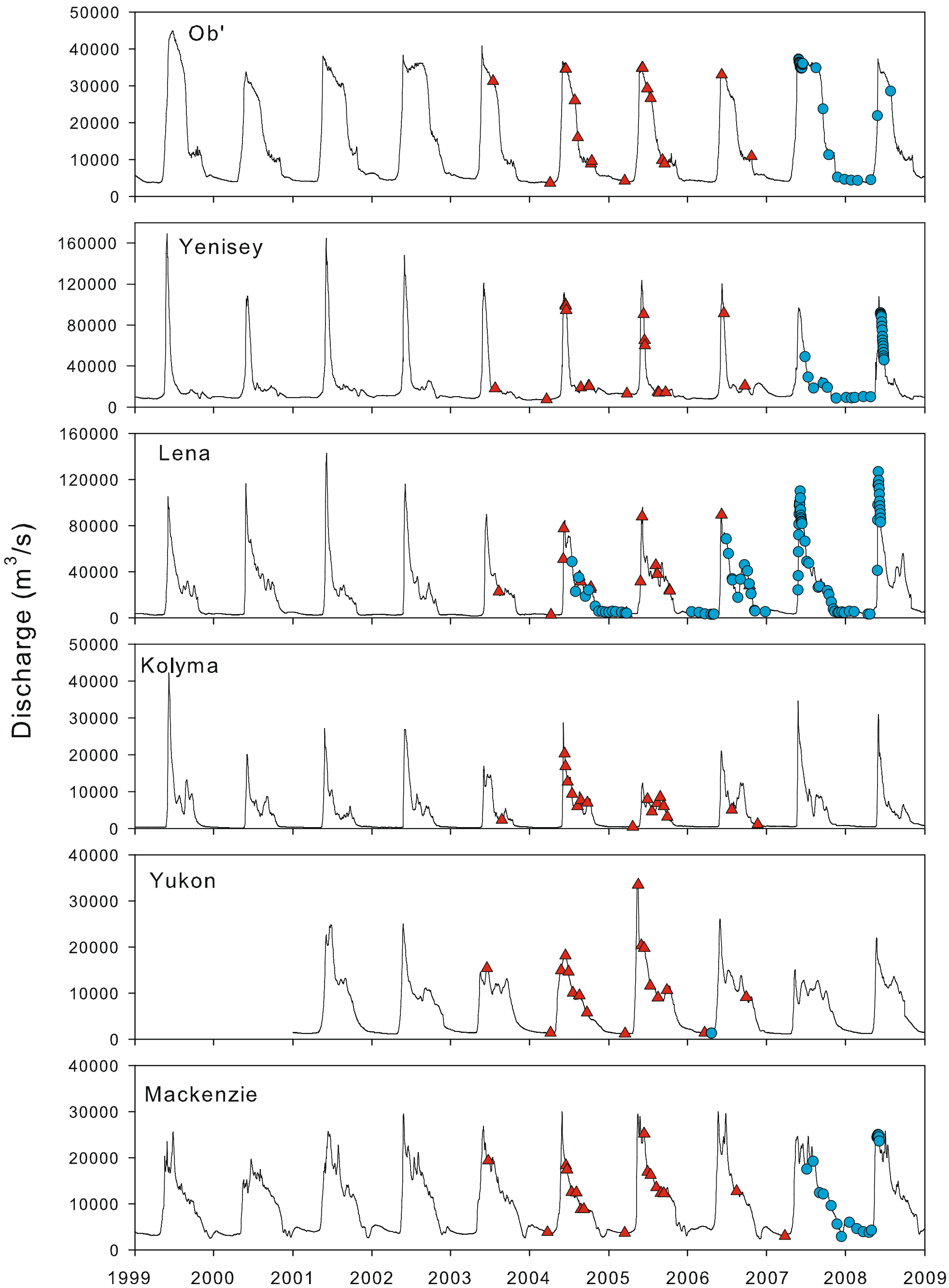

Fig. 2 Daily discharge for each of the six rivers from 1999 to 2008 and dates when PARTNERS and Student Partners samples were collected. The *red triangles* show the dates when samples were collected as part of the PARTNERS Project (17 times per river). The *blue circles* indicate the dates that samples were collected as part of the Student Partners Project

program (LOADEST; Runkel et al. 2004). LOADEST uses a time series of paired streamflow and constituent concentration data to construct a calibration regression, which is then applied to a continuous daily discharge record to obtain daily constituent loads (mass per day). The LOADEST calibration equation is chosen from a suite of predetermined multiple regression models using Akaike's information criterion. The LOADEST models we considered included discharge and seasonality as independent variables, with discharge and time centered to avoid multicollinearity. We excluded all models containing long-term time functions because our short data series did not lend itself to detecting such trends. We used the adjusted maximum likelihood estimator to fit the calibration equation, which is used when the residuals are normally distributed. To facilitate comparisons among rivers, PARTNERS data (which have consistent coverage among rivers) were used to calibrate the model, but Student Partners data (which vary greatly in abundance among rivers) were not (Fig. 2).

On the Lena River, PARTNERS constituent measurements were taken approximately 520 km upstream of the discharge gauging station, while on the Yenisey and Kolyma rivers constituent measurements were taken approximately 250 and 160 km downstream of discharge, respectively. To correct for this offset, we applied our sample concentrations to the downstream locations by determining the lag time between the two sampling stations. We assumed river velocities of 1.5 $m s^{-1}$, which are at the high end of the range modeled and observed for these rivers (Ngo-Duc et al. 2007; Smith and Pavelsky 2008). This ensured that our adjustments were accurate during the high discharge period and that we were not over-correcting our data.

On all rivers except the Ob' and Yukon, there were not enough NH_4-N measurements above the detection limit to meet the minimum LOADEST requirement for uncensored data points. Thus, we modeled fluxes of NO_3-N and DIN ($NO_3 + NH_4$), but not NH_4-N alone. DIN concentrations in the Eurasian rivers drop to near zero in the summer months, as a result of dilution during high flows coupled with biological uptake. We found that LOADEST had difficulty producing models that incorporated these near-zero values. To correct this, we ran LOADEST for the Eurasian rivers using DIN and NO_3-N concentrations that had been increased by a fixed amount and then corrected the modeled output concentrations by subtracting this fixed value. We did this using an increasingly large concentration adjustment until the flux estimate in the corrected model output stabilized. Model fit was considerably improved using this approach. Across all constituents, standard errors of prediction (SEP) ranged from 2.0% to 14.2% (average 5.4%) of modeled constituent export. Because of our method of calculating export for Eurasian NO_3-N and DIN, SEP was not calculated for these export estimates.

We obtained daily discharge for 1999–2008 from the ArcticRIMS Project (http://rims.unh.edu) for the Eurasian rivers, the Water Survey of Canada for the Mackenzie River, and the USGS for the Yukon River (Fig. 2). Calibration regressions were constructed with PARTNERS constituent data collected between 2003 and 2006 and used to extrapolate fluxes over the entire 10-year period for the Ob', Yenisey, Lena, Kolyma, and Mackenzie rivers. Any data gaps in the discharge record were filled by interpolation; there were no gaps during the peak flow period on any river. For the Yukon River, discharge data were not available for 1999 or 2000, or the first 3 months of 2001. Long-term averaged discharge was used to fill the gap at the beginning of 2001 for the Yukon River, but 1999 and 2000 were excluded from the analysis (Fig. 2).

Results and Discussion

The watersheds of the six rivers that are part of the PARTNERS and Student Partners project together cover 11.3×10^6 km^2, 55% of the pan-Arctic watershed (Fig. 1, Table 1) or 67% of the Arctic Ocean's drainage basin. Thus, accurately assessing biogeochemical fluxes in these six rivers makes a major contribution to the goal of determining total fluvial fluxes to the Arctic Ocean and surrounding seas. The combined discharge of the six rivers also accounts for well over half of the river water inputs to the Arctic Ocean. Below we first address the seasonality of discharge and constituent fluxes, then consider our estimates of annual constituent fluxes, and finally compare our estimates to a selection of previously published estimates.

Seasonality of Fluxes

PARTNERS samples were collected throughout the year (Fig. 2), both in the open water season and through the ice, enabling us to investigate how constituent fluxes vary seasonally. Though this has rarely been done in previous studies, it is important for three reasons. First and most obviously, we can only confidently estimate annual fluxes if we can also accurately quantify seasonal fluxes. Second, shifts in the seasonality of constituent fluxes from large rivers over time may be a sensitive indicator of widespread terrestrial change (Holmes et al. 2000a; Striegl et al. 2005; Walvoord and Striegl 2007; McClelland et al. 2008). And third, the significance of fluvial fluxes to the biogeochemistry of recipient estuarine and coastal ecosystems depends greatly on the timing of the fluxes (McClelland et al. 2011).

The strong relationships observed among discharge, season, and constituent concentrations illustrate the necessity of adequate seasonal coverage in sampling for accurately determining seasonal and annual constituent fluxes (Fig. 3). In many cases, such as for nitrate and silica, concentrations tend to be highest during winter baseflow but then decrease in spring and summer due to the combined effects of dilution and biological uptake. In other cases, such as for DOC, concentrations are at their highest during the spring freshet. The extreme seasonal variability in both discharge and constituent concentrations means that annual constituent flux estimates based on a small number of samples collected during a single season are tenuous. This also means that assessment of fluvial fluxes derived from sampling during oceanographic cruises is uncertain because ice conditions during the high discharge period generally preclude access to the river plumes from the ocean. When access from the ocean is feasible (late summer and early autumn), river discharge and constituent concentrations are generally not representative of annual fluxes.

We have binned results into seasons that correspond to distinct hydrologic phases of northern rivers (the Spring freshet during May and June, the more biologically active Summer period from July through October, and Winter low-flow conditions from November through April). These same seasons have been used in studies of nutrient and

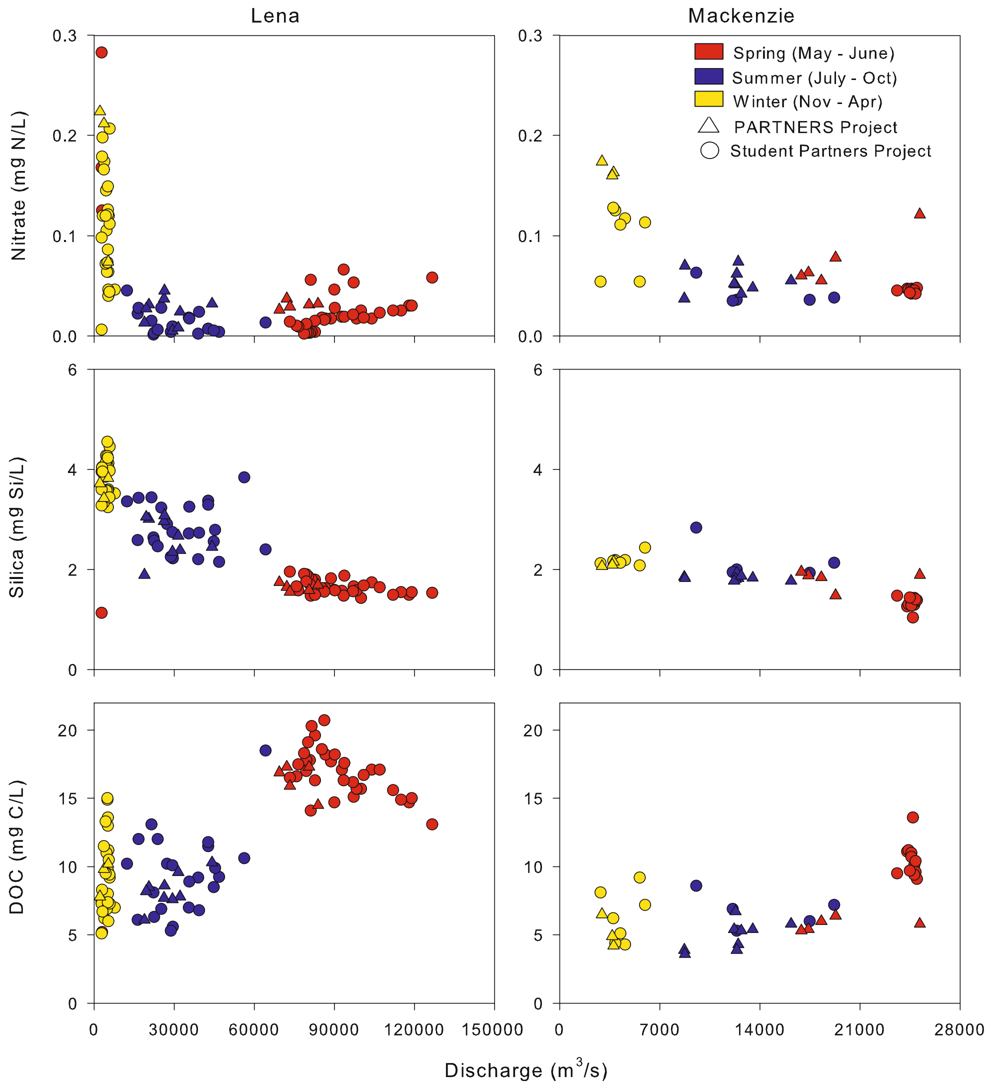

Fig. 3 Relationships between discharge and nitrate, silica, and DOC concentrations on the Lena and Mackenzie rivers. *Red* indicates samples that were collected in Spring (May and June), *blue* indicates samples that were collected in Summer (July through October), and *yellow* indicates samples that were collected in Winter (November through April). *Triangles* indicate samples that were collected as part of the PARTNERS Project, and *circles* indicate samples that were collected as part of the Student Partners Project

organic matter fluxes in the Yukon River (Dornblaser and Striegl 2007; Striegl et al. 2007). When comparing constituent fluxes among these seasons, it is important to note that as defined, spring lasts 2 months, summer lasts 4 months, and winter lasts 6 months (Table 2).

In spite of the fact that the spring season lasts just 2 months, it is the dominant period for the fluxes of several constituents, particularly those related to organic matter (Table 2). For example, DON flux from the six PARTNERS rivers during the 2-month spring period (208×10^9 g) exceeds the flux during the entire 6-month winter period by more than 400% (47×10^9 g). Similarly, spring DOC flux ($8{,}809\times10^9$ g) exceeds winter DOC flux by more than 400% ($2{,}151\times10^9$ g). The high organic matter fluxes during spring are the combined result of high discharge and high organic matter concentrations during that period (Figs. 2 and 3). In contrast, fluxes of inorganic nutrients such as silica and nitrate are much more similar among seasons. For example, the six-river flux of silica in spring ($1{,}972\times10^9$ g) only slightly exceeds the winter flux ($1{,}641\times10^9$ g), while the spring nitrate flux (58×10^9 g) is less than the winter nitrate flux (78×10^9 g). It is important to remember that, as defined, winter is three times longer than spring. In the case of the seasonality of the fluxes of these inorganic nutrients, the patterns of discharge and concentrations work in opposing directions: High spring discharge (Fig. 2) is countered by lower concentrations during spring (Fig. 3).

The focus above on the combined fluxes from the six PARTNERS rivers masks differences in seasonality among the rivers. With respect to discharge, at one extreme only 6% of annual discharge in the Kolyma River occurs during the 6-month winter period, whereas winter discharge in the Yenisey and Mackenzie rivers reaches ~25% of annual values (Fig. 4). There are also marked differences in the proportional contribution of spring discharge. In the Yenisey and Kolyma rivers, sharp ascending and descending limbs of the hydrograph during the freshet lead to almost half of annual discharge occurring during the spring season (Figs. 2 and 4). Far broader peaks in the Ob' and Mackenzie rivers decrease

Table 2 Average seasonal and annual constituent fluxes (1999 through 2008) for the six rivers that were part of the PARTNERS Project

Constituent	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie	Sum	Pan-Arctic
Spring, May–June (2 months)								
Q	136	284	216	47	72	92	847	
TDN	57	81	80	13	28	20	280	526
DON	31	65	69	9	24	10	208	391
DIN	25	16	13	3	7	8	72	135
NO_3-N	20	13	8	2	6	8	58	109
TDP	4.9	5.0	3.2	0.6	0.8	1.0	15	28
Si	537	599	379	105	185	166	1,972	3,707
DOC	1,338	2,924	2,823	449	783	493	8,809	16,559
Summer, July–October (4 months)								
Q	214	190	306	57	106	139	1,011	
TDN	81	38	66	10	26	24	245	461
DON	69	32	57	8	15	15	195	367
DIN	14	6	9	3	11	10	53	100
NO_3-N	15	3	7	2	10	9	46	86
TDP	9.8	2.2	2.2	0.5	0.9	1.4	17	32
Si	410	565	729	144	344	257	2,449	4,604
DOC	2,171	1,183	2,350	329	508	610	7,150	13,441
Winter, November–April (6 months)								
Q	78	162	59	7	30	66	403	
TDN	48	44	21	1.4	14	16	144	271
DON	9	13	10	0.7	8	6	47	88
DIN	47	29	11	0.6	8	8	104	196
NO_3-N	22	32	10	0.5	7	7	78	147
TDP	2.6	2.5	0.6	0.06	0.3	0.7	7	13
Si	505	575	238	26	165	131	1,641	3,085
DOC	609	537	508	40	182	275	2,151	4,043
Annual fluxes								
Q	427	636	581	111	208	298	2,261	
TDN	186	163	168	25	67	60	669	1,258
DON	110	111	135	17	47	31	450	846
DIN	86	51	33	7	26	27	229	430
NO_3-N	57	49	24	5	24	24	182	342
TDP	17	10	6	1	2	3	39	73
Si	1,453	1,740	1,347	276	694	554	6,062	11,395
DOC	4,119	4,645	5,681	818	1,472	1,377	18,109	34,042

All units are 10^9 g (as N, P, Si, or C), except for discharge (Q) which is given in cubic kilometers. Missing discharge data restricted the Yukon estimates to 2001–2008. The pan-Arctic constituent flux estimates are derived by scaling the fluxes calculated for the six rivers to the unsampled portion of the pan-Arctic watershed assuming that areal yields in the unmonitored region were equivalent to those in the monitored region

the contribution of the spring freshwater discharge to ~30% of annual values.

The contrasts in seasonality among rivers are even greater for constituent fluxes than they are for water discharge. For example, the Yenisey River transports 66% of its annual nitrate flux during winter when the ocean is largely ice-covered and primary productivity is low, compared to just 10% for the Kolyma River (Fig. 4; Table 2). For DON, spring fluxes account for more than half of the annual loads in the Yenisey and Kolyma rivers but only about 30% in the Ob' and Mackenzie rivers.

The impact of fluvial fluxes on the biogeochemistry of the receiving estuaries and coastal zones in the Arctic depends on their timing and magnitudes as well as on the relative abundances of the different constituents. In all rivers, on an annual basis as well as in all seasons except winter, DON fluxes exceed DIN fluxes (Fig. 5, upper panel). This highlights the potential significance of nutrients regenerated in the spring and summer by the decomposition of dissolved organic matter that enters the coastal system during the spring freshet (Holmes et al. 2008; McClelland et al. 2011; Tank et al. in review). On the

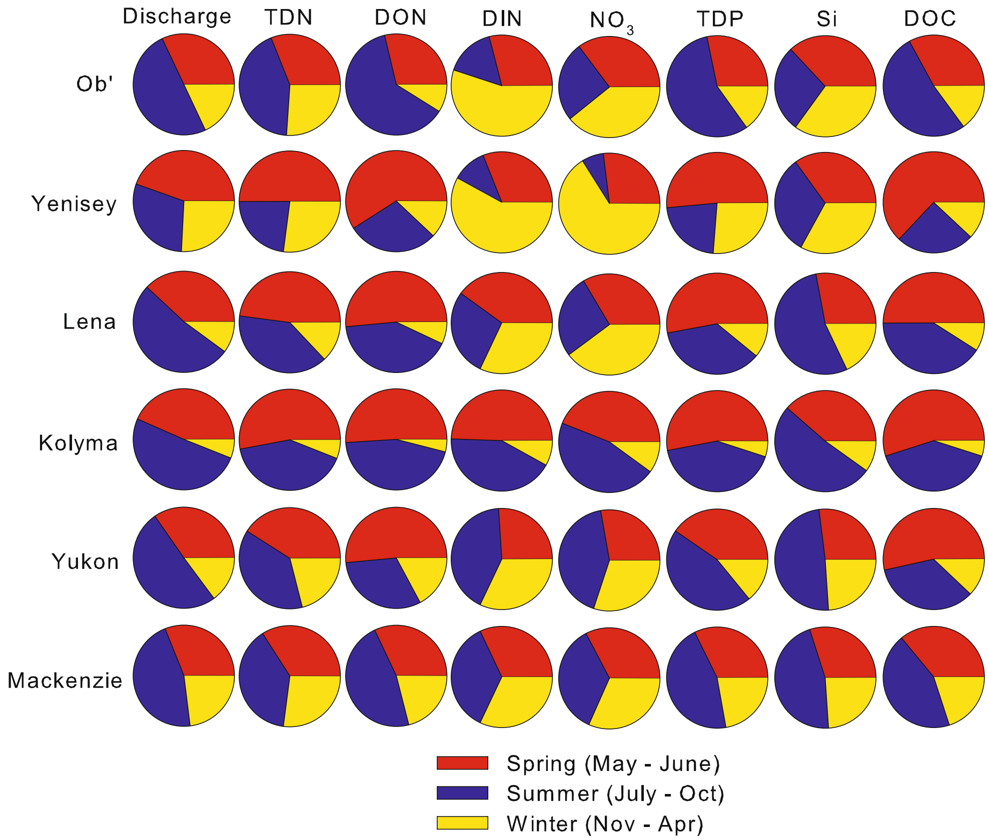

Fig. 4 Percentage of annual water and constituent fluxes in the different seasons. As described in the text, constituent fluxes were estimated for the 1999–2008 period (2001–2008 for the Yukon River) using LOADEST. *Red* indicates samples that were collected in Spring (May and June), *blue* indicates samples that were collected in Summer (July through October), and *yellow* indicates samples that were jcollected in Winter (November through April)

other hand, molar TDN-to-TDP ratios are generally well in excess of Redfield ratios (16:1 N/P; Fig. 5, middle panel), suggesting a relative scarcity of phosphorus in the river water delivered to the coastal zone (assuming that all N and P in organic forms becomes available, and at similar rates). High silica-to-inorganic nitrogen ratios (the Redfield ratio for Si to N is 1) suggest that ample silica is available to support diatom production, which is a major component of the Arctic Ocean's primary production (Sakshaug 2004).

Annual Fluxes and Yields

Our estimates of average annual constituent fluxes and yields (normalized to watershed area) for the six largest arctic rivers during the 1999–2008 time period are presented in the lower section of Table 2 (fluxes) and in Table 3 (yields). Here we highlight a few interesting patterns that emerge, recognizing that many more comparisons are possible.

On an annual basis, the six PARTNERS rivers combined transport about twice as much DON as DIN (Table 2 and Fig. 5). The rivers with the lowest permafrost coverage in their watersheds (Ob' and Mackenzie) each transport roughly equal amounts of DON and DIN on an annual basis, compared to the Lena which transports 4× more DON than DIN. These results further highlight the previously identified problems with some of the historical chemical data for Russian rivers, which suggested very high DIN yields for the Ob' and Yenisey rivers (Holmes et al. 2000a, 2001).

The Mackenzie River stands out as having relatively low yields (mass of constituent per watershed area per time) for all constituents we examined (Table 3). This may be in part related to the presence of a large lake (Great Slave Lake) in the middle of the watershed, which could allow for efficient processing and retention of constituents transported to the lake from the upper part of the watershed. However, the high suspended sediment fluxes observed in the downstream reaches of the Mackenzie River (Holmes et al. 2002) indicate that tributaries entering the river below Great Slave Lake have the potential to greatly modify its constituent load.

Raymond et al. (2007) noted a relationship between annual water yield (or runoff) and annual DOC yield for the six PARTNERS rivers: As water yield increased, so did DOC yield. We find a similar relationship for DON and Si: The rivers with the highest water yields (Yenisey, Yukon, and Lena; Table 1) also have the highest DON and Si yields (Table 3). In contrast, when comparing all six rivers, there is no clear relationship between water yield and annual yields of TDP, DIN, or NO_3. However, the Ob' River is notable in that it has the lowest water yield but high DIN and TDP yields (Table 3), perhaps reflecting the greater population density and development in the Ob' watershed as compared to the other basins (Table 1).

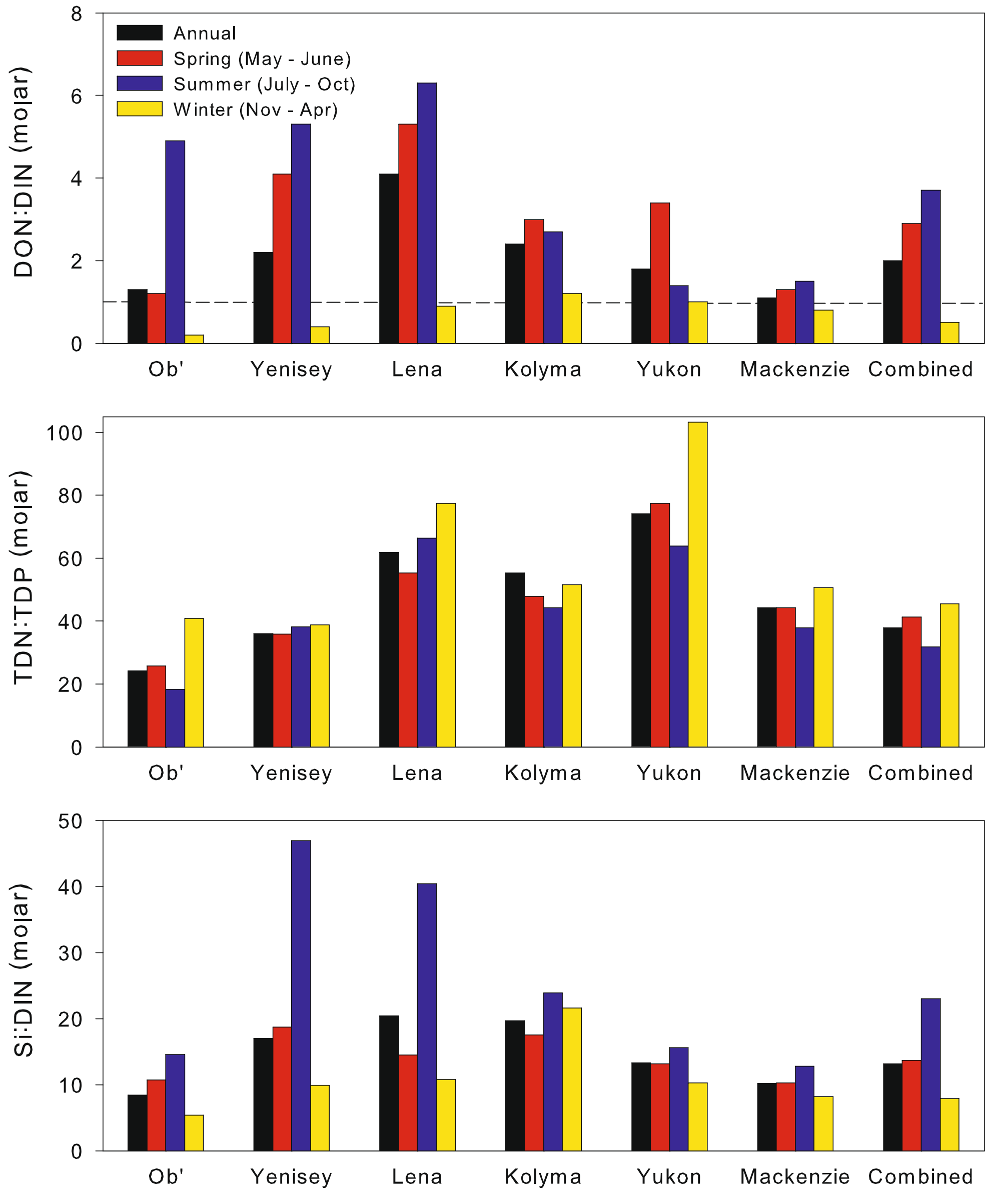

Fig. 5 Annual and seasonal molar flux ratios of DON/DIN (*upper panel*), TDN/TDP (*middle panel*), and Si/DIN (*lower panel*). As described in the text, constituent fluxes were estimated for the 1999–2008 period (2001–2008 for the Yukon River) using LOADEST. The *horizontal dashed line in the upper panel* indicates a flux ratio of 1. The final set in each figure, labeled "Combined," indicates the ratios when the fluxes from all six rivers are summed

Comparison with Previous Estimates

How do the flux estimates presented here compare with previous studies? Few comparisons are possible for seasonal fluxes because most previous studies only presented annual flux estimates. One exception is with work on seasonal N and P fluxes in the Yukon River during the 2001–2005 period (Dornblaser and Striegl 2007). The

Table 3 Average annual constituent yields (kilograms per square kilometer per year) and water yield (cubic meters per square kilometer per year)

	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie
TDN	63	67	69	48	81	36
DON	37	45	56	32	57	18
DIN	29	21	14	13	31	16
NO_3	19	20	10	10	29	14
TDP	6	4	2	2	2	2
Si	493	713	554	525	835	330
DOC	1,396	1,904	2,338	1,555	1,771	820
Water yield	1,430	2,590	2,400	1,660	2,480	1,770

seasonal and annual flux estimates for NO_3, DIN, TDN, and TDP are generally within 10–20% of those presented here, but the comparisons are confounded because the estimates are not really independent since they each use some of the same data (the USGS and the PARTNERS project collaborated for sampling on the Yukon River at Pilot Station).

In contrast to the situation for seasonal flux estimates, more comparisons are possible for annual flux estimates. Coverage is best for DOC, which has received the most attention in previous studies: Still, we know of no other studies that report annual flux estimates for each of the six rivers considered here. Several studies, however, provide composite estimates that we can compare to our six rivers and pan-Arctic estimates (18.1 and 34.0 Tg year^{-1}, respectively; Table 2). Dittmar and Kattner (2003) estimate that the total amount of DOC discharged by rivers into the Arctic Ocean is 18–26 Tg year^{-1}. For rivers draining directly into the Arctic Ocean, Raymond et al. (2007) estimate a flux of ~25 Tg year^{-1}, increasing to 36 Tg year^{-1} if the entire pan-Arctic watershed is considered. A very similar pan-Arctic estimate (37.7 Tg year^{-1}) is obtained by Manizza et al. (2009). Thus, several recent studies (including ours) point to an annual fluvial DOC flux estimate from the pan-Arctic watershed of 34–38 Tg, with ~25 Tg year^{-1} being discharged directly into the Arctic Ocean, although again it should be noted that these estimates are not all truly independent as both the Raymond et al. (2007) and Manizza et al. (2009) estimates rely at least in part on PARTNERS data.

Fewer comparisons are possible for the other constituents we consider (TDN, DON, DIN, NO_3, TDP, and Si). Moreover, in most cases, the raw concentration and discharge data used to generate the flux estimates are not published or widely available, making critical evaluation of the flux estimates difficult or impossible. That being said, we find cases where the estimates we provide are very close to previously published estimates, whereas in other cases there are large differences. For example, our annual nitrate flux estimates for the Yenisey, Lena, and Kolyma rivers are within 10% of the values given by Gordeev et al. (1996), one of the most widely used references regarding biogeochemical fluxes from large arctic rivers. On the other hand, our annual DON flux estimates for the Lena and Kolyma rivers are two to three times lower than those reported in that same paper. Furthermore, our TDP estimates are generally only one half to one third of those reported by Gordeev et al. (1996), whereas our silica flux estimates, though variable, differ on average by only ~3%. Rigorous explanations for differences or similarities are elusive except in cases when discharge and concentration data are readily available for comparison, along with detailed descriptions of the methods used to calculate annual fluxes from periodic measurements of constituent concentrations. Prior to the PARTNERS project, this sort of information has not been readily available for large-scale studies of biogeochemical fluxes in arctic rivers.

Conclusions

The PARTNERS project was an unprecedented effort to capture the seasonal dynamics of constituent fluxes from the major arctic rivers in Russia, Canada, and Alaska over a multi-year period using standardized sampling and analytical protocols. The 17 major sampling campaigns on each of the rivers spanned most of the range of annual discharge extremes in each river and covered all seasons (Fig. 2). Increased temporal resolution was achieved on several of the rivers as part of the Student Partners Project. The resulting data sets, available without restriction at www.arcticgreatrivers.org and at the AON-CADIS as part of the Arctic-GRO data portal, allow for improved understanding of seasonal and annual constituent fluxes and set the baseline against which to judge future changes.

The focus of this paper is on mean fluxes, annual and seasonal, over the 1999 to 2008 period. However, just as discharge varies from year to year within each river (Fig. 2), so to do constituent fluxes. For example, from 1999 to 2008, our model results suggest that annual fluxes in the Lena River varied from 4.1 to 7.4 Tg for DOC and from 1.1 to 1.6 Tg Si. It is important to recognize that the impact of fluvial inputs on the receiving coastal waters at any particular time is a function of the actual fluxes over a relatively short time frame, more so than the long-term mean fluxes. As estimates of long-term mean constituent fluxes become better constrained, increased attention should be directed toward consideration of the implications of interannual variability in constituent fluxes.

The watersheds of the rivers that are the focus of the PARTNERS project and its successor (the Arctic-GRO) together cover more than 50% of the pan-Arctic watershed. To estimate total fluxes to the Arctic Ocean and surrounding seas, we assumed that constituent yields were the same in the unmonitored portion of the watershed and scaled-up accordingly (Table 2). However, the unmonitored rivers tend to have smaller, more northerly watersheds that ring the Arctic Ocean, so it is likely that at least for some constituents yields may be considerably different than for the larger rivers whose watersheds extend much further south. Moreover, trajectories of change with future warming may differ among these classes of rivers. Although biogeochemical fluxes from some smaller arctic watersheds have received considerable attention, particularly on the North Slope of Alaska (Kling et al. 1991; Peterson et al. 1992; McClelland et al. 2007; Bowden et al. 2008), at the pan-Arctic scale, they represent a significant gap in our ability to confidently assess land–ocean fluxes.

Finally, we recognize that what we often consider to be fluxes to the ocean may in fact be better characterized as fluxes to estuaries or the coastal zone. As is widely understood in temperature or tropical estuarine systems, this distinction is important because extensive processing in estuaries and coastal zones often substantially modifies fluvial constituent fluxes before they reach the open ocean (Nixon et al. 1996; Kemp et al. 1997; Holmes et al. 2000b; Tobias et al. 2003). The same is true in arctic estuaries and nearshore zones (Emmerton et al. 2008b), although our understanding of estuarine processes in the Arctic is far less developed than in other regions, particularly with respect to seasonality (McClelland et al. 2011 and references therein). Improved understanding of the impact of fluvial inputs on the biogeochemistry of the Arctic Ocean as a whole, as well as on the coastal zone of the Arctic, will require increased attention on estuarine and coastal processes despite the daunting logistical challenges facing nearshore research in the Arctic.

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