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

Robert M. Holmes[1*], James W. McClelland[2], Bruce J. Peterson[3], Suzanne E. Tank[3], Ekaterina Bulygina[1], Timothy I. Eglinton[4], Viacheslav V. Gordeev[5], Tatiana Y. Gurtovaya[6], Peter A. Raymond[7], Daniel J. Repeta[4], Robin Staples[8], Robert G. Striegl[9], Alexander V. Zhulidov[6], Sergey A. Zimov[10]

[1]The Woods Hole Research Center, Falmouth, Massachusetts USA
[2]The University of Texas at Austin, Port Aransas, Texas USA
[3]Marine Biological Laboratory, Woods Hole, Massachusetts USA
[4]Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA
[5]P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia
[6]South Russia Centre for Preparation and Implementation of International Projects, Rostov-on-DON, Russia
[7]Yale School of Forestry and Environmental Studies, Yale University, Connecticut, USA
[8]Department of Indian and Northern Affairs, Yellowknife, Canada
[9]USGS, Boulder, Colorado USA
[10]Northeast Science Station, Cherskiy, Russia

*Corresponding Author: Robert M. Holmes
rmholmes@whrc.org, phone 508-444-1548, fax 508-444-1848

Abstract

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

Introduction

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

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

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

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

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

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

As a response to these challenges and to facilitate understanding of fluvial constituent fluxes to the Arctic Ocean at the pan-arctic scale, we began the PARTNERS project (Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments) in 2002, an effort to obtain a coherent data set using identical sampling and analytical methods for the six largest arctic rivers in Russia, Canada, and Alaska (Figure 1) (McClelland et al. 2008). A related effort, the Student Partners Project, began in 2005. Recent papers have used data generated from these projects to investigate dissolved organic carbon (DOC), barium, alkalinity, and $H_2{}^{18}O$ concentrations and fluxes over the 2-4 year period of data collection (Cooper et al. 2005; Raymond et al. 2007; Cooper et al.

2008). Here we focus on seasonal and annual fluxes of total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), nitrate (NO_3), total dissolved phosphorus (TDP), silica (Si), and DOC and extend the flux estimates to cover a 10-year period (1999-2008) using a statistical modeling approach. For constituents other than DOC, the estimates provided here represent the first time that seasonal and annual fluxes have been determined using consistent sampling and analytical methods at the pan-arctic scale and as such provide the best available estimates for constituent flux from land to the Arctic Ocean and surrounding seas.

Methods

Field Sampling

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

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

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

Sample Analysis

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

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

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 NH_4-N
207 measurements above the detection limit to meet the minimum LOADEST requirement
208 for uncensored data points. Thus, we modeled fluxes of NO_3-N and DIN (NO_3 + NH_4),
209 but not NH_4-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 NO_3-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 NO_3-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 x 10^6 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 x 10^9 g) exceeds the flux during the entire six-month winter period by
280 more than 400% (47 x 10^9 g). Similarly, spring DOC flux (8809 x 10^9 g) exceeds winter
281 DOC flux by more than 400% (2151 x 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 x 10^9 g) only slightly exceeds the winter flux (1641 x 10^9 g), while
286 the spring nitrate flux (58 x 10^9 g) is less than the winter nitrate flux (78 x 10^9g). 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 NO_3. 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 NO_3, 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, NO_3, 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

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

Conclusions

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

The focus of this paper is on mean fluxes, annual and seasonal, over the 1999 to 2008 period. However, just as discharge varies from year to year within each river (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 temperature or tropical estuarine systems, this distinction is important

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

Acknowledgments

This work was supported by the National Science Foundation through grants OPP-0229302, OPP-0519840, OPP-0732522, and OPP-0732944. Additional support was provided by the U. S. Geological Survey (Yukon River) and the Department of Indian and Northern Affairs (Mackenzie River). We thank Suzanne Thomas and Kate Morkeski for assistance using Loadest to model constituent fluxes, and Rainer Amon, Tim Brabets, Ludmila Boeva, Ludmila Kosmenko, Charlie Couvillon, Elena Dunaeva, Martin Kelly, Dave Milburn, Yana Adreeva, Anna Suslova, and Mikhail Suslov for assistance with sample collection or project coordination. Greg Fiske assisted with GIS analysis and figures and Alexander Shiklomanov provided additional discharge data for the Kolyma River.

References

Aagaard, K. and E. C. Carmack. 1989. The role of sea ice and other fresh water in the arctic circulation. Journal of Geophysical Research 94:14485-14498.

ACIA. 2004. Impacts of a Warming Climate - Arctic Climate Impact Assessment. Cambridge University Press.

Adam, J. C., I. Haddeland, F. Su, and D. P. Lettenmaier. 2007. Simulation of reservoir influences on annual and seasonal streamflow changes for the Lena, Yenisei, and Ob' rivers. Journal of Geophysical Research-Atmospheres 112:D24114, doi:24110.21029/22007JD008525.

Booth, G., P. Raymond, and N.-H. Oh. 2007. *LoadRunner*. Software and website, Yale University, New Haven, CT <http://research.yale.edu/environment/loadrunner/>.

Bowden, W. B., M. N. Gooseff, A. Balser, A. Green, B. J. Peterson, and J. Bradford. 2008. Sediment and nutrient delivery from thermokarst features in the foothills of the North Slope, Alaska: Potential impacts on headwater stream ecosystems. Journal of Geophysical Research-Biogeosciences 113:G02026, doi:02010.01029/02007JG000470.

Bring, A. and G. Destouni. 2009. Hydrological and hydrochemical observation status in the pan-Arctic drainage basin. Polar Research 28:327-338.

Brown, J., O. J. Ferrians, Jr., J. A. Heginbottom, and E. S. Melnikov. 1998, revised February 2001. *Circum-arctic map of permafrost and ground ice conditions.* Boulder, CO: National Snow and Ice Data Center/World Data Center for Glaciology. Digital media.

Clesceri, L. S., A. E. Greenberg, and A. E. Eaton, editors. 1998. Standard Methods for the Examination of Water and Wastewater. 20th edition. American Pubic Health Association, Washington DC.

Cooper, L. W., R. Benner, J. W. McClelland, B. J. Peterson, R. M. Holmes, P. A. Raymond, D. A. Hansell, J. M. Grebmeier, and L. A. Codispoti. 2005. Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. Journal of Geophysical Research-Biogeosciences 110:G02013, doi:02010.01029/02005JG000031.

Cooper, L. W., J. W. McClelland, R. M. Holmes, P. A. Raymond, J. J. Gibson, C. K. Guay, and B. J. Peterson. 2008. Flow-weighted values of runoff tracers (delta 18O, DOC, Ba, alkalinity) from the six largest Arctic rivers. Geophysical Research Letters 35:L18606, doi:18610.11029/12008GL035007.

Déry, S. J., M. A. Hernandez-Henriquez, J. E. Burford, and E. F. Wood. 2009. Observational evidence of an intensifying hydrological cycle in northern Canada. Geophysical Research Letters 36:L13402, doi:13410.11029/12009GL038852.

Déry, S. J. and E. F. Wood. 2005. Decreasing river discharge in northern Canada. Geophysical Research Letters 32:L10401, doi:10410.11029/12005GL022845.

Dittmar, T. and G. Kattner. 2003. The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review. Marine Chemistry 83:103-120.

Dornblaser, M. M. and R. G. Striegl. 2007. Nutrient (N, P) loads and yields at multiple scales and subbasin types in the Yukon River basin, Alaska. Journal of Geophysical Research-Biogeosciences 112:G04S57, doi:10.1029/2006JG000366.

Emmerton, C. A., L. F. W. Lesack, and W. F. Vincent. 2008a. Mackenzie River nutrient delivery to the Arctic Ocean and effects of the Mackenzie Delta during open water conditions. Global Biogeochemical Cycles 22:GB1024, doi:1010.1029/2006GB002856.

Emmerton, C. A., L. F. W. Lesack, and W. F. Vincent. 2008b. Nutrient and organic matter patterns across the Mackenzie River, estuary and shelf during the seasonal recession of sea-ice. Journal of Marine Systems 74:741-755.

Finlay, J., J. Neff, S. Zimov, A. Davydova, and S. Davydov. 2006. Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC. Geophysical Research Letters 33:L10401, doi:10410.11029/12006GL025754.

Gordeev, V. V., J. M. Martin, I. S. Sidorov, and M. V. Sidorova. 1996. A reassessment of the Eurasian river input of water, sediment, major elements, and nutrients to the Arctic Ocean. American Journal of Science 296:664-691.

Holmes, R. M., B. J. Peterson, V. V. Gordeev, A. V. Zhulidov, M. Meybeck, R. B. Lammers, and C. J. Vorosmarty. 2000a. Flux of nutrients from Russian rivers to the Arctic Ocean: Can we establish a baseline against which to judge future changes? Water Resources Research 36:2309-2320.

Holmes, R. M., B. J. Peterson, L. Deegan, J. Hughes, and B. Fry. 2000b. Nitrogen biogeochemistry in the oligohaline zone of a New England estuary. Ecology 81:416-432.

Holmes, R. M., B. J. Peterson, A. V. Zhulidov, V. V. Gordeev, P. N. Makkaveev, P. A. Stunzhas, L. S. Kosmenko, G. H. Kohler, and A. I. Shiklomanov. 2001. Nutrient

chemistry of the Ob' and Yenisey Rivers, Siberia: results from June 2000 expedition and evaluation of long-term data sets (vol 75, pg 219, 2001). Marine Chemistry 76:135-135.

Holmes, R. M., J. W. McClelland, B. J. Peterson, I. A. Shiklomanov, A. I. Shiklomanov, A. V. Zhulidov, V. V. Gordeev, and N. N. Bobrovitskaya. 2002. A circumpolar perspective on fluvial sediment flux to the Arctic Ocean. Global Biogeochemical Cycles 16:1098, doi:1010.1029/2001GB001849.

Holmes, R. M., J. W. McClelland, P. A. Raymond, B. B. Frazer, B. J. Peterson, and M. Stieglitz. 2008. Lability of DOC transported by Alaskan rivers to the arctic ocean. Geophysical Research Letters 35:L03402, doi:03410.01029/02007gl032837.

IPCC. 2007. Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Kemp, W. M., E. M. Smith, M. MarvinDiPasquale, and W. R. Boynton. 1997. Organic carbon balance and net ecosystem metabolism in Chesapeake Bay. Marine Ecology-Progress Series 150:229-248.

Kling, G. W., G. W. Kipphut, and M. C. Miller. 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 251:298-301.

Lobbes, J. M., H. P. Fitznar, and G. Kattner. 2000. Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. Geochimica Et Cosmochimica Acta 64:2973-2983.

McClelland, J. W., S. J. Dery, B. J. Peterson, R. M. Holmes, and E. F. Wood. 2006. A pan-arctic evaluation of changes in river discharge during the latter half of the 20th century. Geophysical Research Letters 33:L06715, doi:06710.01029/02006GL025753.

McClelland, J. W., R. M. Holmes, B. J. Peterson, R. Amon, T. Brabets, L. Cooper, J. Gibson, V. V. Gordeev, C. Guay, D. Milburn, T. Staples, P. A. Raymond, I. Shiklomanov, R. Striegl, A. Zhulidov, T. Gurtovaya, and S. Zimov. 2008. Development of a pan-arctic database for river chemistry. EOS 89:217-218.

McClelland, J. W., R. M. Holmes, B. J. Peterson, and M. Stieglitz. 2004. Increasing river discharge in the Eurasian Arctic: Consideration of dams, permafrost thaw, and fires as potential agents of change. Journal of Geophysical Research-Atmospheres 109:D18102, doi:18110.11029/12004JD004583.

McClelland, J. W., M. Stieglitz, F. Pan, R. M. Holmes, and B. J. Peterson. 2007. Recent changes in nitrate and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska. Journal of Geophysical Research 112:G04S60, doi:10.1029/2006JG000371.

McClelland, J. W., R. M. Holmes, K. H. Dunton, and R. Macdonald. in press. The Arctic Ocean estuary. Estuaries and Coasts, 10.1007/s12237-010-9357-3.

Neff, J. C., J. C. Finlay, S. A. Zimov, S. P. Davydov, J. J. Carrasco, E. A. G. Schuur, and A. I. Davydova. 2006. Seasonal changes in the age and structure of dissolved

organic carbon in Siberian rivers and streams. Geophysical Research Letters 33:L23401, doi:23410.21029/22006GL028222.

Ngo-Duc, T., T. Oki, and S. Kanae. 2007. A variable streamflow velocity method for global river routing model: model description and preliminary results. Hydrology and Earth System Sciences Discussions 4:4389-4414.

Nixon, S. W., J. W. Ammerman, L. P. Atkinson, V. M. Berounsky, G. Billen, W. C. Boicourt, W. R. Boynton, T. M. Church, D. M. Ditoro, R. Elmgren, J. H. Garber, A. E. Giblin, R. A. Jahnke, N. J. P. Owens, M. E. Q. Pilson, and S. P. Seitzinger. 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35:141-180.

Peterson, B. J., T. Corliss, K. Kriet, and J. E. Hobbie. 1992. Nitrogen and phosphorus concentrations and export for the upeer Kuparuk River on the North Slope of Alaska in 1980. Hydrobiologia 240:61-69.

Peterson, B. J., R. M. Holmes, J. W. McClelland, C. J. Vorosmarty, R. B. Lammers, A. I. Shiklomanov, I. A. Shiklomanov, and S. Rahmstorf. 2002. Increasing river discharge to the Arctic Ocean. Science 298:2171-2173.

Peterson, B. J., J. McClelland, R. Curry, R. M. Holmes, J. E. Walsh, and K. Aagaard. 2006. Trajectory shifts in the Arctic and subarctic freshwater cycle. Science 313:1061-1066.

Rawlins, M. A., M. Steele, M. M. Holland, J. C. Adam, J. E. Cherry, J. A. Francis, P. Y. Groisman, L. D. Hinzman, T. G. Huntington, D. L. Kane, J. S. Kimball, R. Kwok, R. B. Lammers, C. M. Lee, D. P. Lettenmaier, K. C. McDonald, E. Podest, J. W. Pundsack, B. Rudels, M. C. Serreze, A. Shiklomanov, O. Skagseth, T. J. Troy, C.

J. Vorosmarty, M. Wensnahan, E. F. Wood, R. Woodgate, D. Yang, K. Zhang, and T. Zhang. Analysis of the arctic system for freshwater cycle intensification: observations and expectations. Journal of Climate 23:5715-5737.

Raymond, P. A., J. W. McClelland, R. M. Holmes, A. V. Zhulidov, K. Mull, B. J. Peterson, R. G. Striegl, G. R. Aiken, and T. Y. Gurtovaya. 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochemical Cycles 21:GB4011, doi:4010.1029/2007GB002934.

Runkel, R. L., C. G. Crawford, and T. A. Cohn. 2004. Load Estimator (LOADEST): A FORTRAN Program for Estimating Constituent Loads in Streams and Rivers. Page 69 p. U.S. Geological Survey Techniques and Methods Book 4.

Sakshaug, E. 2004. Primary and secondary production in the arctic seas. Pages 57-81 *in* R. Stein and R. W. Macdonald, editors. The organic carbon cycle in the Arctic Ocean. Springer-Verlag, Berlin.

Serreze, M. C., A. P. Barrett, A. G. Slater, R. A. Woodgate, K. Aagaard, R. B. Lammers, M. Steele, R. Moritz, M. Meredith, and C. M. Lee. 2006. The large-scale freshwater cycle of the Arctic. Journal of Geophysical Research-Oceans 111:C11010, doi:11010.11029/12005JC003424.

Serreze, M. C., D. H. Bromwich, M. P. Clark, A. J. Etringer, T. Zhang, and R. Lammers. 2003. Large-scale hydro-climatology of terrestrial arctic drainage system. Journal of Geophysical Research 108:D2, 8160, doi:8110.1029/2001JD000919.

Smith, L. C. and T. M. Pavelsky. 2008. Estimation of river discharge, propagation speed, and hydraulic geometry from space: Lena River, Siberia. Water Resources Research 44:W03427, 03410.01029/02007wr006133.

Spencer, R. G. M., G. R. Aiken, K. D. Butler, M. M. Dornblaser, R. G. Striegl, and P. J. Hernes. 2009. Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. Geophysical Research Letters 36:L06401, 06410.01029/02008gl036831.

Spencer, R. G. M., G. R. Aiken, K. P. Wickland, R. G. Striegl, and P. J. Hernes. 2008. Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. Global Biogeochemical Cycles 22:GB4002, doi:4010.1029/2008GB003231.

Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. Geophysical Research Letters 32:L21413, doi:21410.21029/22005gl024413.

Striegl, R. G., M. M. Dornblaser, G. R. Aiken, K. P. Wickland, and P. A. Raymond. 2007. Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001-2005. Water Resources Research 43:W02411, doi:02410.01029/02006WR005201.

Tank, S. E., M. Manizza, R. M. Holmes, J. W. McClelland, and B. J. Peterson. in press. The input of nutrients and organic matter to the Arctic Ocean and their potential impact on ocean processes. Estuaries and Coasts.

Tobias, C. R., M. Cieri, B. J. Peterson, L. A. Deegan, J. Vallino, and J. Hughes. 2003. Processing watershed-derived nitrogen in a well-flushed New England estuary. Limnology and Oceanography 48:1766-1778.

Walvoord, M. A. and R. G. Striegl. 2007. Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen. Geophysical Research Letters 34.

Welp, L. R., J. T. Randerson, J. C. Finlay, S. P. Davydov, G. M. Zimova, A. I. Davydova, and S. A. Zimov. 2005. A high-resolution time series of oxygen isotopes from the Kolyma River: implications for the seasonal dynamics of discharge and basin-scale water use. Geophysical Research Letters 32:L14404, doi:14410.11029/12005GL022857.

White, D., L. Hinzman, L. Alessa, J. Cassano, M. Chambers, K. Falkner, J. Francis, W. J. Gutowski, M. Holland, R. M. Holmes, H. Huntington, D. Kane, A. Kliskey, C. Lee, J. McClelland, B. Peterson, T. S. Rupp, F. Straneo, M. Steele, R. Woodgate, D. Yang, K. Yoshikawa, and T. Zhang. 2007. The arctic freshwater system: Changes and impacts. Journal of Geophysical Research-Biogeosciences 112:G04S54, doi:10.1029/2006JG000353.

Zhulidov, A. V., V. V. Khlobystov, R. D. Robarts, and D. F. Pavlov. 2000. Critical analysis of water quality monitoring in the Russian Federation and former Soviet Union. Canadian Journal of Fisheries and Aquatic Sciences 57:1932-1939.

Zhulidov, A. V., R. D. Robarts, and V. V. Khlobystov. 2001. The need and requirements for modernizing surface water quality monitoring in the Russian Federation. Water International 26:536-546.

Figure Captions

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

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

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

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

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

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

Figure 1

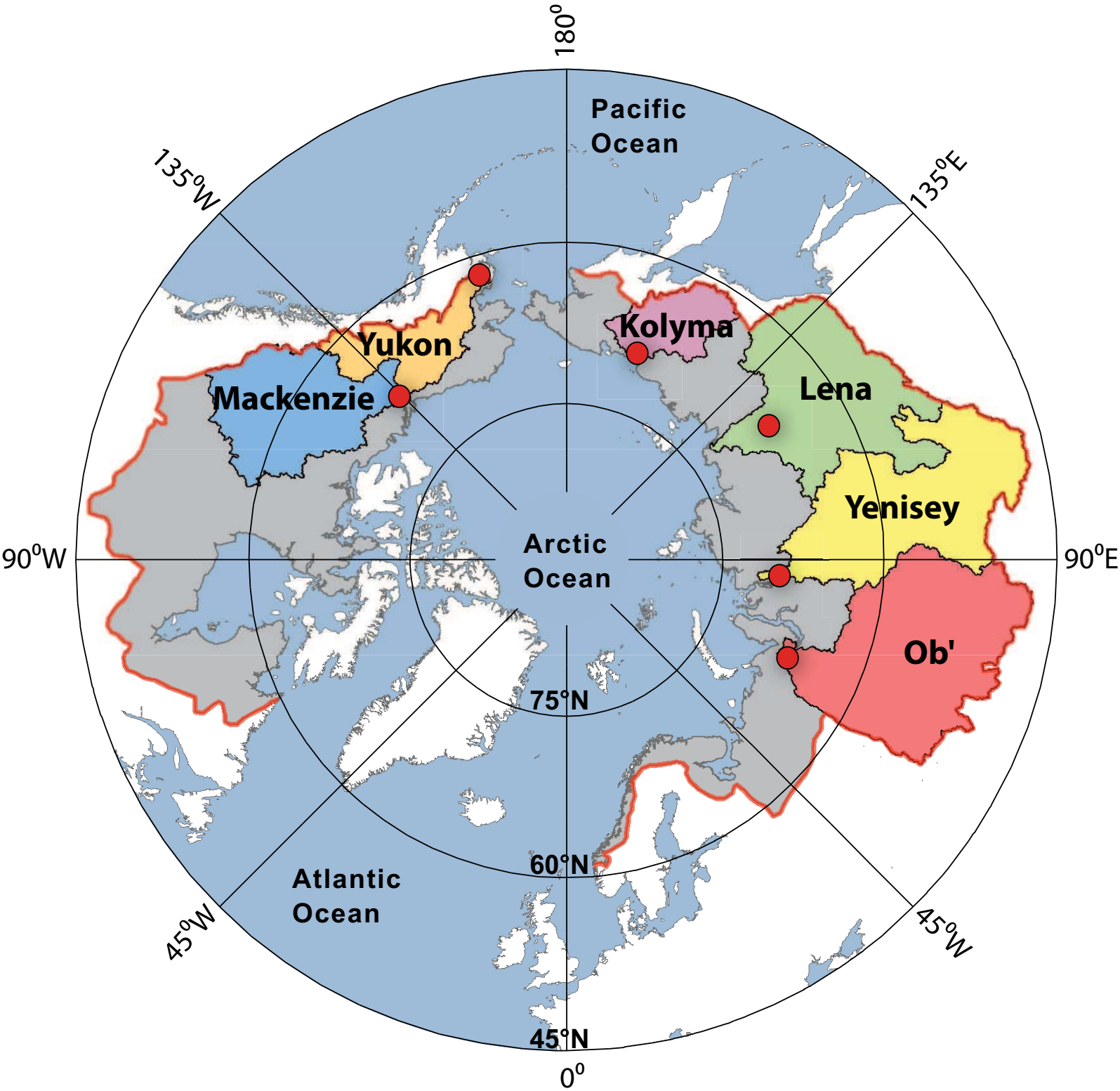
180°
Pacific
Ocean
135°W
135°E
Kolyma
Yukon
Mackenzie
Lena
Yenisey
90°W
Arctic
Ocean
90°E
Ob'
75°N
60°N
Atlantic
Ocean
45°W
45°W
45°N
0°

Figure 2

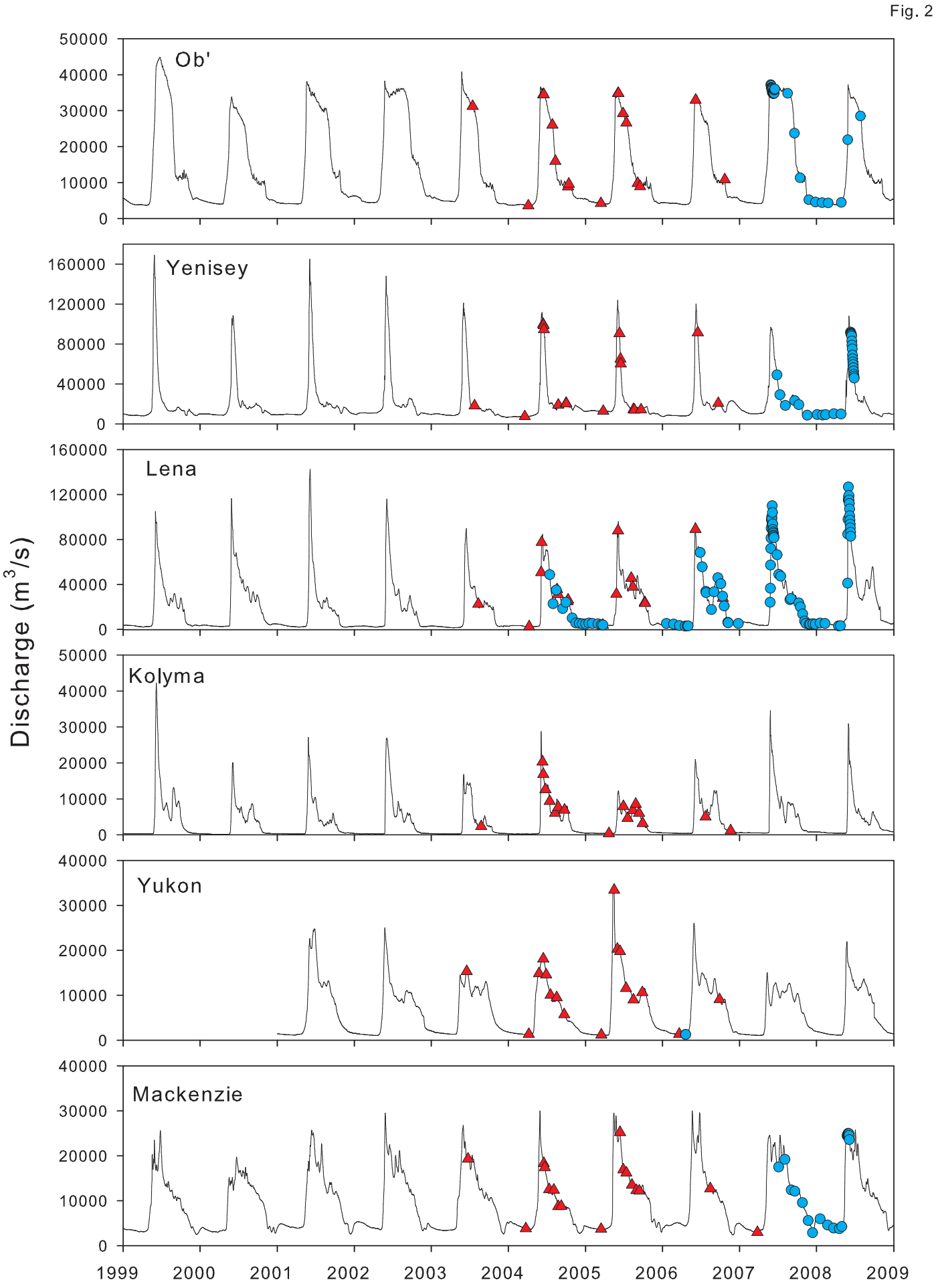
Fig. 2
Ob'
Yenisey
Lena
Kolyma
Yukon
Mackenzie
Discharge (m3/s)
50000
40000
30000
20000
10000
0
160000
120000
80000
40000
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009

Figure 3

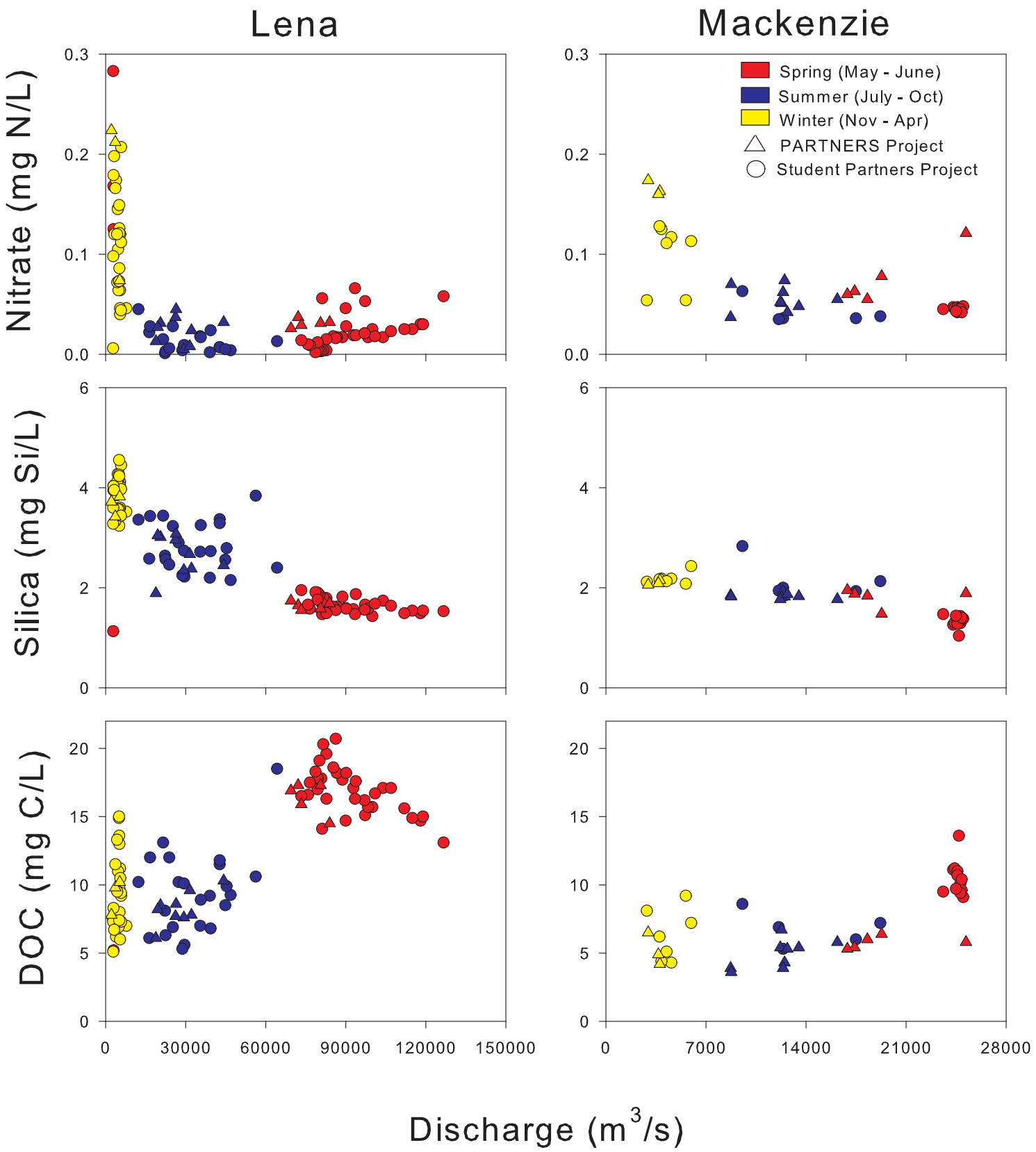
Lena
Mackenzie
Nitrate (mg N/L)
Silica (mg Si/L)
DOC (mg C/L)
Spring (May - June)
Summer (July - Oct)
Winter (Nov - Apr)
PARTNERS Project
Student Partners Project
0.0
0.1
0.2
0.3
0
2
4
6
0
5
10
15
20
0
30000
60000
90000
120000
150000
0
7000
14000
21000
28000
Discharge (m3/s)

Figure 4

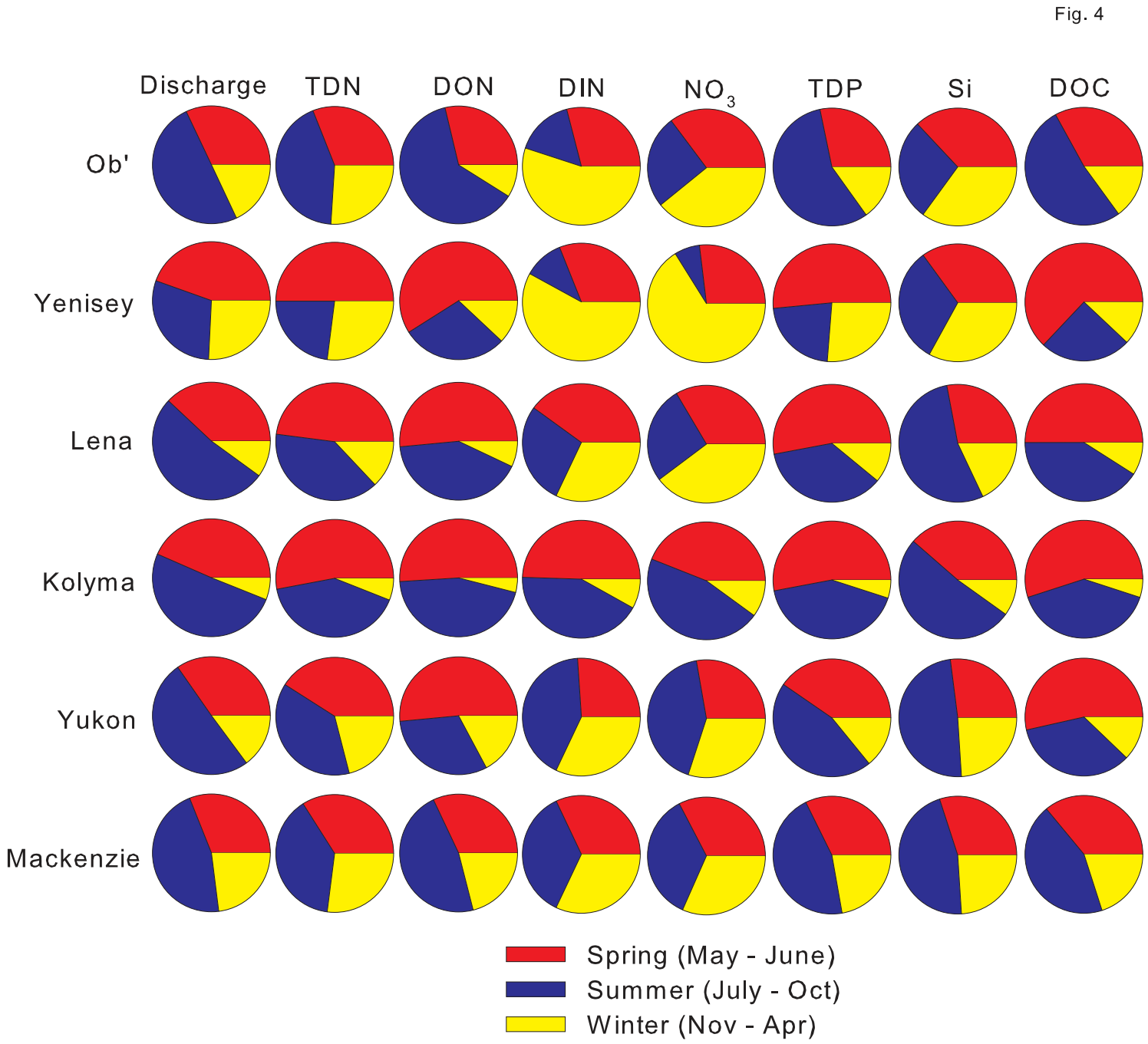
Fig. 4
Discharge
TDN
DON
DIN
NO_3
TDP
Si
DOC
Ob'
Yenisey
Lena
Kolyma
Yukon
Mackenzie
Spring (May - June)
Summer (July - Oct)
Winter (Nov - Apr)

Figure 5

Fig. 5

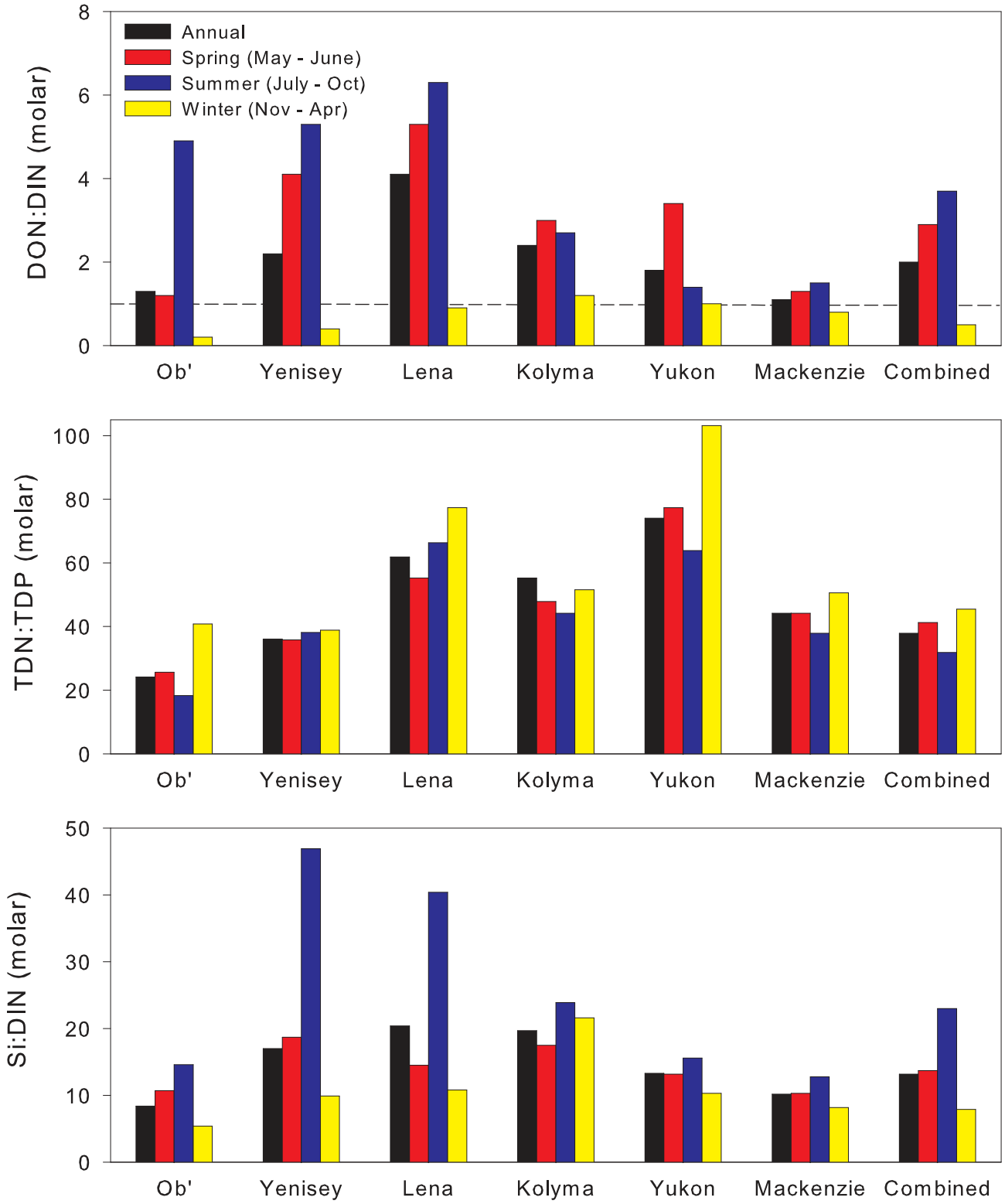

Table 1

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 10^9g (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

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