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Seasonal and Annual Fluxes of Nutrients and Organic Matter

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from Large Rivers to the Arctic Ocean and Surrounding Seas

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24

25 Abstract

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

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42

43 Introduction

44 Massive inputs of river water make terrestrial influences particularly strong in the
45 Arctic Ocean. Containing only ~1% of global ocean volume, the Arctic Ocean receives
46 more than 10% of global river discharge. The three largest arctic rivers, the Yenisey,
47 Lena, and Ob', are each comparable in watershed area and annual discharge to the
48 Mississippi River, North America's largest river. The large river inputs to the Arctic
49 Ocean strongly influence its salinity structure and impart estuarine characteristics
50 throughout the basin (Aagaard and Carmack 1989; Serreze et al. 2003; Serreze et al.
51 2006; McClelland et al. in press).

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

66 water chemistry is expected to change as permafrost thaws, and speculate that increases
67 in major ion concentrations associated with greater weathering of mineral soils as water
68 flow paths deepen may be a particularly robust indicator.

69 Observational records extending back to the 1930's demonstrate that river
70 discharge to the Arctic Ocean from the major rivers in Russia has increased almost 10%
71 since the records began (Peterson et al. 2002). Patterns are less clear for rivers in the
72 North American Arctic, in part due to much shorter discharge records. However, a recent
73 analysis of rivers in northern Canada did detect a large increase over the 1989-2007
74 period (Déry et al. 2009), reversing the apparently declining discharge observed from
75 1964-2003 (Déry and Wood 2005). At the pan-arctic scale, total river discharge to the
76 Arctic Ocean and surrounding seas is estimated to have increased about 5.6 km³/y/y
77 during the 1964-2000 timeframe, with the rate of increase accelerating recently
78 (McClelland et al. 2006). These river discharge increases are part of a suite of changes in
79 the freshwater cycle of the Arctic that are impacting salinity in both the Arctic and North
80 Atlantic oceans, with potential implications for ocean circulation and climate (Peterson et
81 al. 2006). Changes in the seasonality of discharge have also been observed, which may
82 impact coastal biogeochemistry and physics (McClelland et al. 2004; Adam et al. 2007).

83 In contrast to the rapidly evolving understanding of arctic river discharge,
84 considerably less work has investigated the chemistry of arctic rivers. Although detailed
85 studies have been undertaken on specific aspects of individual rivers including the Yukon
86 (Striegl et al. 2005; Dornblaser and Striegl 2007; Spencer et al. 2008; Spencer et al.
87 2009), Kolyma (Welp et al. 2005; Finlay et al. 2006; Neff et al. 2006), and Mackenzie
88 (Emmerton et al. 2008a), relatively few studies have examined river fluxes to the Arctic

89 Ocean at the continental or pan-arctic scale (Gordeev et al. 1996; Holmes et al. 2000a;
90 Lobbes et al. 2000; Holmes et al. 2002; Dittmar and Kattner 2003). Those that have
91 attempted large-scale syntheses have been hampered by a number of factors including
92 inconsistent sampling and analytical methods across sites, lack of sufficient seasonal
93 coverage, and data quality issues (Bring and Destouni 2009). For example, an analysis of
94 historical nutrient data sets for 16 rivers across the Russian Arctic concluded that unusual
95 patterns in the data (such as very high estimates of ammonium concentrations) were of
96 sufficient concern that independent verification would be required (Holmes et al. 2000a).
97 When these independent analyses were done as part of an expedition to the Ob' and
98 Yenisey rivers during summer 2000, it became clear that at least some of the historical
99 data for river chemistry in the Russian Arctic were grossly in error (Holmes et al. 2001).
100 While much of the historical data for Russian arctic rivers may in fact be good,
101 systematic quality control concerns have made it extremely difficult to separate the good
102 from the bad (Zhulidov et al. 2000; Zhulidov et al. 2001).

103 As a response to these challenges and to facilitate understanding of fluvial
104 constituent fluxes to the Arctic Ocean at the pan-arctic scale, we began the PARTNERS
105 project (Pan-Arctic River Transport of Nutrients, Organic Matter, and Ssuspended
106 Sediments) in 2002, an effort to obtain a coherent data set using identical sampling and
107 analytical methods for the six largest arctic rivers in Russia, Canada, and Alaska (Figure
108 1) (McClelland et al. 2008). A related effort, the Student Partners Project, began in 2005.
109 Recent papers have used data generated from these projects to investigate dissolved
110 organic carbon (DOC), barium, alkalinity, and H₂¹⁸O concentrations and fluxes over the
111 2-4 year period of data collection (Cooper et al. 2005; Raymond et al. 2007; Cooper et al.

112 2008). Here we focus on seasonal and annual fluxes of total dissolved nitrogen (TDN),
113 dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), nitrate (NO₃),
114 total dissolved phosphorus (TDP), silica (Si), and DOC and extend the flux estimates to
115 cover a 10-year period (1999-2008) using a statistical modeling approach. For
116 constituents other than DOC, the estimates provided here represent the first time that
117 seasonal and annual fluxes have been determined using consistent sampling and
118 analytical methods at the pan-arctic scale and as such provide the best available estimates
119 for constituent flux from land to the Arctic Ocean and surrounding seas.

120 Methods

121 *Field Sampling*

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

134 for the transit time of water between the discharge and chemistry stations when they
135 differed.

136 Sampling for the PARTNERS Project began in 2003 and continued through 2006,
137 with each of the six rivers being sampled a total of 17 times (Figure 2). This effort was
138 explicitly designed to capture low flow in late winter (through the ice), high flow in the
139 spring, and intermediate flow during mid to late summer. Sampling frequency for the
140 Student Partners Project varied greatly among rivers (Figure 2).

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

151 PARTNERS samples for all analyses except DOC were collected in Nalgene
152 high-density polyethylene bottles after having been filtered through Pall Aquaprep 600
153 capsule filters (0.45 μm pore size). PARTNERS DOC samples were collected in acid-
154 leached Nalgene polycarbonate bottles after filtration through precombusted Whatman
155 QMA quartz filters (1 μm nominal pore size). Student Partners samples were collected in
156 Nalgene high-density polyethylene bottles after filtration through Millipore Sterivex-HF

157 capsule filters (0.45 μm pore size) or Whatman GFF filters (0.7 μm nominal pore size).
158 All PARTNERS and Student Partners samples were frozen until analyzed.

159 *Sample Analysis*

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

174 PARTNERS and Student Partners constituent concentration data and modeled
175 constituent fluxes are available without restriction at www.arcticgreatrivers.org and at the
176 Arctic Observing Network's Cooperative Arctic Data and Information Center (AON-
177 CADIS) as part of the Arctic Great Rivers Observatory (Arctic-GRO) data portal
178 (McClelland et al. 2008). No systematic differences in constituent concentrations,

179 attributable to either difference in sampling or analytical protocols, are apparent between
180 the PARTNERS and Student Partners data sets.

181 *Modeling*

182 Constituent fluxes from each of the six rivers were estimated using the
183 LoadRunner software package (Booth et al. 2007) to automate runs of the USGS
184 LoadEstimator program (LOADEST; Runkel et al. 2004). LOADEST uses a time series
185 of paired streamflow and constituent concentration data to construct a calibration
186 regression, which is then applied to a continuous daily discharge record to obtain daily
187 constituent loads (mass day⁻¹). The LOADEST calibration equation is chosen from a
188 suite of predetermined multiple regression models using Akaike's Information Criterion.
189 The LOADEST models we considered included discharge and seasonality as independent
190 variables, with discharge and time centered to avoid multicollinearity. We excluded all
191 models containing long-term time functions because our short data series did not lend
192 itself to detecting such trends. We used the Adjusted Maximum Likelihood Estimator
193 (AMLE) to fit the calibration equation, which is used when the residuals are normally
194 distributed. To facilitate comparisons among rivers, PARTNERS data (which have
195 consistent coverage among rivers) were used to calibrate the model, but Student Partners
196 data (which vary greatly in abundance among rivers) were not (Figure 2).

197 On the Lena River, PARTNERS constituent measurements were taken
198 approximately 520 km upstream of the discharge gauging station, while on the Yenisey
199 and Kolyma rivers constituent measurements were taken approximately 250 and 160 km
200 downstream of discharge, respectively. To correct for this offset, we applied our sample
201 concentrations to the downstream locations by determining the lag time between the two

202 sampling stations. We assumed river velocities of 1.5 m s^{-1} , which are at the high end of
203 the range modeled and observed for these rivers (Ngo-Duc et al. 2007; Smith and
204 Pavelsky 2008). This ensured that our adjustments were accurate during the high
205 discharge period, and that we were not over-correcting our data.

206 On all rivers except the Ob' and Yukon, there were not enough $\text{NH}_4\text{-N}$
207 measurements above the detection limit to meet the minimum LOADEST requirement
208 for uncensored data points. Thus, we modeled fluxes of $\text{NO}_3\text{-N}$ and DIN ($\text{NO}_3 + \text{NH}_4$),
209 but not $\text{NH}_4\text{-N}$ alone. DIN concentrations in the Eurasian rivers drop to near zero in the
210 summer months, as a result of dilution during high flows coupled with biological uptake.
211 We found that LOADEST had difficulty producing models that incorporated these near-
212 zero values. To correct this, we ran LOADEST for the Eurasian rivers using DIN and
213 $\text{NO}_3\text{-N}$ concentrations that had been increased by a fixed amount, and then corrected the
214 modeled output concentrations by subtracting this fixed value. We did this using an
215 increasingly large concentration adjustment until the flux estimate in the corrected model
216 output stabilized. Model fit was considerably improved using this approach. Across all
217 constituents, standard errors of prediction (SEP) ranged from 2.0 to 14.2 % (average
218 5.4%) of modeled constituent export. Because of our method of calculating export for
219 Eurasian $\text{NO}_3\text{-N}$ and DIN, SEP was not calculated for these export estimates.

220 We obtained daily discharge for 1999-2008 from the ArcticRIMS Project
221 (<http://rims.unh.edu>) for the Eurasian rivers, the Water Survey of Canada for the
222 Mackenzie River, and the USGS for the Yukon River (Figure 2). Calibration regressions
223 were constructed with PARTNERS constituent data collected between 2003 and 2006,
224 and used to extrapolate fluxes over the entire 10-year period for the Ob', Yenisey, Lena,

225 Kolyma, and Mackenzie rivers. Any data gaps in the discharge record were filled by
226 interpolation; there were no gaps during the peak flow period on any river. For the
227 Yukon River, discharge data were not available for 1999 or 2000, or the first three
228 months of 2001. Long-term averaged discharge was used to fill the gap at the beginning
229 of 2001 for the Yukon River, but 1999 and 2000 were excluded from the analysis (Figure
230 2).

231

232 Results and Discussion

233 The watersheds of the six rivers that are part of the PARTNERS and Student
234 Partners project together cover $11.3 \times 10^6 \text{ km}^2$, 55% of the pan-arctic watershed (Figure
235 1, Table 1) or 67% of the Arctic Ocean's drainage basin. Thus, accurately assessing
236 biogeochemical fluxes in these six rivers makes a major contribution to the goal of
237 determining total fluvial fluxes to the Arctic Ocean and surrounding seas. The combined
238 discharge of the six rivers also accounts for well over half of the river water inputs to the
239 Arctic Ocean.

240 Below we first address the seasonality of discharge and constituent fluxes, then
241 consider our estimates of annual constituent fluxes, and finally compare our estimates to
242 a selection of previously published estimates.

243 *Seasonality of Fluxes*

244 PARTNERS samples were collected throughout the year (Figure 2), both in the
245 open water season and through the ice, enabling us to investigate how constituent fluxes
246 vary seasonally. Though this has rarely been done in previous studies, it is important for
247 three reasons. First and most obviously, we can only confidently estimate annual fluxes
248 if we can also accurately quantify seasonal fluxes. Second, shifts in the seasonality of

249 constituent fluxes from large rivers over time may be a sensitive indicator of widespread
250 terrestrial change (Holmes et al. 2000a; Striegl et al. 2005; Walvoord and Striegl 2007;
251 McClelland et al. 2008). And third, the significance of fluvial fluxes to the
252 biogeochemistry of recipient estuarine and coastal ecosystems depends greatly on the
253 timing of the fluxes (McClelland et al. in press).

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

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

272 organic matter fluxes in the Yukon River (Dornblaser and Striegl 2007; Striegl et al.
273 2007). When comparing constituent fluxes among these seasons, it is important to note
274 that as defined, “spring” lasts two months, “summer” lasts 4 months, and “winter” lasts
275 six months (Table 2).

276 In spite of the fact that the spring season lasts just two months, it is the dominant
277 period for the fluxes of several constituents, particularly those related to organic matter
278 (Table 2). For example, DON flux from the six PARTNERS rivers during the two-month
279 spring period (208×10^9 g) exceeds the flux during the entire six-month winter period by
280 more than 400% (47×10^9 g). Similarly, spring DOC flux (8809×10^9 g) exceeds winter
281 DOC flux by more than 400% (2151×10^9 g). The high organic matter fluxes during
282 spring are the combined result of high discharge and high organic matter concentrations
283 during that period (Figure 2, 3). In contrast, fluxes of inorganic nutrients such as silica
284 and nitrate are much more similar among seasons. For example, the six-river flux of
285 silica in spring (1972×10^9 g) only slightly exceeds the winter flux (1641×10^9 g), while
286 the spring nitrate flux (58×10^9 g) is less than the winter nitrate flux (78×10^9 g). It is
287 important to remember that, as defined, winter is three times longer than spring. In the
288 case of the seasonality of the fluxes of these inorganic nutrients, the patterns of discharge
289 and concentrations work in opposing directions: high spring discharge (Figure 2) is
290 countered by lower concentrations during spring (Figure 3).

291 The focus above on the combined fluxes from the six PARTNERS rivers masks
292 differences in seasonality among the rivers. With respect to discharge, at one extreme
293 only 6% of annual discharge in the Kolyma River occurs during the six-month winter
294 period, whereas winter discharge in the Yenisey and Mackenzie rivers reaches ~25% of

295 annual values (Figure 4). There are also marked differences in the proportional
296 contribution of spring discharge. In the Yenisey and Kolyma rivers, sharp ascending and
297 descending limbs of the hydrograph during the freshet lead to almost half of annual
298 discharge occurring during the spring season (Figure 2 and Figure 4). Far broader peaks
299 in the Ob' and Mackenzie rivers decrease the contribution of the spring freshwater
300 discharge to ~30% of annual values.

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

307 The impact of fluvial fluxes on the biogeochemistry of the receiving estuaries and
308 coastal zones in the Arctic depends on their timing and magnitudes as well as on the
309 relative abundances of the different constituents. In all rivers, on an annual basis as well
310 as in all seasons except winter, DON fluxes exceed DIN fluxes (Figure 5, upper panel).
311 This highlights the potential significance of nutrients regenerated in the spring and
312 summer by the decomposition of dissolved organic matter that enters the coastal system
313 during the spring freshet (Holmes et al. 2008; McClelland et al. in press; Tank et al. in
314 press). On the other hand, molar TDN to TDP ratios are generally well in excess of
315 Redfield Ratios (16N:1P; Figure 5, middle panel), suggesting a relative scarcity of
316 phosphorus in the river water delivered to the coastal zone (assuming that all N and P in
317 organic forms becomes available, and at similar rates). High silica to inorganic nitrogen

318 ratios (the Redfield ratio for Si to N is 1) suggest that ample silica is available to support
319 diatom production, which is a major component of the Arctic Ocean's primary
320 production (Sakshaug 2004).

321 *Annual Fluxes and Yields*

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

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

334 The Mackenzie River stands out as having relatively low yields (mass of
335 constituent per watershed area per time) for all constituents we examined (Table 3). This
336 may be in part related to the presence of a large lake (Great Slave Lake) in the middle of
337 the watershed, which could allow for efficient processing and retention of constituents
338 transported to the lake from the upper part of the watershed. However, the high
339 suspended sediment fluxes observed in the downstream reaches of the Mackenzie River

340 (Holmes et al. 2002) indicate that tributaries entering the river below Great Slave Lake
341 have the potential to greatly modify its constituent load.

342 Raymond et al. (2007) noted a relationship between annual water yield (or runoff)
343 and annual DOC yield for the six PARTNERS rivers: as water yield increased, so did
344 DOC yield. We find a similar relationship for DON and Si: the rivers with the highest
345 water yields (Yenisey, Yukon, and Lena; Table 1) also have the highest DON and Si
346 yields (Table 3). In contrast, when comparing all six rivers there is no clear relationship
347 between water yield and annual yields of TDP, DIN, or NO₃. However, the Ob' River is
348 notable in that it has the lowest water yield but high DIN and TDP yields (Table 3),
349 perhaps reflecting the greater population density and development in the Ob' watershed
350 as compared to the other basins (Table 1).

351 *Comparison with Previous Estimates*

352 How do the flux estimates presented here compare with previous studies? Few
353 comparisons are possible for seasonal fluxes because most previous studies only
354 presented annual flux estimates. One exception is with work on seasonal N and P fluxes
355 in the Yukon River during the 2001-2005 period (Dornblaser and Striegl 2007). The
356 seasonal and annual flux estimates for NO₃, DIN, TDN, and TDP are generally within
357 10-20% of those presented here, but the comparisons are confounded because the
358 estimates are not really independent since they each use some of the same data (the
359 USGS and the PARTNERS project collaborated for sampling on the Yukon River at Pilot
360 Station).

361 In contrast to the situation for seasonal flux estimates, more comparisons are
362 possible for annual flux estimates. Coverage is best for DOC, which has received the

363 most attention in previous studies: still, we know of no other studies that report annual
364 flux estimates for each of the six rivers considered here. Several studies, however,
365 provide composite estimates that we can compare to our six rivers and pan-arctic
366 estimates (18.1 Tg yr⁻¹ and 34.0 Tg yr⁻¹, respectively) (Table 2). Dittmar and Kattner
367 (2003) estimate that the total amount of DOC discharged by rivers into the Arctic Ocean
368 is 18-26 Tg yr⁻¹. For rivers draining directly into the Arctic Ocean, Raymond et al.
369 (2007) estimate a flux of ~25 Tg yr⁻¹, increasing to 36 Tg yr⁻¹ if the entire pan-arctic
370 watershed is considered. A very similar pan-arctic estimate (37.7 Tg yr⁻¹) is obtained by
371 Manizza et al. (2009). Thus, several recent studies (including ours) point to an annual
372 fluvial DOC flux estimate from the pan-arctic watershed of 34-38 Tg, with ~25 Tg yr⁻¹
373 being discharged directly into the Arctic Ocean, although again it should be noted that
374 these estimates are not all truly independent as both the Raymond et al. (2007) and
375 Manizza et al. (2009) estimates rely at least in part on PARTNERS data.

376 Fewer comparisons are possible for the other constituents we consider (TDN,
377 DON, DIN, NO₃, TDP, and Si). Moreover, in most cases the raw concentration and
378 discharge data used to generate the flux estimates are not published or widely available,
379 making critical evaluation of the flux estimates difficult or impossible. That being said,
380 we find cases where the estimates we provide are very close to previously published
381 estimates, whereas in other cases there are large differences. For example, our annual
382 nitrate flux estimates for the Yenisey, Lena, and Kolyma rivers are within 10% of the
383 values given by Gordeev et al. (1996), one of the most widely used references regarding
384 biogeochemical fluxes from large arctic rivers. On the other hand, our annual DON flux
385 estimates for the Lena and Kolyma rivers are 2-3 times lower than those reported in that

386 same paper. Furthermore, our TDP estimates are generally only one-half to one-third of
387 those reported by Gordeev et al. (1996), whereas our silica flux estimates, though
388 variable, differ on average by only ~3%. Rigorous explanations for differences or
389 similarities are elusive except in cases when discharge and concentration data are readily
390 available for comparison, along with detailed descriptions of the methods used to
391 calculate annual fluxes from periodic measurements of constituent concentrations. Prior
392 to the PARTNERS project, this sort of information has not been readily available for
393 large-scale studies of biogeochemical fluxes in arctic rivers.

394 Conclusions

395 The PARTNERS project was an unprecedented effort to capture the seasonal
396 dynamics of constituent fluxes from the major arctic rivers in Russia, Canada, and Alaska
397 over a multi-year period using standardized sampling and analytical protocols. The 17
398 major sampling campaigns on each of the rivers spanned most of the range of annual
399 discharge extremes in each river and covered all seasons (Figure 2). Increased temporal
400 resolution was achieved on several of the rivers as part of the Student Partners Project.
401 The resulting data sets, available without restriction at www.arcticgreatrivers.org and at
402 the Arctic Observing Network's Cooperative Arctic Data and Information Center (AON-
403 CADIS) as part of the Arctic Great Rivers Observatory (Arctic-GRO) data portal, allow
404 for improved understanding of seasonal and annual constituent fluxes and set the baseline
405 against which to judge future changes.

406 The focus of this paper is on mean fluxes, annual and seasonal, over the 1999 to
407 2008 period. However, just as discharge varies from year to year within each river
408 (Figure 2), so to do constituent fluxes. For example, from 1999-2008, our model results

409 suggest that annual fluxes in the Lena River varied from 4.1 to 7.4 Tg for DOC and from
410 1.1 to 1.6 Tg Si. It is important to recognize that the impact of fluvial inputs on the
411 receiving coastal waters at any particular time is a function of the actual fluxes over a
412 relatively short time frame, more so than the long-term mean fluxes. As estimates of
413 long-term mean constituent fluxes become better constrained, increased attention should
414 be directed toward consideration of the implications of interannual variability in
415 constituent fluxes.

416 The watersheds of the rivers that are the focus of the PARTNERS project and its
417 successor (the Arctic Great Rivers Observatory; Arctic-GRO) together cover more than
418 50% of the pan-arctic watershed. To estimate total fluxes to the Arctic Ocean and
419 surrounding seas, we assumed that constituent yields were the same in the unmonitored
420 portion of the watershed and scaled-up accordingly (Table 2). However, the unmonitored
421 rivers tend to have smaller, more northerly watersheds that ring the Arctic Ocean, so it is
422 likely that at least for some constituents yields may be considerably different than for the
423 larger rivers whose watersheds extend much further south. Moreover, trajectories of
424 change with future warming may differ among these classes of rivers. Although
425 biogeochemical fluxes from some smaller arctic watersheds have received considerable
426 attention, particularly on the North Slope of Alaska (Kling et al. 1991; Peterson et al.
427 1992; McClelland et al. 2007; Bowden et al. 2008), at the pan-arctic scale they represent
428 a significant gap in our ability to confidently assess land-ocean fluxes.

429 Finally, we recognize that what we often consider to be fluxes to the ocean may in
430 fact be better characterized as fluxes to estuaries or the coastal zone. As is widely
431 understood in temperate or tropical estuarine systems, this distinction is important

432 because extensive processing in estuaries and coastal zones often substantially modifies
433 fluvial constituent fluxes before they reach the open ocean (Nixon et al. 1996; Kemp et
434 al. 1997; Holmes et al. 2000b; Tobias et al. 2003). The same is true in arctic estuaries
435 and near-shore zones (Emmerton et al. 2008b), although our understanding of estuarine
436 processes in the Arctic is far less developed than in other regions, particularly with
437 respect to seasonality (McClelland et al. in press and references therein). Improved
438 understanding of the impact of fluvial inputs on the biogeochemistry of the Arctic Ocean
439 as a whole, as well as on the coastal zone of the Arctic, will require increased attention on
440 estuarine and coastal processes despite the daunting logistical challenges facing near-
441 shore research in the Arctic.

442

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656 Figure Captions

657 Figure 1. Map showing the watersheds of the six rivers included in this study. Red dots
658 show sampling locations (Ob' at Salekhard, Yenisey at Dudinka, Lena at
659 Zhigansk, Kolyma at Cherskiy, Yukon at Pilot Station, Mackenzie at Tsiigehtchic
660 or Inuvik), generally located close to the mouths of the rivers to facilitate
661 estimation of constituent fluxes to the ocean. The bold red line shows the
662 boundary of the 20.5×10^6 km² pan-arctic watershed. Together the six rivers
663 cover 53% of the pan-arctic watershed.

664 Figure 2. Daily discharge for each of the six rivers from 1999 through 2008 and dates
665 when PARTNERS and Student Partners samples were collected. The red
666 triangles show the dates where samples when samples were collected as part of
667 the PARTNERS Project (17 times per river). The blue circles indicate the dates
668 that samples were collected as part of the Student Partners Project.

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

676 Figure 4. Percentage of annual water and constituent fluxes in the different seasons. As
677 described in the text, constituent fluxes were estimated for the 1999-2008 period
678 (2001-2008 for the Yukon River) using LOADEST. Red indicates samples that

679 were collected in Spring (May and June), blue indicates samples that were
680 collected in Summer (July through October), and yellow indicates samples that
681 were collected in Winter (November through April).

682 Figure 5. Annual and seasonal molar flux ratios of DON:DIN (upper panel), TDN:TDP
683 (middle panel), and Si:DIN (lower panel). As described in the text, constituent
684 fluxes were estimated for the 1999-2008 period (2001-2008 for the Yukon River)
685 using LOADEST. The horizontal dashed line in the upper panel indicates a flux
686 ratio of 1. The final set in each figure, labeled “Combined”, indicates the ratios
687 when the fluxes from all six rivers are summed.

688

689

Figure 1

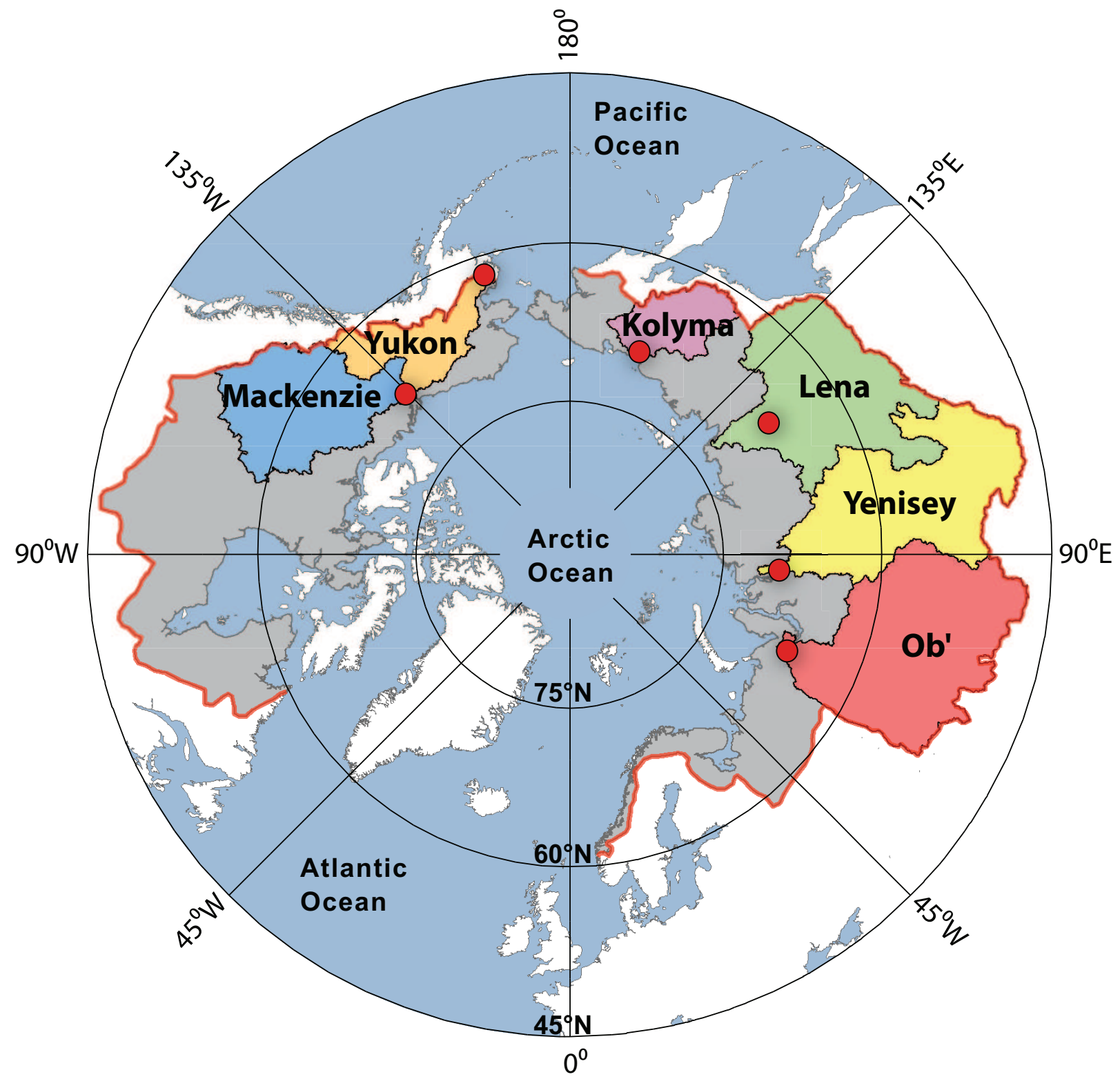
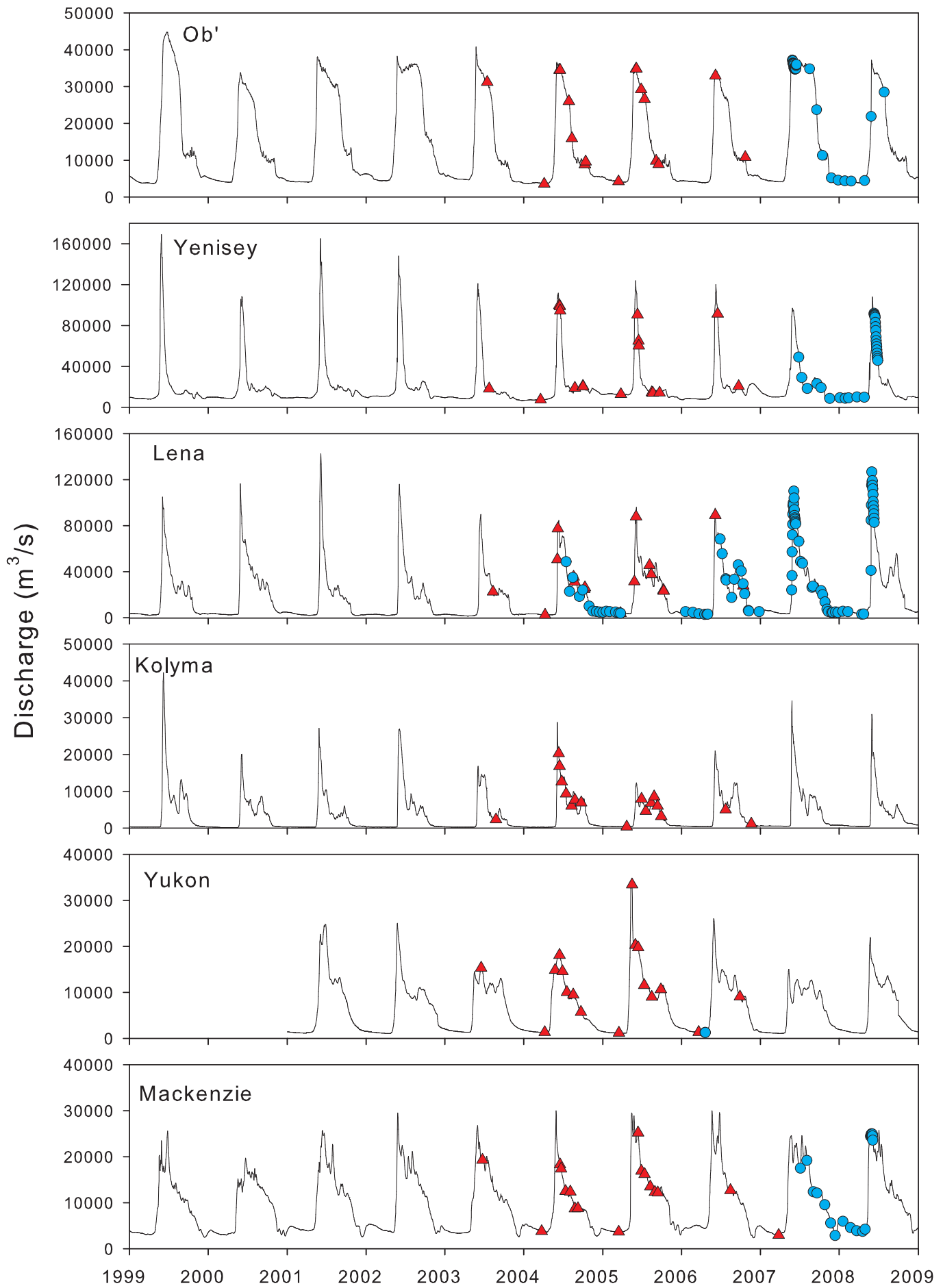


Figure 2

Fig. 2



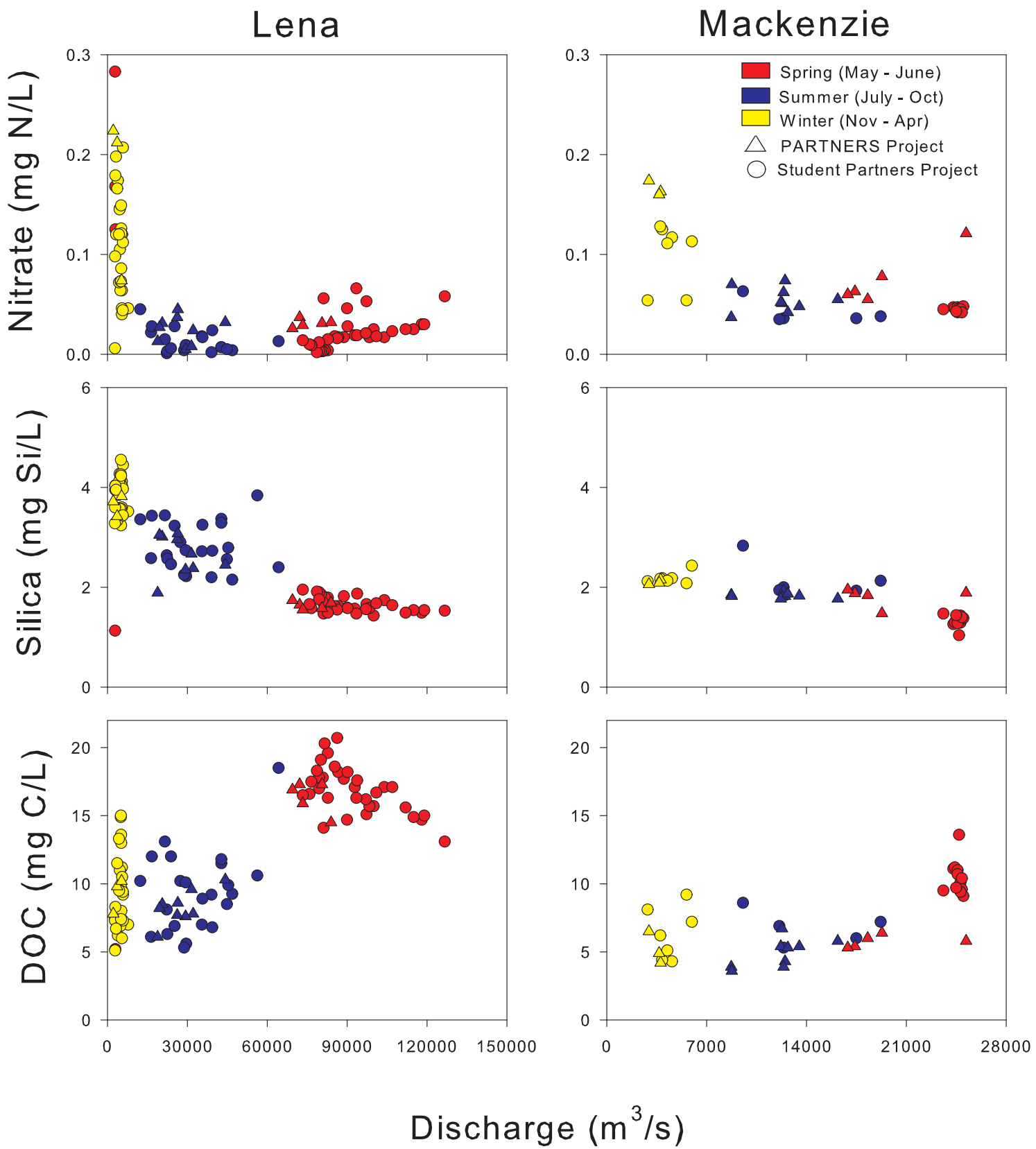


Figure 4

Fig. 4

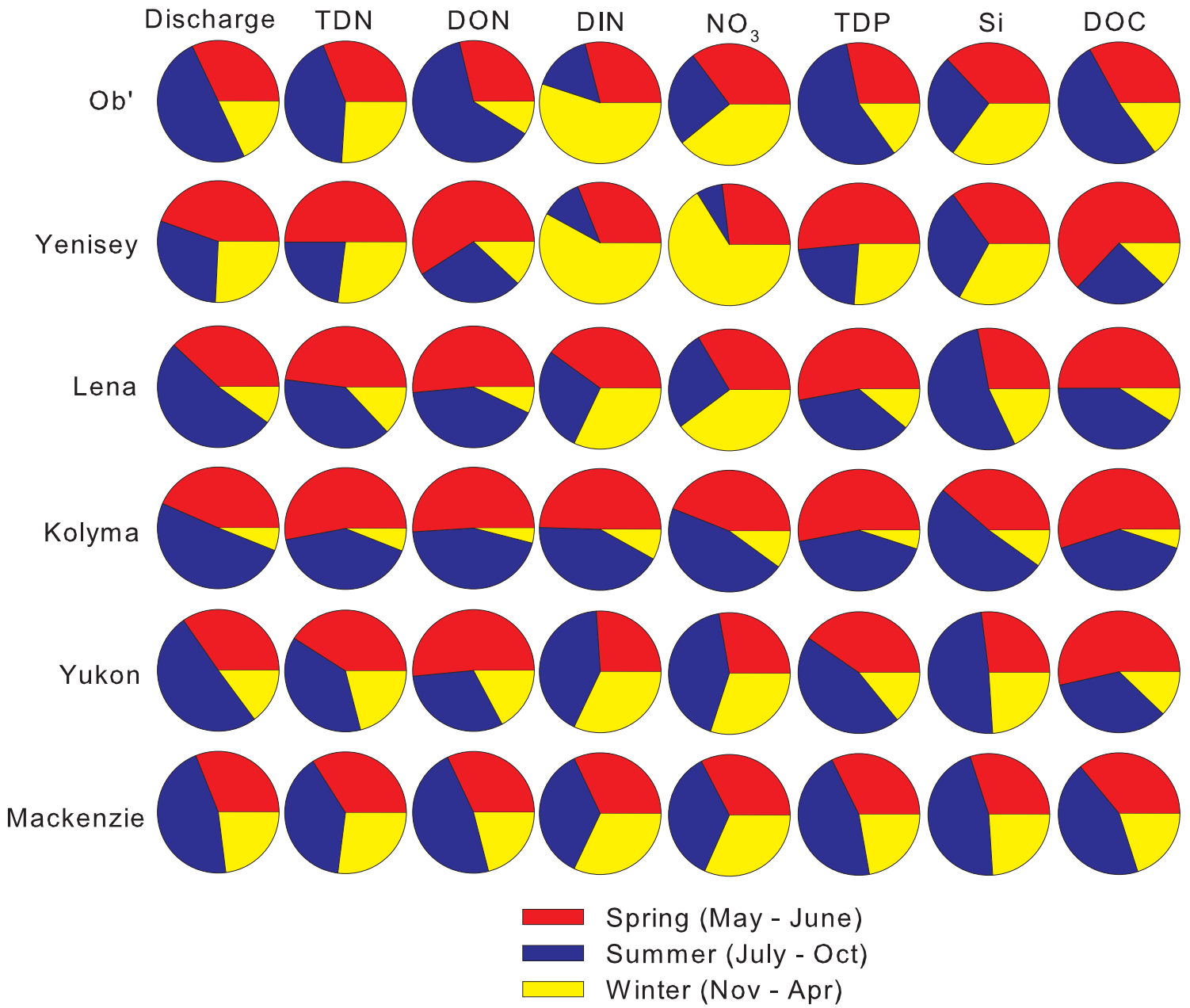


Figure 5

Fig. 5

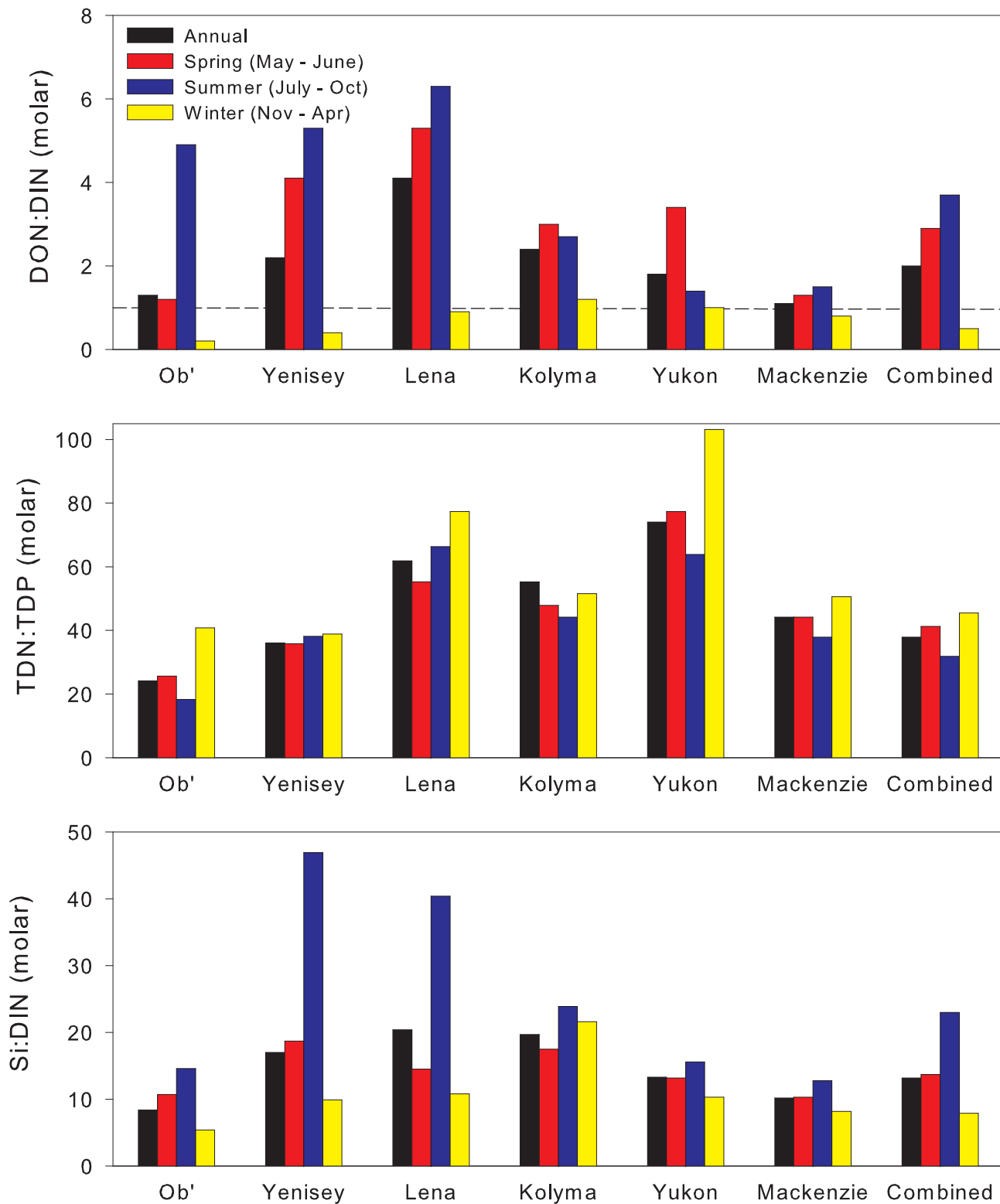


Table 1

Table 1. Discharge gauging stations, PARTNERS sampling locations, and watershed characteristics. 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 the Center for International Earth Science Information Network (<http://sedac.ciesin.columbia.edu/gpw>).

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 yr ⁻¹) – at gauging station	427	636	581	111	208	298	2261
Discharge (km ³ yr ⁻¹) – total	427	673	588	136	208	316	2348
Runoff (mm yr ⁻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)	10	3	0.3	<0.1	0.1	0.2	-

Table 2

Table 2. Average seasonal and annual constituent fluxes (1999 through 2008) for the six rivers that were part of the PARTNERS Project. All units are 10^9 g (as N, P, Si, or C), except for discharge (Q) which is given in km^3 . 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.

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	1972	3707
DOC	1338	2924	2823	449	783	493	8809	16,559
Summer, July – October (4 months)								
Q	214	190	306	57	106	139	1011	
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	2449	4604
DOC	2171	1183	2350	329	508	610	7150	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	1641	3085
DOC	609	537	508	40	182	275	2151	4043
Annual Fluxes								
Q	427	636	581	111	208	298	2261	
TDN	186	163	168	25	67	60	669	1258
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	1453	1740	1347	276	694	554	6062	11,395
DOC	4119	4645	5681	818	1472	1377	18,109	34,042

Table 3. Average annual constituent yields ($\text{kg km}^{-2} \text{yr}^{-1}$) and water yield ($\text{m}^3 \text{km}^{-2} \text{yr}^{-1}$).

	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	1396	1904	2338	1555	1771	820
Water Yield	1430	2590	2400	1660	2480	1770