



# **Global Biogeochemical Cycles**

## **RESEARCH ARTICLE**

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#### **Kev Points:**

- River export of POC and PN from pan-Arctic watershed is constrained using multiyear data set
- Together, the six largest Arctic rivers export ~3.1 Tg/yr of POC and ~0.4 Tg/yr of PN
- Export estimates for pan-Arctic watershed as a whole are ~5.8 Tg/yr of POC and 0.7 Tg/yr of PN

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# Particulate organic carbon and nitrogen export from major Arctic rivers

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**Abstract** Northern rivers connect a land area of approximately 20.5 million km² to the Arctic Ocean and surrounding seas. These rivers account for ~10% of global river discharge and transport massive quantities of dissolved and particulate materials that reflect watershed sources and impact biogeochemical cycling in the ocean. In this paper, multiyear data sets from a coordinated sampling program are used to characterize particulate organic carbon (POC) and particulate nitrogen (PN) export from the six largest rivers within the pan-Arctic watershed (Yenisey, Lena, Ob', Mackenzie, Yukon, Kolyma). Together, these rivers export an average of  $3055 \times 10^9$  g of POC and  $368 \times 10^9$  g of PN each year. Scaled up to the pan-Arctic watershed as a whole, fluvial export estimates increase to  $5767 \times 10^9$  g and  $695 \times 10^9$  g of POC and PN per year, respectively. POC export is substantially lower than dissolved organic carbon export by these rivers, whereas PN export is roughly equal to dissolved nitrogen export. Seasonal patterns in concentrations and source/composition indicators (C:N,  $\delta^{13}$ C,  $\Delta^{14}$ C,  $\delta^{15}$ N) are broadly similar among rivers, but distinct regional differences are also evident. For example, average radiocarbon ages of POC range from ~2000 (Ob') to ~5500 (Mackenzie) years before present. Rapid changes within the Arctic system as a consequence of global warming make it challenging to establish a contemporary baseline of fluvial export, but the results presented in this paper capture variability and quantify average conditions for nearly a decade at the beginning of the 21st century.

### 1. Introduction

Six large rivers, the Yukon and Mackenzie in North America and the Yenisey, Ob', Lena, and Kolyma in Eurasia, drain over half of the watershed area surrounding the Arctic Ocean (Figure 1). Seasonally explicit sampling programs were established at downstream locations on these rivers in 2003 to improve estimates of fluvial export and establish benchmarks for tracking large-scale perturbations associated with climate change [McClelland et al., 2008]. Sampling was initiated by the Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments (PARTNERS) project and later continued through the Arctic Great Rivers Observatory (Arctic-GRO; www.arcticgreatrivers.org). These efforts have led to major revisions of flux estimates for dissolved organic matter (DOM) and inorganic nutrients [Holmes et al., 2012], as well as improved understanding of the composition of DOM delivered to Arctic coastal waters [Raymond et al., 2007; Amon et al., 2012]. Particulate organic carbon (POC) and particulate nitrogen (PN) data from PARTNERS/Arctic-GRO have received less attention to date. Although literature estimates for POC and PN fluxes from the major Arctic rivers do exist, these are largely hampered by short data records, lack of seasonally explicit sampling, or variations in sampling methodology among rivers. For example, although concentrations of suspended particulates in rivers often vary with water depth [Millman and Meade, 1983], methods for capturing this variability have not been consistent. Here we present rigorous new estimates of POC and PN fluxes for the major Arctic rivers, which are based on 9 years of depth-integrated, seasonally explicit sampling. We also present a new data set for  $\delta^{15}$ N,  $\delta^{13}$ C,  $\Delta^{14}$ C, and C:N ratios that provide fresh insights into seasonal and geographical variability in particulate organic matter sources and composition.

Scientific understanding of how terrestrial inputs influence biogeochemical cycles [Anderson et al., 2011; Manizza et al., 2011; Tank et al., 2012; Vonk et al., 2012; Karlsson et al., 2015] and food webs [Dunton et al., 2012; Casper et al., 2015]

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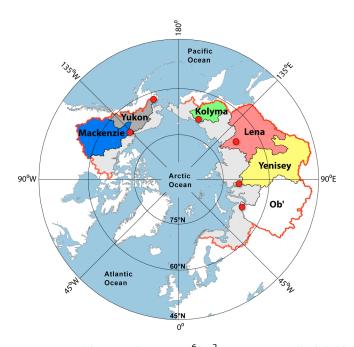


Figure 1. Map delineating the  $20.5 \times 10^6 \text{ km}^2$  pan-Arctic watershed (bold red line) and the drainage basins of the six rivers included in this study. Red dots show sampling locations (Mackenzie at Tsiigehtchic, Yukon at Pilot Station, Kolyma at Cherskiy, Lena at Zhigansk, Yenisey at Dudinka, and Ob' at Salekhard).

2014] in Arctic coastal waters is rapidly improving. Characterization of these land-ocean linkages is, however, still hindered by a lack of well-constrained estimates of some inputs such as particulate organic matter. Historically, it has been particularly difficult to capture seasonal dynamics. Although seasonality is recognized as a defining feature of the Arctic, much of the research focusing on riverine systems and coastal waters in this region has been conducted during middle to late summer because of logistical challenges associated with winter and spring field conditions [McClelland et al., 2012].

While better constrained estimates of fluvial export are required to improve fundamental understanding of landocean coupling in the Arctic, climate change adds some urgency to this need. Thawing permafrost and changes in net precipitation and runoff associated with warming are hav-

ing widespread impacts on the Arctic hydrologic system [White et al., 2007; Rawlins et al., 2010], including changes in water and water-borne constituent fluxes to the ocean [Holmes et al., 2013]. These changes in land-to-ocean fluxes may be altering estuarine ecology and biogeochemistry in ways that challenge local communities (e.g., through effects on subsistence harvests) and have broader impacts on global carbon cycling. The role that rivers play in mobilizing terrestrial carbon stocks, including those derived from thawing permafrost, is of particular interest from a climate feedback perspective. Organic carbon in northern permafrost soils accounts for roughly one half of the global standing stock of soil organic carbon [Tarnocai et al., 2009], and fluvial transport of soil carbon from the pan-Arctic watershed to the ocean may facilitate significant storage or carbon release (via CO<sub>2</sub> and methane) to the atmosphere depending on the relative importance of sequestration and decomposition processes within the marine environment [Letscher et al., 2011; Alling et al., 2012; Hilton et al., 2015]. Decomposition of permafrost-derived carbon during transport through river networks in the Arctic may also contribute significantly to atmospheric CO<sub>2</sub> increases [Spencer et al., 2015].

# 2. Methods

## 2.1. Sample Collection and Analysis

Water samples for POC and PN analyses were collected from the Mackenzie River at Tsiigehtchic, Yukon River at Pilot Station, Kolyma River at Cherskiy, Lena River at Zhigansk, Yenisey River at Dudinka, and Ob' River at Salekhard (Figure 1). Sampling at Tsiigetchic was conducted upstream of the Arctic Red River. Key characteristics of the watersheds drained by the PARTNERS/Arctic-GRO rivers, including catchment area, permafrost coverage, and human population density, are provided in Holmes et al. [2012]. This paper describes results from sampling between summer 2003 and early 2012. Samples were collected for the PARTNERS project from 2003 to 2006 and for the Arctic-GRO thereafter. Samples were collected during different hydrographic stages and seasons, with particular emphasis on depth-integrated sampling of high flow conditions during the spring thaw period (Figure 2). All data generated from the PARTNERS project and Arctic-GRO are available at www.arcticgreatrivers.org.

Water was collected using United States Geological Survey (USGS) D-96 samplers equipped with Teflon nozzles and bags to acquire depth-integrated, flow-weighted samples during open water conditions. The

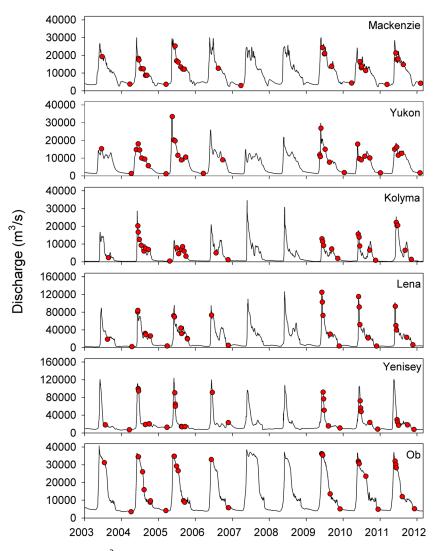


Figure 2. River discharge records (m<sup>3</sup>/s at a daily time step) between January 2003 and February 2012. Red dots along the hydrographs show when samples were collected for suspended POC and PN analyses. Note that the discharge scales for the Lena and Yenisey are 4 times greater than those shown for the other rivers.

samplers were deployed at five approximately equally spaced intervals across each river channel, and the water from these deployments was combined in a single 14L Teflon churn to create composites representing the cross sections as a whole. While this sampling approach was designed to capture vertical and cross-sectional variability in water column constituents, it was not designed to quantify bed load. The D-96 samplers were not deployed during ice covered periods. Samples from these (low flow) periods were from surface waters only, collected through holes cut in the ice.

Samples of river water were placed in coolers and processed within 1-4 h of collection to isolate POC and PN for concentration and isotopic measurements. Water volumes ranging from ~50 to 1000 mL, depending on the particulate concentrations, were filtered through precombusted (24 h at 450°C) 25 mm Whatman GF/F filters. The filters were then stored frozen prior to shipment from field sites. Subsequent processing and analysis of these filters was done at the Marine Biological Laboratory. Filters were dried at 60°C and stored in a desiccator cabinet thereafter. Filters for POC measurements were treated with direct applications of sulfurous acid (H<sub>2</sub>SO<sub>3</sub>, ACS 6% SO<sub>2</sub> minimum, applied through three wetting/drying cycles) to remove inorganic carbon prior to analysis. Filters for PN analysis were not acidified. Samples were run on a Europa 20-20 continuous flow isotope ratio mass spectrometer coupled to an Automated Nitrogen Carbon Analyzer-Solids and Liquids (ANCA-SL) elemental analyzer to determine the concentrations and stable isotope ratios of POC



and PN. Stable isotope results are reported in  $\delta$  notation relative to Vienna Pee Dee Belemnite and atmospheric N<sub>2</sub> for  $\delta^{13}$ C and  $\delta^{15}$ N, respectively (analytical precision of ±0.1‰ on homogenous IAEA reference materials). The analytical precision of POC and PN concentration measurements was ±1%.

Collection and field processing of samples for POC radiocarbon measurements were the same as described for POC concentration/ $\delta^{13}$ C samples, except that 47 mm quartz filters (Whatman QM-A, precombusted at 850°C for 6 h) were used. Frozen filters for radiocarbon analysis were shipped to Yale University for subsequent processing, and  $^{14}$ C measurements were conducted at the National Ocean Sciences Accelerator Mass Spectrometry facility at the Woods Hole Oceanographic Institution. All  $^{14}$ C measurements were performed within a 2 year collection. Filters from 2004 and 2005 were acidified by immersion in 1 mL of concentrated sulfurous acid in quartz tubes. After 6 h the acid was removed using a Pierce Reacti-Therm III (no. 18835). After 2005, the same acidification protocol that was used for  $^{13}$ C (described here) was used for  $^{14}$ C samples. After acidification, POC samples were oxidized to CO<sub>2</sub> by off-line dry combustion with CuO and Ag metal at 850°C in 9 mm quartz tubes [*Sofer*, 1980].

#### 2.2. Estimation of Constituent Fluxes and Discharge-Weighted Averages

The USGS Load Estimator (LOADEST) program [Runkel et al., 2004] was used in combination with LoadRunner version 1.2 [http://environment.yale.edu/loadrunner/] to calculate fluxes. LoadRunner is a program that automates runs of LOADEST and performs additional data processing and output options. LOADEST includes a range of regression models that can be used for flux estimation. For this study, LOADEST model 6 was applied for POC and PN in all rivers:

$$ln(Flux) = a_0 + a_1 lnQ + a_2 lnQ^2 + a_3 \sin (2 \pi d_{time}) + a_4 \cos (2 \pi d_{time})$$
 (1)

where flux is provided in kg/d, Q equals water discharge (ft<sup>3</sup>/s), lnQ equals ln (Q) minus center of ln (Q), and  $d_{\text{time}}$  equals decimal time minus center of decimal time in this model. The centering routine is applied to account for multicolinearity [Helsel and Hirsch, 2002] associated with the use of linear and quadratic expressions of time and discharge. Model 6 was chosen because it provided the best overall fit for the six rivers without including functions for "long-term" change over the calibration period. LOADEST calculates daily flux values using maximum likelihood estimation (MLE), adjusted maximum likelihood estimation (AMLE), and least absolute deviation (LAD) statistical approaches. The AMLE output was used in this study, but all three output types provided similar results.

Water discharge data were acquired from Roshydromet (Federal Service for Hydrometeorology and Environmental Monitoring, Ministry of Natural Resources and Environment, Russian Federation), the Water Survey of Canada, and the USGS. PARTNERS/Arctic-GRO samples were collected at the same locations as discharge gauging stations on the Yukon (Pilot Station), Mackenzie (Tsiigehtchic), and Ob' (Salekhard) rivers. Discharge gauging and water sampling locations on the other rivers were not coincident. Discharge data from the Yenisey at Igarka, Lena at Kyusyur, and Kolyma at Kolymskoye were used to calculate POC and PN fluxes. Temporal corrections of 1 (Kolyma), 2 (Yenisey), and 4 (Lena) days were applied in these cases to align the water quality and discharge data before using LoadRunner/LOADEST. See *Holmes et al.* [2012] for a more detailed explanation of these temporal corrections.

LOADEST model 6 explains a large proportion of the variability in POC and PN fluxes in all rivers (Table 1).  $R^2$  values range from 0.78 to 0.96 for POC and 0.86–0.97 for PN. Not all model coefficients are statistically significant for all rivers, reflecting differences in the importance of water discharge (coefficients  $a_1$  and  $a_2$ ) and temporal oscillations (e.g., seasonality; coefficients  $a_3$  and  $a_4$ ) unrelated to discharge as explanatory variables. Significant coefficients also vary between POC and PN. Coefficients  $a_0$  (y intercept) and  $a_1$  are significant for POC and PN in all rivers. Coefficient  $a_2$  is significant for POC and PN in the Kolyma River and for PN in the Ob' River. Coefficient  $a_3$  is significant for POC in the Kolyma and Lena and for PN in the Yukon, Kolyma, Lena, and Yenisey. Coefficient  $a_4$  is significant for POC and PN in the Ob' River.

Discharge-weighted annual averages of POC and PN concentrations, C:N ratios, and isotope values ( $\delta^{15}$ N,  $\delta^{13}$ C, and  $\Delta^{14}$ C) were calculated using two different approaches. For the concentration data, daily flux estimates from LOADEST were converted to daily concentration estimates and averaged on a monthly basis. These monthly concentrations were then multiplied by the corresponding average water discharge for each month, summed, and divided by average annual discharge. For the C:N ratios and isotope values, we simply

**Table 1.** Coefficients (+/- 1 Standard Deviation) and  $R^2$  Values for LOADEST Model 6 [In (Flux) =  $a_0 + a_1 \ln Q$  $+ a_2 \ln Q^2 + a_3 \sin (2 \pi d_{\text{time}}) + a_4 \cos (2 \pi d_{\text{time}})]$  as Applied to Each River for Flux Estimation<sup>a</sup>

	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$R^2$
POC						
Mackenzie	13.21 ± 0.56	$3.07 \pm 0.76$	$-0.21 \pm 0.92$	$1.01 \pm 0.61$	$0.17 \pm 0.70$	0.78
Yukon	$13.28 \pm 0.30$	$1.46 \pm 0.24$	$-0.03 \pm 0.22$	$-0.47 \pm 0.39$	$-0.07 \pm 0.25$	0.90
Kolyma	11.13 ± 0.33	$1.40 \pm 0.13$	0.37 ± 0.11	$-0.93 \pm 0.39$	$-0.07 \pm 0.19$	0.94
Lena	13.54 ± 0.27	1.53 ± 0.13	$0.03 \pm 0.11$	$-0.72 \pm 0.35$	$-0.23 \pm 0.17$	0.96
Yenisey	13.26 ± 0.29	1.17 ± 0.18	$0.29 \pm 0.24$	$-0.52 \pm 0.28$	$-0.10 \pm 0.19$	0.83
Ob'	14.23 ± 0.25	$1.09 \pm 0.13$	$-0.29 \pm 0.28$	$-0.23 \pm 0.23$	$-0.45 \pm 0.16$	0.96
PN						
Mackenzie	11.12 ± 0.43	$2.75 \pm 0.58$	$-0.41 \pm 0.71$	$0.70 \pm 0.46$	$-0.14 \pm 0.54$	0.86
Yukon	11.01 ± 0.24	1.46 ± 0.19	$-0.01 \pm 0.18$	$-0.60 \pm 0.32$	$0.07 \pm 0.21$	0.94
Kolyma	$8.73 \pm 0.33$	$1.36 \pm 0.13$	$0.47 \pm 0.12$	$-1.64 \pm 0.39$	$-0.10 \pm 0.19$	0.95
Lena	11.68 ± 0.25	$1.49 \pm 0.12$	$-0.06 \pm 0.10$	$-0.63 \pm 0.33$	$-0.17 \pm 0.15$	0.97
Yenisey	11.29 ± 0.25	1.03 ± 0.16	$0.30 \pm 0.20$	$-0.69 \pm 0.24$	$-0.05 \pm 0.17$	0.84
Ob'	12.44 ± 0.31	$1.00 \pm 0.16$	$-0.83 \pm 0.35$	$-0.52 \pm 0.28$	$-0.69 \pm 0.19$	0.96

<sup>&</sup>lt;sup>a</sup>Values in bold type are statistically different from zero (alpha 0.05). Flux = kg/d, Q = discharge,  $\ln Q$  =  $\ln (Q)$  — center of In (Q),  $d_{\text{time}}$  = decimal time – center of decimal time.

used measured values as available. All data for each month when sampling occurred were averaged, and averages for missing months were estimated by linear interpolation. Discharge weighting was then done as described for the concentration data.

#### 3. Results

#### 3.1. POC and PN Concentrations

Strong seasonal variations in POC and PN concentrations are evident in all of the rivers, with lowest values occurring during the winter months and peak values occurring during late May to early June (Figure 3). These variations in concentration are, in part, linked to variations in river discharge: POC and PN concentrations are positively correlated with water yield (discharge divided by watershed area) in all of the rivers ( Figure 4 and Table 2). However, the discharge-concentration relationships differ markedly among rivers. Concentrations increase much less in the Yenisey than in the Mackenzie, Yukon, and Ob' rivers as water yields increase (Figure 4 and Table 2). Changes in concentration with water yield are intermediate in the Lena and Kolyma (Figure 4 and Table 2). The seasonal differences in concentrations among rivers translate into average annual values that range from 26 to 145 µM for POC and 3.3-13.1 µM for PN (Table 3). In both cases, the lowest values come from the Yenisey River and the highest values come from the Yukon River. Annualized POC and PN concentration estimates increase for all of the rivers when discharge-weighted averages are calculated (Table 3). Discharge-weighted averages exceed straight averages by 23% (Yenisey) to 85% (Lena) for POC concentrations and by 18% (Yenisey) to 76% (Lena) for PN concentrations. Increases from straight averages to discharge-weighted averages of POC concentrations are much greater in the Yukon and Mackenzie than the Ob'. As a result, the discharge-weighted averages of POC concentrations in the Mackenzie and Yukon rivers are substantially higher than all of the Eurasian rivers (Table 3).

#### 3.2. Indicators of Particulate Sources and Composition

Seasonal concentration changes are accompanied by major differences in the composition of suspended particulates in all of the rivers. Average C:N ratios are lowest during summer (p < 0.05, Tukey-Kramer honest significant difference (HSD) test for all rivers combined), while patterns for winter and spring are less consistent (Table 4). In some cases, such as the Yenisey, winter and spring C:N ratios are very similar. In other cases, such as the Ob', winter values are substantially higher than spring values for C:N. Average  $\delta^{13}$ C values are lowest during winter and highest during spring (p < 0.05, Tukey-Kramer HSD test for all rivers combined), although the Yenisey River stands out as an exception with lower  $\delta^{13}$ C values during summer (Table 4). While there is substantial variability in average  $\Delta^{14}C$  and  $\delta^{15}N$  values among seasons, no consistent seasonal patterns among rivers are evident (Table 4).

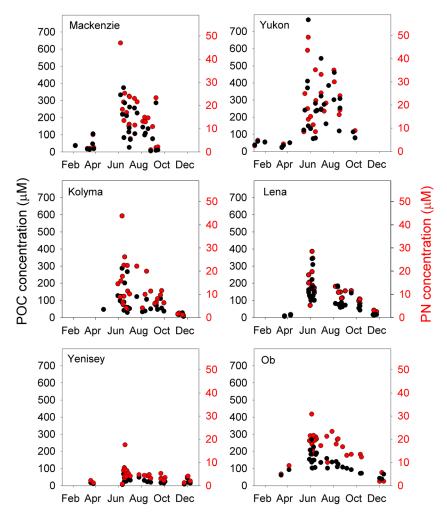


Figure 3. Variations in suspended POC (black dots, left y axis) and PN (red dots, right y axis) concentrations in river water over the calendar year. Daily values for all water samples collected during the 2003-2012 time frame are shown.

Plots of organic matter quality parameters (C:N,  $\delta^{13}$ C,  $\Delta^{14}$ C, and  $\delta^{15}$ N) versus water yields show a variety of relationships (Figure 5). Water yield is not a strong predictor of C:N ratios but is tightly linked to  $\delta^{13}$ C values of POC ( $R^2 = 0.44$  and p < 0.05 for  $\delta^{13}$ C versus log water yield, all rivers combined). The  $\delta^{13}$ C values are most negative (minimum of -38% in the Ob' River) at low water yields, and they rapidly increase as water yields approach 1 mm/d. Above this threshold, most  $\delta^{13}$ C values range between -26% and -30% and do not show further changes as a function of water yield (Figure 5).  $\Delta^{14}$ C values of POC (ranging from approximately -650% to -150%) also appear to show a positive relationship with water yield when the data are considered in aggregate, but the relationships for  $\Delta^{14}$ C are not strong or consistent when rivers are considered individually. In fact, the only river with a strong relationship between  $\Delta^{14}$ C and water yield is the Mackenzie, and in that case the slope is negative. The  $\delta^{15}$ N values of PN, which range from approximately -4% to +12%, show no clear increases or decreases with water yield, but like the other quality indicators they do show a consistent pattern of decreasing variability as water yields increase (Figure 5).

Estimates of average annual C:N,  $\delta^{13}$ C, and  $\delta^{15}$ N vary significantly among rivers, but do not separate into distinct geographic groupings, even after discharge-weighting is applied (Table 3). The discharge-weighting procedure does, however, result in lower estimates of average annual C:N ratios in four of the six rivers (Mackenzie, Yukon, Kolyma, and Ob'). Overall, discharge-weighted averages of C:N ratios range from 8.1 to 11.7, discharge-weighted averages of  $\delta^{13}$ C values range from -31.7% to -28.0%, and discharge-weighted averages of  $\delta^{15}N$  values range from 1.9% to 5.0% among rivers (Table 3).

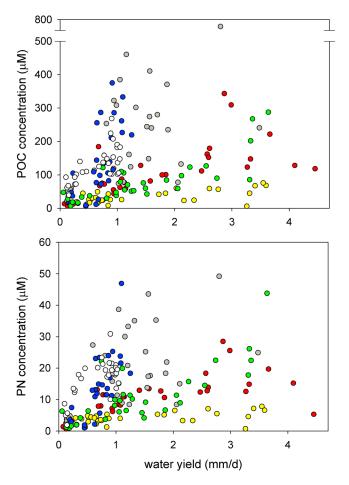


Figure 4. Relationships between water yield and concentrations of suspended (top) POC and (bottom) PN in river water. Blue = Mackenzie, gray = Yukon, green = Kolyma, red = Lena, yellow = Yenisey, and white = Ob'.

In contrast to the other organic matter source/composition indicators, average annual  $\Delta^{14}$ C values do show geographic groupings. distinct Overall, the discharge-weighted averages for  $\Delta^{14}C$  range between -535% and -220%. This range equates with ages of approximately 5500 (Mackenzie) to 2000 (Ob') years before present (years BP). The average annual age of POC in the Kolyma (~5000 years BP) is similar to that of the Mackenzie, whereas average annual POC ages in the Yenisey (~2900 years BP) and Lena (~2700 years BP) are closer to that of the Ob'. Although data coverage was not adequate to support estimates of average annual POC age for the Yukon, the  $\Delta^{14}$ C values measured during summer and winter (Table 4) show that POC age in the Yukon is similar to POC age in the Mackenzie and Kolyma.

## 3.3. Seasonal and Annual Fluxes of **POC and PN**

Average annual fluxes of POC and PN are highest in the Lena River and lowest in the Kolyma River (Table 5). The POC flux estimates range from  $123 - 814 \times 10^9$  g/year, while the PN flux estimates range

from 20 –  $99 \times 10^9$  g/year. The six river total is  $3055 \times 10^9$  g/year for POC and  $368 \times 10^9$  g/year for PN. Scaled to the pan-Arctic watershed, riverine POC fluxes are estimated to be  $5767 \times 10^9$  g/year, and riverine PN fluxes are estimated to be  $695 \times 10^9$  g/year. While average annual POC fluxes from the Mackenzie and

**Table 2.** Linear Regression (Standard Least Squares) Statistics for Concentration (μM) versus Water Yield (mm/d) Relationships<sup>a</sup>

	R <sup>-</sup>	Slope	Lower 95%	Upper 95%
POC				
Mackenzie	0.50	246.1	148.0	344.1
Yukon	0.27	113.8	42.8	184.7
Kolyma	0.63	50.9	36.1	65.7
Lena	0.45	42.5	25.0	59.9
Yenisey	0.40	10.7	5.7	15.6
Ob'	0.50	108.0	65.8	150.2
PN				
Mackenzie	0.56	25.1	16.4	33.8
Yukon	0.29	8.7	3.5	13.9
Kolyma	0.59	6.8	4.7	9.0
Lena	0.43	3.4	1.9	4.8
Yenisey	0.27	0.8	0.3	1.3
Ob'	0.45	12.6	7.3	18.0

<sup>&</sup>lt;sup>a</sup>All slopes are significant with 95% confidence. Lower and upper bounds of 95% confidence intervals are shown in the last two columns, respectively.

# **CAGU** Global Biogeochemical Cycles

	Mackenzie	Yukon	Kolyma	Lena	Yenisey	Ob'
	Mackenzie	TUKOH	KOIYIIIa	Lena	remsey	Ob
POC (μM)						
Average ± SE	$126 \pm 48^{AB}$	145 ± 29 <sup>A</sup>	52 ± 10 <sup>AB</sup>	60 ± 16 <sup>AB</sup>	$26 \pm 3^{B}$	97 ± 12 <sup>AB</sup>
Discharge-weighted average	201	217	84	111	32	122
PN (μM)						
Average ± SE	$10.4 \pm 3.4^{AB}$	13.1 ± 2.8 <sup>A</sup>	6.7 ± 1.5 <sup>AB</sup>	6.6 ± 1.6 <sup>AB</sup>	$3.3 \pm 0.4^{B}$	11.5 ± 2.1 <sup>AB</sup>
Discharge-weighted average	16.3	19.7	11.7	11.6	3.9	16.1
C:N (Molar Ratio)						
Average ± SE	$10.7 \pm 0.5^{ABC}$	12.2 ± 0.4 <sup>A</sup>	$9.0 \pm 0.6^{BC}$	$9.4 \pm 0.3^{ABC}$	$7.9 \pm 0.3^{C}$	11.3 ± 1.4 <sup>AB</sup>
Discharge-weighted average	10.1	11.7	8.1	9.7	8.1	9.2
POC $\delta^{13}$ C (‰)						
Average ± SE	$-28.4 \pm 0.2^{A}$	$-31.5 \pm 1.0^{B}$	$-31.8 \pm 0.8^{B}$	$-31.1 \pm 0.8^{AB}$	$-30.3 \pm 0.3^{AB}$	$-33.0 \pm 0.7^{B}$
Discharge-weighted average	-28.0	-29.0	-29.4	-29.0	-30.2	-31.7
POC Δ14C (‰)						
Average ± SE	−504 ± 17 <sup>C</sup>		−467 ± 33 <sup>C</sup>	$-293 \pm 13^{AB}$	$-309 \pm 23^{B}$	$-226 \pm 8^{A}$
Discharge-weighted average	-535		-426	-283	-274	-220
PN δ <sup>15</sup> N (‰)						
Average ± SE	$3.5 \pm 0.1^{A}$	$0.6 \pm 0.6^{B}$	$5.4 \pm 0.4^{A}$	$5.0 \pm 0.5^{A}$	$5.2 \pm 0.3^{A}$	3.1 ± 1.0 <sup>A</sup>
Discharge-weighted average	3.4	1.9	4.4	4.6	5.0	4.8

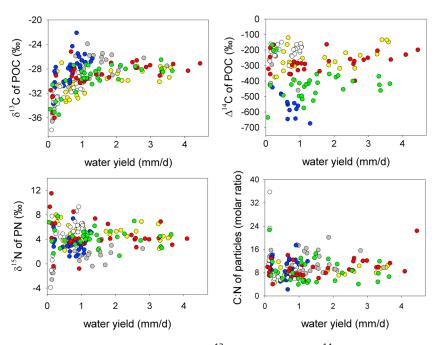
<sup>a</sup>Data were binned by month and then used to calculate straight averages (average ± 1 standard error) and discharge-weighted averages for each parameter. See methods section for a description of the monthly binning and discharge-weighting procedures. Superscript letters show results of pairwise comparisons using Tukey-Kramer HSD test. Values not connected by the same letter are significantly different (alpha 0.05).

> Yukon rivers are not markedly different from average annual POC fluxes from the Lena and Ob' rivers (Table 5), POC yields for the Mackenzie and Yukon are significantly higher than POC yields for all of the Eurasian rivers (Figure 6). The same general pattern exists for PN (i.e. the Yukon and Mackenzie have the two highest average PN yields), although the differences in PN yields between the North American and Eurasian rivers are not as stark as the differences in POC yields (Figure 6). In particular, the Mackenzie PN yield is not statistically discernable from those of the Kolyma, Lena and Ob' at a 95% confidence threshold.

> While the magnitudes of POC and PN fluxes differ greatly among rivers, the seasonality of these fluxes is broadly similar. In most cases, cumulative amounts of POC and PN exported from the beginning of May to the end of June (which include the spring freshet) are similar to, or higher than, the cumulative amounts exported over the next four open water months (Table 5). Cumulative amounts of POC and PN exported while the rivers are largely ice covered, between the beginning of November and the end of April, are much lower. POC and PN fluxes during this 6 month time frame are less than 5% of annual fluxes for the Mackenzie, Yukon,

<b>Table 4.</b> Seasonal C:N Ratios and Isotope Values of Suspended POC and PN <sup>a</sup>										
	Mackenzie	Yukon	Kolyma	Lena	Yenisey	Ob'				
C:N (Molar Ratio)										
Spring	$9.6 \pm 1.2$	12.1 ± 1.0	$8.7 \pm 1.0$	11.1 ± 1.0	$8.5 \pm 0.3$	$8.4 \pm 0.5$				
Summer	$8.8 \pm 0.7$	11.5 ± 1.2	$7.0 \pm 0.8$	$8.5 \pm 0.8$	$7.0 \pm 0.4$	$6.9 \pm 0.4$				
Winter	$11.7 \pm 0.9$	$13.0 \pm 0.7$	$12.5 \pm 3.2$	$8.6 \pm 1.2$	$8.0 \pm 1.0$	$17.8 \pm 4.8$				
POC $\delta^{13}$ C (‰)										
Spring	$-27.0 \pm 0.3$	$-27.5 \pm 0.4$	$-28.3 \pm 0.3$	$-27.8 \pm 0.2$	$-29.3 \pm 0.4$	$-30.1 \pm 0.2$				
Summer	$-28.0 \pm 0.6$	$-27.7 \pm 0.6$	$-29.0 \pm 0.4$	$-29.0 \pm 0.4$	$-31.7 \pm 0.4$	$-31.9 \pm 0.4$				
Winter	$-30.0 \pm 0.9$	$-35.0 \pm 0.5$	$-32.8 \pm 1.0$	$-32.8 \pm 1.0$	$-30.0 \pm 0.8$	$-33.9 \pm 1.0$				
POC Δ14C (‰)	)									
Spring	$-614 \pm 27$		$-404 \pm 12$	$-255 \pm 15$	$-230 \pm 17$	$-203 \pm 10$				
Summer	$-547 \pm 19$	-460	$-463 \pm 15$	$-313 \pm 9$	$-253 \pm 22$	$-217 \pm 13$				
Winter	-441	$-378 \pm 51$	$-326 \pm 90$	$-255 \pm 33$	$-374 \pm 36$	$-220 \pm 19$				
PN δ <sup>15</sup> N (‰)										
Spring	$3.1 \pm 0.4$	$1.9 \pm 0.3$	$4.1 \pm 0.4$	$4.6 \pm 0.4$	$4.9 \pm 0.3$	$6.3 \pm 0.3$				
Summer	$3.3 \pm 0.4$	$2.6 \pm 0.7$	$4.2 \pm 0.2$	$3.9 \pm 0.6$	$3.9 \pm 0.4$	$5.3 \pm 0.2$				
Winter	$4.0 \pm 0.4$	$-1.4 \pm 0.3$	5.1 ± 1.1	$6.3 \pm 1.7$	$6.2 \pm 0.9$	1.4 ± 1.7				

 $<sup>^{</sup>a}$ Averages  $\pm$  1 standard error are reported for data collected during May–June (spring), July–October (summer), and November-April (winter).



**Figure 5.** Relationships between water yield and (top left)  $\delta^{13}$ C of POC, (top right)  $\Delta^{14}$ C of POC, (bottom left)  $\delta^{15}$ N of PN, and (bottom right) C:N of particulates suspended in river water. Blue = Mackenzie, gray = Yukon, green = Kolyma, red = Lena, yellow = Yenisey, and white = Ob'.

Kolyma, and Lena (Table 5). November-April fluxes of POC and PN are proportionally higher in the Yenisey and Ob' rivers but still amount to less than 15% of annual fluxes.

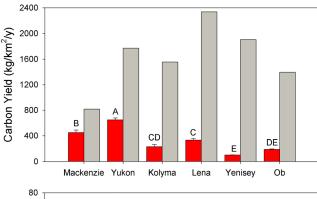
### 4. Discussion

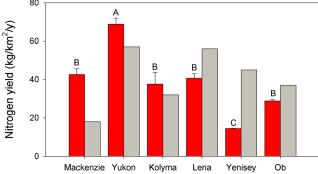
While a variety of POC and PN flux and quality estimates have been published for the major Arctic rivers (see section 4.2 for a discussion of previous flux estimates), the results presented here provide a unique opportunity for making comparisons among rivers because standardized sample collection, processing, and analysis

**Table 5.** Average Seasonal and Annual Water Discharge (km<sup>3</sup>) and Flux Estimates for POC and PN ( $10^9$  g)  $\pm 1$ Standard Error<sup>a</sup>

	Mackenzie	Yukon	Kolyma	Lena	Yenisey	Ob'	Sum	Pan-Arctic		
Spring: M	Spring: May–June (2 months)									
Q	97 ± 4	$70 \pm 6$	$43 \pm 4$	$209 \pm 13$	$274 \pm 7$	$132 \pm 5$				
POC	$540 \pm 53$	$218 \pm 24$	$72 \pm 15$	$382 \pm 32$	$142 \pm 4$	$250 \pm 10$	1604	3028		
PN	$46 \pm 4$	$21 \pm 2$	11 ± 3	$42 \pm 3$	$18 \pm 4$	$38 \pm 2$	176	332		
Summer:	July-October (4	months)								
Q	$141 \pm 6$	$104 \pm 4$	$58 \pm 4$	$319 \pm 13$	196 ± 8	$183 \pm 14$				
POC	191 ± 22	$300 \pm 15$	$49 \pm 5$	$422 \pm 26$	$73 \pm 3$	$260 \pm 15$	1293	2442		
PN	$23 \pm 2$	$34 \pm 2$	8 ± 1	$56 \pm 3$	$12 \pm 0$	$42 \pm 1$	175	331		
Winter: No	ovember-April (	(6 months)								
Q	$69 \pm 2$	$30 \pm 1$	9 ± 1	$67 \pm 5$	$160 \pm 7$	$77 \pm 1$				
POC	$29 \pm 3$	$21 \pm 1$	$2\pm0$	11 ± 1	$33 \pm 1$	$63 \pm 2$	159	300		
PN	$2.8 \pm 0.3$	$2.1 \pm 0.1$	$0.2 \pm 0.0$	$1.6 \pm 0.2$	$4.9 \pm 0.1$	$6.1 \pm 0.4$	18	34		
Annual										
Q	$306 \pm 10$	$204 \pm 7$	$109 \pm 7$	$596 \pm 28$	$630 \pm 10$	$392 \pm 17$				
POC	$758 \pm 66$	$539 \pm 26$	$123 \pm 19$	$814 \pm 52$	$249 \pm 3$	$572 \pm 20$	3055	5767		
PN	$72 \pm 5$	$57 \pm 3$	$20 \pm 3$	$99 \pm 6$	$35 \pm 4$	$86 \pm 2$	368	695		

 $<sup>^{</sup>m a}$ Averages for the Mackenzie River cover the 2004–2011 time frame. Averages for all other rivers cover 2003–2011. The pan-Arctic estimates were derived by scaling up from the combined watershed area of the six rivers to the watershed area of the pan-Arctic drainage basin (Figure 1), assuming equivalent areal yields of POC and PN.





**Figure 6.** (top) Carbon and (bottom) nitrogen yields for the major Arctic rivers. Values are annual averages  $\pm$  1 standard error for suspended POC and PN (red bars) from this study and previously published averages for DOC and DON (gray bars) from *Holmes et al.* [2012] that were calculated using PARTNERS data. Watershed areas (10 $^6$  km $^2$ ) used to calculate yields were 1.68 (Mackenzie), 0.83 (Yukon), 0.53 (Kolyma), 2.43 (Lena), 2.40 (Yenisey), and 2.99 (Ob'). Yield estimates not connected by the same letter are significantly different (Tukey-Kramer HSD test, p < 0.05).

protocols were used at all of the PARTNERS/Arctic-GRO sites. Perhaps most importantly, seasonal coverage was similar at all rivers and included sampling during winter and spring that was missing from many previous efforts. Robustness of comparisons is also strengthened by multiyear sampling that has captured a wide range of interannual variability.

# 4.1. Pan-Arctic Patterns and Regional Distinctions

Common patterns among the major Arctic rivers are primarily related to seasonality. Higher proportional fluxes of POC and PN during May and June (Table 5), lower C:N ratios during summer as compared to other seasons (Table 4), and consistent seasonal shifts in  $\delta^{13}$ C values (lowest during winter and highest during spring; Table 4) point to shared drivers controlling these variables. Key among these drivers is the timing of seasonal warming and thaw across the pan-Arctic drainage area. The resulting snowmelt pulse mobilizes large amounts of soil as well as sediment deposits within river channels in the spring. In general, suspended

particulate concentrations are positively correlated with water velocity [Meybeck et al., 2003], and thus, high particulate fluxes associated with the spring freshet are expected. However, frozen ground in the watersheds of the major Arctic rivers during the spring may limit soil mobilization. Previous work has highlighted this process as it relates to the Yukon and Mackenzie, noting that relatively old suspended POC in the rivers implicates bank erosion as the primary source of suspended sediment, as opposed to recently produced organic matter near the soil surface [Guo and Macdonald, 2006; Guo et al., 2007; Striegl et al., 2007]. For  $\delta^{13}$ C, the shift from lower values to higher values with increasing discharge (Figure 5) suggests a shift from aquatic to terrestrially derived material [Finlay, 2001; Cai et al., 2008; McClelland et al., 2014]. The  $\delta^{13}$ C values of terrestrial organic matter typically range between -26 and -29, whereas  $\delta^{13}$ C values below -30 are indicative of in situ production in lotic systems [Finlay, 2001; Alin et al., 2008; Spencer et al., 2012]. Relatively low C:N molar ratios during summer (Table 4) are also consistent with greater contributions from in situ sources. Alternatively, lower  $\delta^{13}$ C and C:N could be related to seasonal changes in the composition of soil organic matter inputs. Depleted  $\delta^{13}$ C values have been associated with contributions from methanotrophs in previous studies [Freeman et al., 1990], and although C:N ratios of organic-rich surface soils tend to have elevated C:N ratios, values of deeper soils can have C:N ratios of less than 10 [Schädel et al., 2014].

Another Arctic-wide pattern is that annual POC yields are consistently smaller than annual DOC yields for the major rivers (Figure 6). This finding generally agrees with an earlier synthesis effort by *Rachold et al.* [2004]. Our specific result that POC yields are smaller than DOC yields in the Mackenzie, however, departs from previous understanding. This is partly explained by the fact that DOC yield estimates have increased [Holmes et al., 2012] but also reflect a lower POC yield estimate for the Mackenzie as compared to some previous estimates (discussed further in section 4.2).



Relationships between PN and DON yields are less consistent. Our findings that (1) the annual PN yield is much lower than the annual DON yield in the Yenisey and (2) annual PN yields exceed annual DON yields in the Kolyma and Mackenzie (Figure 6) are consistent with Dittmar and Kattner [2003]. However, our results for the Lena and Ob' indicate that PN and DON yields (Figure 6) are more evenly matched than previously thought: Dittmar and Kattner [2003] report substantially greater DON than PON export from the Lena and Ob' rivers. This could be important for understanding the role that terrestrial inputs play in supporting productivity in Arctic coastal waters. While focused attention on the fate of riverine DOC (as has been the case during recent years) may be warranted by its dominant contribution to the total organic carbon flux, a more balanced approach is needed when considering the fate of terrestrial nitrogen inputs. Suspended PN [Mayer et al., 1998] and DON [Seitzinger and Sanders, 1997] inputs are both important sources of regenerated nitrogen supporting primary production in coastal waters (as well as direct sources of nitrogen supporting secondary production), but they impact coastal systems over different temporal and spatial domains. The importance of DON as a nitrogen source supporting productivity along the nearshore to offshore continuum is tightly coupled to water residence times [Seitzinger and Sanders, 1997]. In contrast, deposition of fluvial PN is disproportionately focused near river mouths/deltas and drops off relatively quickly with distance off shore. For example, a study of the Mackenzie estuary showed that river-supplied PN was largely depleted from the water column within 40 km of the river delta [Emmerton et al., 2008]. The losses were shown to be nonconservative and were attributed to biological uptake as well as sedimentation.

Relatively high POC yields in the Mackenzie and Yukon as compared to the other rivers (Figure 6) generally match findings for total suspended sediment yields among the major Arctic rivers [Holmes et al., 2002]. However, whereas Holmes et al. [2002] showed that the Kolyma sediment yield was higher than those of the Lena, Yenisey, and Ob', our results for POC suggest that the Kolyma aligns closely with the other Eurasian rivers. Multiple factors undoubtedly contribute to the observed difference in POC yields between the North American and Eurasian rivers, but it is particularly noteworthy that mean topographic slope (steepness) values of the Mackenzie and Yukon drainage basins are greater than those of the other major drainage basins [Amon et al., 2012]. The Mackenzie and Yukon also both receive inputs from the North American Cordillera [Millot et al., 2003]. Carson et al. [1998] showed that a majority of the total suspended sediment load carried by the Mackenzie comes from west bank tributaries that drain the North American Cordillera (specifically the Rocky and Mackenzie mountain belts). Higher sediment yields in west bank tributaries as compared to east bank tributaries of the Mackenzie have been attributed to steeper topographic gradients and more extensive deposits of fine-grained glacial sediments in mountainous terrain to the west of the Mackenzie [Carson et al., 1998]. While this general argument also applies to rivers draining mountainous versus lower gradient terrain within the adjacent Yukon River drainage area, perennial ice/snow fields and alpine glaciers are identified as particularly important sources of sediment and particulate carbon to the Yukon [Striegl et al., 2007]. Differences in PN yields (Figure 6) may be less distinct than those of POC yields because of variations in inorganic nitrogen contributions (e.g., adsorbed ammonium) to suspended PN among rivers, although these are expected to be small compared to organic nitrogen contributions.

While most of the source/composition indicators that we measured do not support regional grouping of rivers, similar POC ages in the Yukon and Kolyma (Table 4) suggest some potential commonalities in organic matter source contributions and histories within the Beringia region. Organic-rich loess deposits (referred to as yedoma in Siberia) formed during the last glacial maximum may be one source of ancient POC that makes a larger contribution to bulk  $\Delta^{14}$ C values in the Beringia region. The Kolyma River has a particularly high proportion of yedoma deposits within its drainage area, but substantial deposits of yedoma-like soils have also been reported within parts of the Yukon drainage area [Zimov et al., 2006; Walter et al., 2007; Schirrmeister et al., 2013]. These deposits can contribute to riverine POC fluxes through thermokarst activity and bank erosion.

Yedoma-like soils are less likely to be an important source of ancient particulate organic matter to the Mackenzie River because ice sheet coverage inhibited deposit formation over much of the Mackenzie drainage basin during the last glacial maximum. Goñi et al. [2005] suggests that organic matter contributions from petroleum source rocks (i.e., bitumens and kerogens) may account for relatively low bulk POC  $\Delta^{14}$ C values in the Mackenzie. In any case, work by Guo et al. [2007] shows that  $\Delta^{14}$ C values of suspended POM in the Mackenzie are consistent with predominant sourcing from deep active layer and/or permafrost soils as opposed to soils nearer the surface. In contrast, younger bulk  $\Delta^{14}$ C ages in the Ob', Yenisey, and Lena

**Table 6.** Ranges of Published Estimates for Annual POC and PN Fluxes From the Major Arctic Rivers (10<sup>9</sup> g) Compared to the New Estimates Reported Herein (Average ± 1 Standard Error)<sup>a</sup>

	POC		P1	N
River	Published Range	This Study	Published Range	This Study
Mackenzie Yukon Kolyma Lena Yenisey Ob'	317–2100 b,c,d 276–1400 <sup>f,g,h,b,i,j,d</sup> 81–410 <sup>b,l,m</sup> 380–1800 <sup>b,n,l,o,p</sup> 170–570 <sup>q,b,l,m</sup> 270–600 <sup>e,q,r,b</sup>	$758 \pm 66$ $539 \pm 26$ $123 \pm 19$ $814 \pm 52$ $249 \pm 3$ $572 \pm 20$	41–190 <sup>e,b</sup> 22–87 <sup>f,k,g,h,b,d</sup> 13–34 <sup>e,b</sup> 54–94 <sup>e,b</sup> 32–84 <sup>q,b</sup> 27–85 <sup>e,q,b</sup>	$72 \pm 5$ $57 \pm 3$ $20 \pm 3$ $99 \pm 6$ $35 \pm 4$ $86 \pm 2$

<sup>&</sup>lt;sup>a</sup>All published studies used in this compilation are listed alphabetically as footnotes. Superscripts identify the specific studies encompassed by each range. bLe Fouest et al. [2013].

suggest that either organic matter contributions from surface soil layers are proportionally greater or older organic matter sources such as yedoma are less influential. Peatlands that are a prominent feature in the Ob' and Yenisey watersheds are relatively young compared to yedoma deposits [MacDonald et al., 2006].

Although the Yukon River groups with the Mackenzie and Kolyma for POC age (i.e., these three rivers transport much older POC than the Ob', Yenisey, and Lena; Table 4), distinctly high C:N ratios and low  $\delta^{15}$ N values of suspended particulates in the Yukon River (Table 3) point to a unique organic matter profile within this system. Low δ<sup>15</sup>N values of PN (averaging ~0.8%) in the Yukon River were also reported by *Guo and Macdonald* [2006]. These results may indicate that sources of in situ production versus allochthonous contributions to the PN pool are proportionally lower in the Yukon as compared to the other rivers. Although most of the PN- $\delta^{15}$ N values measured by Guo and Macdonald [2006] were below 1%, they found higher values when chlorophyll concentrations increased. The lower  $\delta^{15} N$  values may also be linked to inputs associated with receding glaciers. The Yukon receives inputs from several major glaciers, and discharge from the Tanana River (the Yukon's largest glacierfed tributary) is increasing due to accelerated glacier melt [Brabets and Walvoord, 2009]. Studies in southeast Alaska have shown that plant communities in areas of glacier retreat are dominated by nitrogen fixing species (e.g., Alnus sinuata and Dryas drummondii) for up to a century following deglaciation [Chapin et al., 1994]. The nitrogen fixing plants, which have  $\delta^{15}N$  values between -2% and -1%, impart similar values to the soil nitrogen pool through decomposition/remineralization pathways [Hobbie et al., 1998].

#### 4.2. Comparisons With Previous Estimates of POC and PN Export

Previously published estimates of POC and PN fluxes from the major Arctic rivers were collated for comparison with our new estimates. Sixteen papers contained original POC flux estimates and eight contained original PN flux estimates for one or more of the rivers. Ranges for each river are shown in Table 6. Papers with little or no information on methods used for collecting samples and/or flux calculations were excluded. Modeling studies without direct field measurements were also excluded.

A review focusing on fluxes of total suspended sediments from the major Arctic rivers [Holmes et al., 2002] demonstrated that differences among estimates could largely be explained by differences in sampling time frames, including the number of years represented and the level of seasonal coverage. Most of the studies cited in Table 6 for POC and PN export used only 2-3 years of data to calculate flux estimates. Given the

<sup>&</sup>lt;sup>c</sup>MacDonald et al. [1998]. <sup>d</sup>Telang et al. [1991].

Dittmar and Kattner [2003].

<sup>&</sup>lt;sup>r</sup>Chikita et al. [2012].

<sup>&</sup>lt;sup>9</sup>Guo and Macdonald [2006].

<sup>&</sup>lt;sup>h</sup>Guo et al. [2012].

<sup>&</sup>lt;sup>1</sup>Leenheer [1982].

<sup>&</sup>lt;sup>j</sup>Striegl et al. [2007].

<sup>`</sup>Dornblaser and Striegl [2007].

Lobbes et al. [2000].

<sup>&</sup>lt;sup>m</sup>Vetrov and Romankevich [2004].

<sup>&</sup>lt;sup>n</sup>Lara et al. [1998].

Rachold and Hubberten [1999].

<sup>&</sup>lt;sup>p</sup>Semiletov et al. [2011].

<sup>&</sup>lt;sup>q</sup>Gebhardt et al. [2004].

<sup>&</sup>lt;sup>r</sup>Kohler et al. [2003].



substantial interannual variability in discharge and associated water chemistry exhibited by the major Arctic rivers [Holmes et al., 2012], flux estimates covering longer time frames are more likely to represent average conditions. Thus, it is not surprising that most of our estimates of annual export (Table 5) are intermediate relative to the ranges for previous estimates. Our POC and PN flux estimates for the Ob' River stand out as notable exceptions, both falling near the upper end of the previously published range of estimates. Our PN flux estimate for the Lena falls near the top of the range of previously published values as well.

Differences in calculation methods also contribute to variations among flux estimates. Le Fouest et al. [2013] used PARTNERS/Arctic-GRO data to calculate export from the major Arctic rivers for a study considering the fate of riverine nutrients on Arctic shelves but used monthly average concentrations and river discharge values (rather than a regression approach based on constituent-discharge relationships) to calculate flux estimates. This resulted in substantial differences among estimates for some rivers. For example, their POC flux estimate for the Mackenzie River is less than half of our estimated value. This discrepancy is largely explained by the fact that a regression-based approach accounts for steep changes in concentration as a function of water discharge in the Mackenzie (Figure 4) and allows for projection into peak flow conditions when ice breakup hinders sampling, while monthly averaging does not. At the other extreme, the POC flux estimate reported in Macdonald et al. [1998] for the Mackenzie River is nearly 3 times greater than our estimate. In that case, they applied data on POC content of suspended sediments (i.e., percentage organic carbon) from Yunker et al. [1993] to an estimate of the Mackenzie River sediment flux by Carson et al. [1998]. Interestingly, the dischargeconcentration regression used by Carson et al. [1998] to calculate sediment fluxes included a few extraordinarily high concentration values for July (and to a lesser extent August) that were not observed during the PARTNERS/Arctic-GRO time frame (www.arcticgreatrivers.org/data.html). The explanation for these anomalous concentrations is unclear, but their inclusion when developing discharge-concentration regression equations may have resulted in overestimation of annual sediment loads carried by the Mackenzie River.

While this section emphasizes comparisons with previous POC and PN export estimates for the major Arctic rivers, it is also informative to consider how fluvial export from the pan-Arctic drainage area compares to worldwide estimates of POC and PN export. Global models suggest that contemporary fluvial export of POC ranges from 140,000 to 197,000 Gg yr<sup>-1</sup>, and contemporary fluvial export of PN ranges from 13,500 to 29,600 Gg y<sup>-1</sup> [Beusen et al., 2005; Seitzinger et al., 2010]. Our estimates for the pan-Arctic region (Table 5) amount to approximately 3-4% and 2-5% of these global POC and PN export estimates, respectively. Considering that drainage from the pan-Arctic watershed accounts for >10% of global river water discharge [McClelland et al., 2012], these findings suggest that overall POC and PN yields from the pan-Arctic drainage area are relatively low compared to the global average.

# 5. Concluding Remarks

This paper brings together an unprecedented combination of suspended POC and PN export estimates and source/composition indicators for the major Arctic rivers, taking advantage of shared sample collection and analysis protocols under the PARTNERS/Arctic-GRO umbrella to facilitate comparisons across the pan-Arctic domain. It also provides improved (i.e., better constrained) benchmarks that can be used as a reference for tracking climate change effects on the quantity and quality of suspended particulate fluxes from the major Arctic rivers. Given that the Arctic hydrologic system is rapidly changing already [White et al., 2007; Rawlins et al., 2010], the results presented here cannot be considered a baseline per se. They do, however, capture seasonal to interannual variability and quantify average conditions for nearly a decade at the beginning of the 21st century. While we still have much to learn about the roles that river-supplied carbon and nitrogen play as resources supporting biological production in Arctic coastal waters, it is likely that changes in inputs from the major rivers will have widespread impacts on biogeochemical cycling. As we think about climate impacts on fluvial transport of organic matter in the Arctic, it is important to keep in mind that trajectories and implications of changes in dissolved versus particulate export from watersheds may be different. For example, as highlighted in this paper, changes in particulate organic matter fluxes from the major Arctic rivers have greater potential to influence nitrogen cycling in the coastal ocean than do changes in dissolved organic matter fluxes. It is also essential that we consider how physical, chemical, and biological processes acting across the river-estuary continuum modify organic matter fluxes to Arctic shelf waters and beyond. This paper characterizes fluvial POC and PN before it has started this journey. Very few studies have focused on biogeochemical cycling across the river-estuary continuum in the Arctic, and such studies will be needed to thoroughly understand the implications of changes in riverine fluxes.

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