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Speciation and fluxes of nutrients (N, P, Si) from the upper Yukon River

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[1] Water samples were collected from the Yukon River near the Stevens Village Station from May to September 2002 and analyzed for nutrients (N, P, and Si) in dissolved, particulate, organic, and inorganic forms to examine temporal variations in nutrient concentrations, fluxes, and phase partitioning. Both NO_3 and PO_4 concentrations in the Yukon River were much lower than those of world rivers, with an average concentration of 2.43 ± 0.63 μM-N and 0.053 ± 0.040 μM-P, respectively. $Si(OH)_4$ concentrations were more comparable to those of world rivers, with an average concentration of 82 ± 21 μM-Si. Integrated annual fluxes were 2.4×10^8 mole-NO_3, 3.4×10^6 mole-PO_4, and 8.7×10^9 mole-$Si(OH)_4$, respectively. Nutrient discharge during the river ice open season contributed 73 to 95% of the annual flux depending on nutrient species. Within the total N pool transported by the Yukon River, dissolved inorganic N comprised $7 \pm 4\%$ and particulate N made up $25 \pm 10\%$, while dissolved organic N (DON) was the dominant N species (with an average of $67 \pm 10\%$). In contrast, P was predominantly partitioned in the particulate phase (with an average of $94 \pm 6\%$), leaving $4 \pm 5\%$ of the total P in the dissolved organic phase and $\sim 2 \pm 1\%$ in the dissolved inorganic phase. The partitioning of N and P indicates that the transformation between dissolved and particulate or inorganic and organic phases may play a critical role in controlling the flux of bioavailable nutrients and thus the nutrient dynamics in the Yukon River Basin and its coastal region. Nutrient specific fluxes normalized to drainage area in the Yukon River Basin were 0.57 mmole/m^2/yr for NO_3, 0.012 mmole/m^2/yr for PO_4, and $\sim$19 mmole/m^2/yr for $Si(OH)_4$, respectively. The relatively low specific fluxes of NO_3 and PO_4 in the Yukon River Basin reflect its pristine status or little anthropogenic influence, whereas cold climate in the Arctic/subarctic region may be responsible for its lower $Si(OH)_4$ specific flux, in agreement with a general trend of increasing Si specific flux with decreasing latitude in global river systems. A warming climate and thus deeper permafrost active layer in the Yukon River watershed would likely enhance the export flux of nutrients into the Bering Sea. *INDEX TERMS:* 1030 Geochemistry: Geochemical cycles (0330); 1045 Geochemistry: Low-temperature geochemistry; 1806 Hydrology: Chemistry of fresh water; 1615 Global Change: Biogeochemical processes (4805); *KEYWORDS:* flux, nutrients, Yukon River

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1. Introduction

[2] The Yukon River is one of the largest rivers in the North America. It drains an area of roughly 855,000 km^2 in northwestern Canada and central Alaska (Figure 1). The Yukon River contributes $\sim$8% of the total freshwater input to the Arctic Ocean [*Aagaard and Carmack*, 1989], with an annual discharge of more than 2×10^{11} m^3 of freshwater and $\sim 60 \times 10^6$ tons of suspended sediments [*Brabets et al.*, 2000; *Holmes et al.*, 2002]. Recent studies demonstrate that the northern ecosystems are sensitive to global and regional climate and environmental changes [*Houghton et al.*, 2001;

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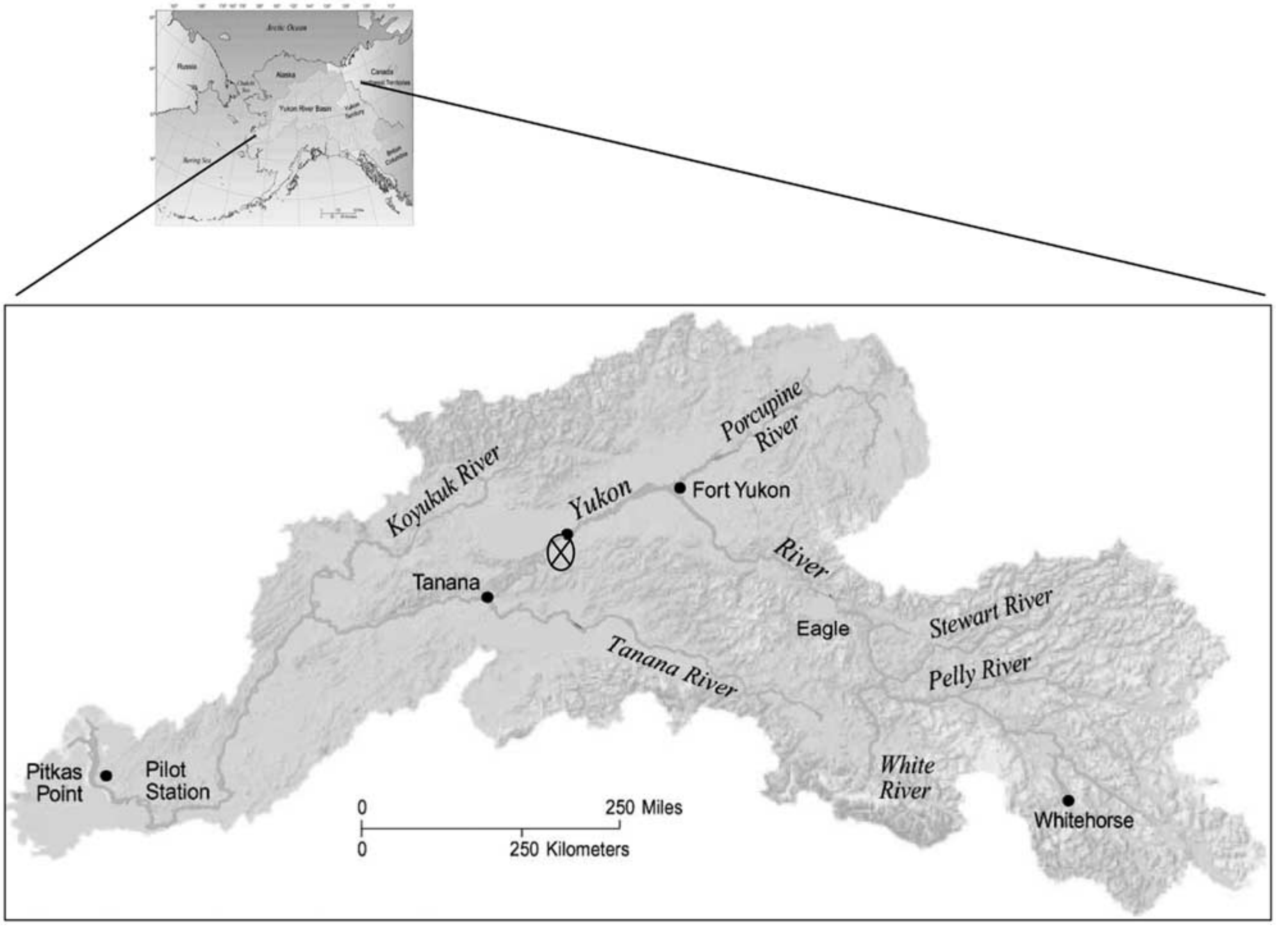

Figure 1. Map of the Yukon River Basin in the northwestern Canada and central Alaska (modified from *Brabets et al.* [2000]) and the sampling location marked by a cross.

Peterson et al., 2002]. Of special concern in the Yukon River Basin are permafrost degradation and its hydrologic changes [e.g., *Jorgenson et al.*, 2001]. Therefore environmental and climate changes in the Arctic and thus increased freshwater runoff in Arctic rivers may have profound impacts on fluxes and biogeochemical cycles of nutrients and other bioactive elements [*Holmes et al.*, 2000; *Freeman et al.*, 2001; *Peterson et al.*, 2002; *Guo et al.*, 2004]. Variations in nutrient concentration, speciation, and flux are the combined effects of physicochemical and biogeochemical processes occurring at various scales in the drainage basin. Thus they could be a useful indicator of climate and environmental change and may provide insights into current status and changes in river basins. However, owing to its remoteness and extreme weather conditions, the Yukon River Basin remains pristine and understudied. Few data are available on nutrient concentrations in the Yukon River Basin. Potential biogeochemical processes as a result of climate and environmental change in the Yukon River watershed are poorly understood. Knowledge of how environmental change influences the fluxes of freshwater and nutrients in Arctic rivers will provide insights into biogeochemical consequences of climate change and human influence in the northern region [*MacLean et al.*, 1999].

[3] Nitrogen (N), phosphorus (P), and silicon (Si) are essential elements for both freshwater and marine organisms. Riverine inputs are considered to be one of the most important nutrient sources to the sea [*Meybeck*, 1982; *Mayer et al.*, 1998]. The Bering Sea ecosystems provide one of the world's most abundant biological resources, contributing over half of the nation's fishery production [*Springer et al.*, 1996, and references therein]. In addition to deep Pacific waters, nutrient inputs through the Yukon River may play an important role in the biogeochemical cycles and sustain primary productivity and the food web in the Bering Sea. Nevertheless, there are few reports on nutrient concentrations in Yukon River waters [e.g., *Brunskill et al.*, 1975; *Brabets et al.*, 2000], and measurements on all nutrient species and their seasonal variations are even scarce. Nutrient dynamics in the Yukon River, such as temporary variations and phase partitioning between dissolved/particulate and inorganic/organic species, remains poorly understood. Furthermore, there is little information on the transport and transformation processes of nutrients in the Yukon River compared to other major rivers in tropical/subtropical and temperate regions [e.g., *Meybeck*, 1982; *Rabalais et al.*, 1996; *McClain et al.*, 2001; *Liu et al.*, 2003; *Smith et al.*, 2003]. Because the Yukon River Basin is

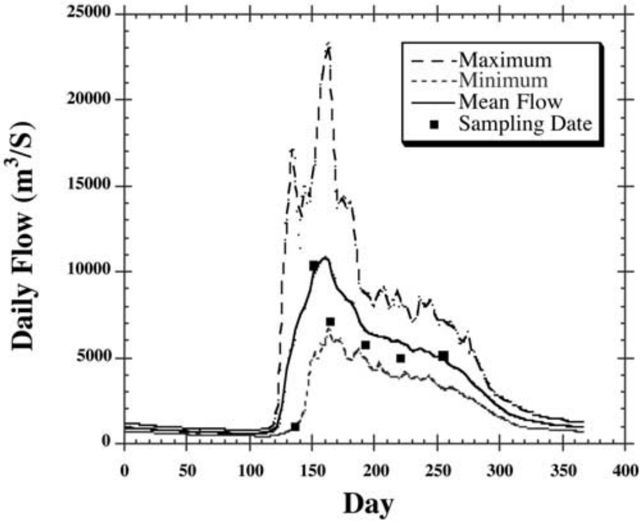

Figure 2. Variations of long-term averaged daily streamflow (m^3/s) at the Stevens Village Station in the Yukon River between 1976 and 2000 (data from USGS at http://waterdata.usgs.gov). Solid circles show our sampling dates and their corresponding instantaneous freshwater discharge in 2002.

predominantly covered with continuous and discontinuous permafrost [*Brabets et al.*, 2000; *Jorgenson et al.*, 2001], fluxes of nutrient and other chemical species may change drastically if ongoing permafrost degradation continues. Therefore it is critical to generate a baseline data set that can be used for future environmental monitoring and trend analysis in the Yukon River Basin.

[4] In order to address the aforementioned gaps in our understanding of the Yukon River system, we undertook a detailed investigation of nutrients (N, P, Si) in the Yukon River. Measurements include nutrient concentrations, fluxes, and their temporal variations during the river ice open season (from May to September 2002). The partitioning of N and P between dissolved and particulate phases and between organic and inorganic phases was also investigated.

2. Methods and Materials

2.1. Study Area

[5] The Yukon River Basin and the sampling station near the USGS Stevens Village Station are shown in Figure 1. Because of its high latitude location (59°N–69°N), the Yukon River is virtually frozen from October to May. The open water season usually starts in late May or early June. Most flow occurs in the summer months through snowmelt, rainfall, and glacier melt, with very low discharge in winter months. Variations of long-term averaged daily streamflow (m^3/s) at the sampling site are given in Figure 2, showing a typical seasonal variation of fresh water discharge for Arctic rivers. For example, mean fresh water discharge during the winter season between 1976 and 2000 was usually less than 1000 m^3/s whereas summer average fresh water discharge was up to an order of magnitude higher, with a high flow range between 7000 and 23,000 m^3/s. While river discharge was the highest during ice opening in the spring, water conductivity increased continuously from snowmelt to ice opening, maintaining a constant value from July to September (Table 1). Concentrations of suspended particulate matter (SPM) were strongly correlated with water discharge.

[6] As shown in Figure 2, our sampling dates and their corresponding instantaneous freshwater discharge seem to capture the general trend of river discharge. For example, flow rates in late May and September 2002 were only slightly higher than the historical average, while the flow rates on the rest of sampling dates were slightly below the historical mean discharge rates (Figure 2). Overall, the flow rates during our sampling dates were within the range of the long-term minimum/maximum flow data collected between 1976 and 2000 by USGS.

2.2. Sampling

[7] From May to September of 2002, six sample sets were obtained at biweekly to monthly intervals from the Yukon River near the USGS hydrological station at Stevens Village, Alaska (Table 1, Figure 1). The first sample (YR-01) was taken on May 15 during snowmelt. The river ice open season started in late May with the typical highest flow rate during 2002, and the flow rate decreased gradually thereafter (Table 1). Using a peristaltic pump fitted with polyethylene tubing, large volumes of river water were pumped on site through a 0.45-μm polycarbonate filter cartridge (Osmonics) to separate the particulate (>0.45 μm) from dissolved (<0.45 μm) phases. Immediately following filtration, aliquots of filtrate samples were collected in acid-cleaned polypropylene bottles and stored frozen for later nutrient analysis. In addition to nutrient samples, aliquots of filtrate were also sampled for measurements of dissolved organic carbon (DOC), dissolved organic nitrogen (DON),

Table 1. Hydrological Data and Concentrations of Suspended Particulate Matter (SPM), Chlorophyll-a (Chl-a), and Different Forms of C, N, P, and Si in the Yukon River Basin Near the USGS Stevens Village Station in 2002[a]

Sample ID	Sampling Date	Discharge, m^3/s	pH	Temp, °C	Conductivity, μS/cm	SPM, g/L	Chl-a, μg/L	DOC, μM	DIC, μM	NO_3, μM	DON, μM	PN, μM	PO_4, μM	DOP, μM	PP, μM	$Si(OH)_4$, μM
YR-01	15-May	991	7.5	2	163	0.092	<0.20	2825	1176	2.98	58.1	10.8	0.127	0.37	2.40	63.6
YR-02	31-May	10337	7.4	6	174	0.331	1.57	1158	1153	1.37	28.9	22.7	0.069	0.18	5.50	53.5
YR-03	14-June	7080	7.7	14	208	0.153	0.97	725	1342	2.71	28.6	10.6	0.039	0.061	1.94	81.4
YR-04	12-July	5721	7.9	15.5	227	0.175	5.07	558	1550	2.21	23.8	5.48	0.025	0.010	2.20	82.2
YR-05	9-August	4984	7.9	14	224	0.130	0.73	508	1465	2.26	17.2	7.49	0.036	0.073	3.13	105
YR-06	12-Sept	5098	7.9	8	226	0.053	0.56	533	1546	3.05	12.5	4.64	0.021	0.014	1.57	107

[a] DOC, dissolved organic carbon; DIC, dissolved inorganic carbon; DON, dissolved organic nitrogen; PN, particulate nitrogen; DOP, dissolved organic phosphorus; PP, particulate phosphorus. Water temperatures were estimated by interpolation from adjacent date.

and dissolved organic phosphorus (DOP). Separate filter membranes (Nuclepore filters and GF/F glass fiber filters) were used to collect particulate samples for the measurement of total suspended particulate matter (SPM), particulate organic carbon (POC), particulate nitrogen (PN), and particulate phosphorus (PP) concentrations. Sampling procedures followed the methods described by *Guo et al.* [2003a].

2.3. Measurements

[8] Concentrations of dissolved nitrate plus nitrite (NO_3 + NO_2) and silicate ($Si(HO)_4$) were measured using an Alpkem gas-segmented continuous flow auto-analyzer. Samples for nitrate analysis were passed through a copperized cadmium column to reduce nitrate to nitrite [*Zhang et al.*, 2000]. Nitrite from the reduction of nitrate plus nitrite in the original sample was then determined by diazotizing with sulfanilamide and coupling with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye, the absorbance of which was measured at 540 nm [*Zhang et al.*, 1997]. Silicate in the sample was reacted with molybdate in an acidic solution to form β-molybdosilicic acid, which was then reduced by ascorbic acid to form molybdenum blue. Absorbances of molybdenum blue were measured at 660 nm [*Zhang and Berberian*, 1997]. Phosphate was determined by reacting with molybdenum (VI) and antimony (III) in an acidic medium to form an antimonyphosphomolybdate complex. This complex was subsequently reduced with ascorbic acid to form a heteropoly blue and the absorbance was measured at 710 nm. The reaction was controlled at room temperature (~23°C) to minimize sample silicate interference [*Zhang et al.*, 1999]. Concentrations of PO_4 in Yukon River waters are lower than the detection limit of the conventional autoanalyzer [*Grasshoff et al.*, 1999]. Therefore an autoanalyzer equipped with a long path length (2 m) liquid waveguide capillary flow-cell was used to measure PO_4 concentrations in Yukon river samples [*Zhang and Chi*, 2002].

[9] Total dissolved phosphorus in river water samples was determined by autoclave-assisted persulfate oxidation of the organic phosphorus at boiling temperature, followed by the standard antimonyphosphomolybdate colorimetric determination of liberated orthophosphate outlined above. The oxidizing reagent, potassium persulfate ($K_2S_2O_8$) solution, was prepared by dissolving 5.0 g $K_2S_2O_8$ in 100 mL of 0.45 N H_2SO_4 solution. A 10.0-mL aliquot of the sample was mixed with 1.0 mL of oxidizing reagent in a 100-mL glass tube. Samples were autoclaved for 60 min. Standard solutions for calibration were also autoclaved and prepared with the same procedures as samples.

[10] Concentrations of total dissolved nitrogen (TDN) were measured using high temperature combustion on a Shimadzu TOC analyzer (TOC-V) interfaced with an N detector. Concentrations of DON were calculated from the difference between TDN and dissolved inorganic nitrogen (DIN) concentrations. Similarly, concentrations of DOP were calculated from total dissolved P and dissolved inorganic P (DIP, or PO_4) concentrations. Concentrations of total dissolved carbon (TDC) were measured by high temperature combustion on a Shimadzu TOC analyzer (TOC-V). Concentrations of DOC were measured by the same instrument after samples were acidified to a pH of ≤ 2 and sparged with ultra-pure air to remove dissolved inorganic carbon (DIC) as CO_2 [*Guo et al.*, 1994]. Concentrations of DIC in the samples were calculated as the difference between TDC and DOC.

[11] Suspended particulate matter concentrations were measured by filtering a known volume of river water through a pre-weighed Nuclepore filter membrane. The filter and samples were repeatedly dried at 60°–80°C and weighed until a constant weight was achieved. Total phosphorus in suspended particulate matter was determined by wetting samples with magnesium nitrate solution and ashing the samples at 550°C to decompose organic phosphorus compounds, followed by a 1 M HCl extraction at 25°C for 16 hours. The extract was determined for liberated orthophosphate by the standard antimonyphosphomolybdate colorimetric method using an HP 8453 spectrophotometer [*Cembella et al.*, 1986; *Solorzano and Sharp*, 1980; *Zhang et al.*, 1999].

[12] Concentrations of particulate organic carbon (POC) and particulate nitrogen (PN) along with their stable isotope composition were measured by continuous flow isotope ratio mass spectrometry [*Guo et al.*, 2003b]. Data of isotopic composition and characterization of dissolved and colored organic matter are reported elsewhere [*Guéguen et al.*, 2003] (also C. Guéguen et al., Chemical characteristics and origins of dissolved organic matter in the Yukon River, submitted to Biogeochemistry, 2004, hereinafter referred to as Guéguen et al., submitted manuscript, 2004; and L. D. Guo et al., Isotopic composition (^{13}C, ^{14}C, ^{15}N) of size fractionated organic matter in the Yukon River Basin: Implications for organic carbon dynamics, manuscript in preparation, 2004, hereinafter referred to as Guo et al., manuscript in preparation, 2004).

3. Results and Discussion

3.1. Variations of Nutrient Concentrations

[13] Concentrations of NO_3 + NO_2 (hereinafter NO_3), PO_4, and $Si(OH)_4$ during the river ice open season (from late May to September) are listed in Table 1 and compared with nutrient data from other Arctic rivers and world rivers in Table 2. Concentrations of NO_3 in Yukon River waters varied from 1.37 μM during the highest river discharge in late May to 3.05 μM in September, with an average concentration of 2.43 ± 0.63 μM. There was no systematic trend in the variation of NO_3 concentrations during the river ice open season between May and September (Figure 3). Concentrations of PO_4 decreased continuously from 0.127 μM during snowmelt in mid-May to 0.021 μM in September, with an average PO_4 concentration of 0.053 ± 0.04 μM. In contrast to PO_4, concentrations of $Si(OH)_4$ increased from 53 μM in May to 107 μM in September, with an average of 82 ± 21 μM (Figure 3), suggesting a distinct source between PO_4 and $Si(OH)_4$.

[14] Concentrations of NO_3 and PO_4 in the Yukon River are considerably lower than those of major world rivers (Table 2) but are similar to those measured from the Mackenzie River in the Arctic region [*Environment Canada*,

Table 2. Comparisons of Nutrient (N, P, Si) Concentrations Between the Yukon River and the World Major Rivers

River	NO_3, μM	PO_4, μM	$Si(OH)_4$, μM	NO_3/PO_4 Ratio	Reference
Amazon	10	0.7	115	14	*DeMaster and Pope* [1996]
Changjiang (Yangtze)	70.3	0.83	102	84	*Liu et al.* [2003]
Lena	0.7–10	0.46	66	<10	*Gordeev* [2000] *Lara et al.* [1998]
Mackenzie	2.42	0.10	48	24	*Environment Canada* [1978], *Millot et al.* [2003]
Mississippi	114	7.7	127	15	*Rabalais et al.* [1996] *Berner and Berner* [1996]
Ob	56	2.3	164	24	*Gordeev* [2000]
Trinity[a]	39.2	1.85	82 ± 35	21	*Warnken* [2002]
Yenisey	26	0.4	107	65	*Gordeev* [2000]
Yukon	1.4–10.7	0.25–8.75[b]	25–125	-	*Brabets et al.* [2000]
Yukon	2.43 ± 0.63	0.053 ± 0.04	82 ± 21	69 ± 47[c]	this work

[a] Data were measured biweekly during September 2000 to August 2001 [*Warnken*, 2002].

[b] Phosphorus concentrations here are not phosphate but total dissolved phosphorus.

[c] NO_3/PO_4 ratio here is calculated from each data point and then averaged.

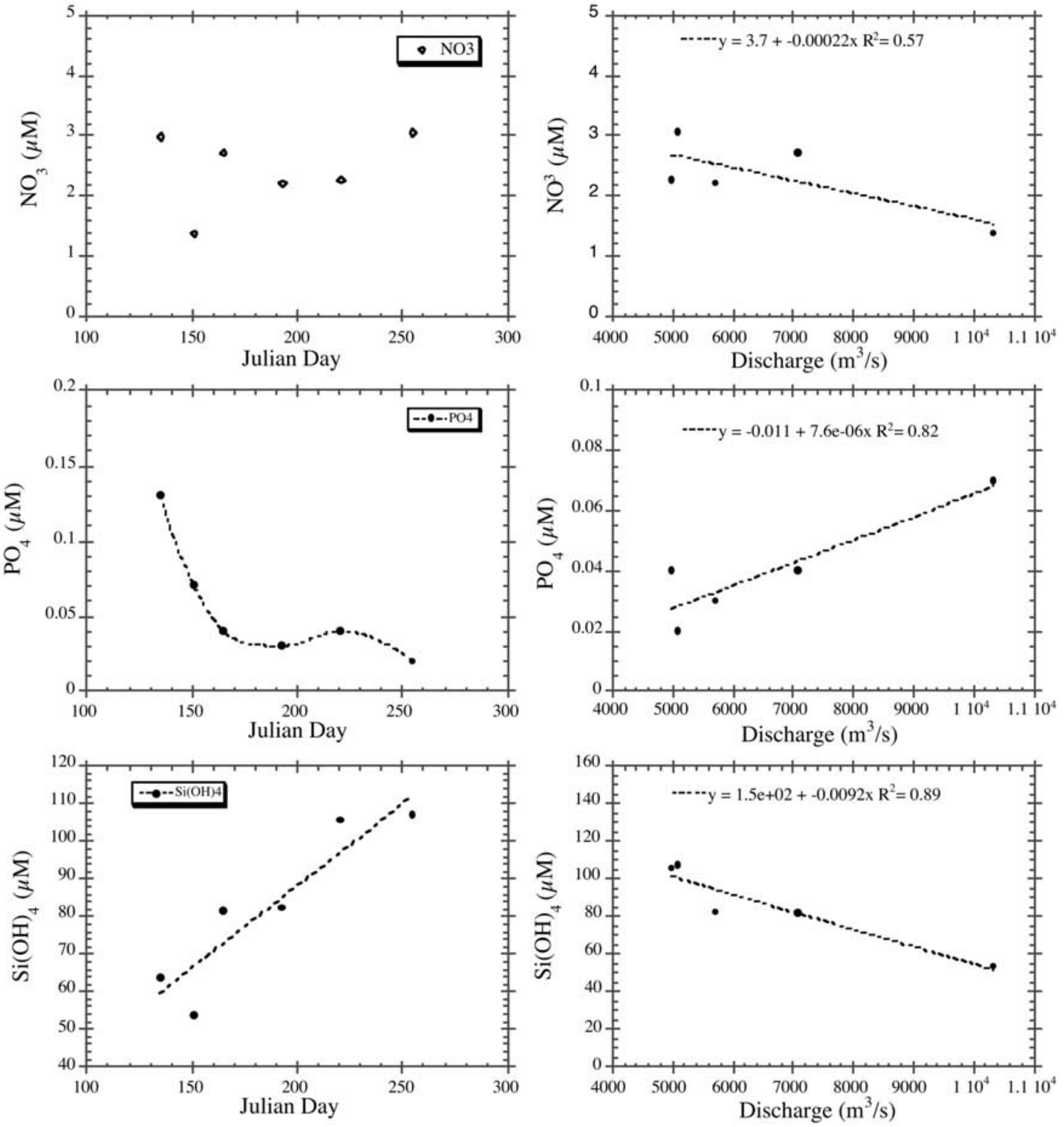

Figure 3. Temporal variations of nutrient (N, P, Si) concentrations (μM) and their relationship to freshwater discharge (m^3/s).

1978] and other oligotrophic rivers in northern Europe [*Humborg et al.*, 2003]. For example, NO_3 concentrations in pristine rivers were usually lower than 10 μM [e.g., *Meybeck*, 1982; *Humborg et al.*, 2003]. In contrast, NO_3 concentration can be as high as 114 μM in the Mississippi River [*Rabalais et al.*, 1996] and about 70 μM in the Yangtze River [*Liu et al.*, 2003]. Compared with average world rivers, PO_4 concentrations observed in the Yukon River Basin are an order of magnitude lower (Table 2). Obviously, higher NO_3 and PO_4 concentrations in tropical/subtropical and temperate rivers are more likely derived from human activities [*Meybeck*, 1982], with a minor contribution from natural sources. Low nitrate and phosphate concentrations reflect the fact that the Yukon River is a relatively pristine river basin with less anthropogenic influence. However, the average concentration of $Si(OH)_4$ in the Yukon River is only slightly lower than those of major world rivers even though there is a general trend of increasing $Si(OH)_4$ concentration with decreasing latitude [e.g., *Huh et al.*, 1998; *Turner et al.*, 2003]. Among the Arctic rivers, the Ob and Yenisey had the highest $Si(OH)_4$ concentration (Table 2).

[15] The nutrient concentrations we report here are within the ranges measured previously for the Yukon River basin [*Brabets et al.*, 2000] (see Table 2). Unfortunately, concentrations of PO_4 are not available from previous reports [e.g., *Brunskill et al.*, 1975; *Brabets et al.*, 2000], likely because of its extremely low concentration in Yukon River waters (Table 2). This prevents a direct comparison for PO_4 concentrations.

[16] Nitrate concentrations were fairly constant throughout the river opening season except during late May. The decrease in NO_3 and PO_4 concentrations during late May could partially result from the biological uptake in the spring (and early summer) phytoplankton bloom in the upstream. Indeed, concentrations of chlorophyll-a (Chl-a) showed a significant increase from early May (<0.2 μg/L) to opening season (0.6–5 μg/L), with the highest Chl-a concentration in July (up to 5.1 μg/L) (Table 1). On the basis of the measured NO_3 and PO_4 concentrations in the Yukon River Basin, an average N/P ratio can be calculated to be 69 ± 47, which is much higher than the Redfield ratio of 16. This high N/P ratio indicates the Yukon River basin is P-limited, similar to most river and freshwater systems [*Wetzel*, 2001; *Turner et al.*, 2003].

[17] Conductivity in Yukon River waters was generally negatively correlated with freshwater discharge except for one sample taken in early May during snowmelt (Table 1). As shown in Figures 3 and 4, $Si(OH)_4$ concentrations were negatively correlated with discharge rate but positively correlated with conductivity in Yukon River waters, suggesting that the concentration of $Si(OH)_4$ was largely controlled by natural weathering processes. However, the opposite is true for PO_4. A quasi-positive correlation between PO_4 concentration and discharge (Figure 3) and negative correlation with conductivity (not shown) suggest that physicochemical and biological degradation processes play an important role in regulating PO_4 concentrations in river waters. Indeed, PO_4 concentrations decreased over the course of the summer while $Si(OH)_4$ concentration increased (Figure 3). In addition, concentrations of DOC, DON, and DOP decreased from snowmelt to river ice opening periods and continuously to autumn (Table 1). It is likely that higher DOC, DON, DOP, and PO_4 concentrations during snowmelt were largely from the leaching of soil organic matter (Guéguen et al., submitted manuscript, 2004; Guo et al., manuscript in preparation, 2004) and the preferential decomposition of organic P relative to organic C and N [*Clark et al.*, 1999]. This hypothesis is further supported by a significant correlation between PO_4 concentration and DOC concentration ($R^2 = 0.96$, Figure 4) in Yukon River waters, and is consistent with higher concentrations of DOP during snowmelt and ice opening seasons. In contrast, the concentration of $Si(OH)_4$ was negatively correlated with DOC concentration, although the correlation was weak ($r^2 = 0.4$). A significant correlation between conductivity and $Si(OH)_4$ (or DIC) ($R^2 = 0.7$, Figure 4) indicates that $Si(OH)_4$ had a similar source function as DIC but different from PO_4, especially during the snowmelt and early ice opening in the Yukon River Basin.

[18] Our results of the temporal variations in PO_4 and $Si(OH)_4$ concentrations and their contrasting source functions are in agreement with stable oxygen isotope ($\delta^{18}O$) data that show a slightly increase from −21.26‰ in May to −21.17‰ in June but a sharp increase from −21.17‰ in June to −20.37 ± 0.07‰ in July/September (Guo et al., manuscript in preparation, 2004). The $\delta^{18}O$ data suggest a shift of sources in river water runoff from snowmelt in late spring/early summer to a combination of rainwater and thawed waters from permafrost active layer and ice/glaciers in late summer/fall. The snowmelt dominated runoff (lower $\delta^{18}O$) is accompanied by intensive leaching of upper soil horizon and thus higher concentration of DOC, DOP, and PO_4. As summer progresses, thawing of the active layer and thus leaching of deeper soil horizon and riverbank erosion gave rise to higher $Si(OH)_4$ and DIC but lower DOC, DOP, and PO_4 concentrations (see also Figures 3 and 4). Therefore river water nutrient chemistry could be a proxy for the active layer and permafrost dynamics in a changing climate.

3.2. Partitioning of N and P Between Dissolved, Particulate, Organic, and Inorganic Phases

[19] N and P species in river waters include dissolved inorganic and organic (e.g., DIN, DON, DIP, and DOP) and particulate phases (e.g., PN and PP). Phase partitioning of N and P was examined by measuring all relevant N and P species in Yukon River waters.

[20] As shown in Table 1, concentrations of DON ranged from 12 to 58 μM with an average of 28 ± 16 μM and particulate nitrogen (PN) ranged from 4.6 to 23 μM, with an average of 10 ± 6 μM. The organic and particulate N concentrations were considerably higher than NO_3 concentrations (Table 1 and Figure 5). Similarly, concentrations of DOP, ranging from 0.010 to 0.37 μM-P with an average concentration of 0.12 ± 0.14 μM-P, were also significantly higher than DIP (i.e., PO_4). More importantly, concentrations of particulate phosphorus (PP) were almost 2 orders of magnitude higher than those of PO_4, ranging from 1.6 to 5.5 μM with an average of 2.8 ± 1.4 μM (Table 1).

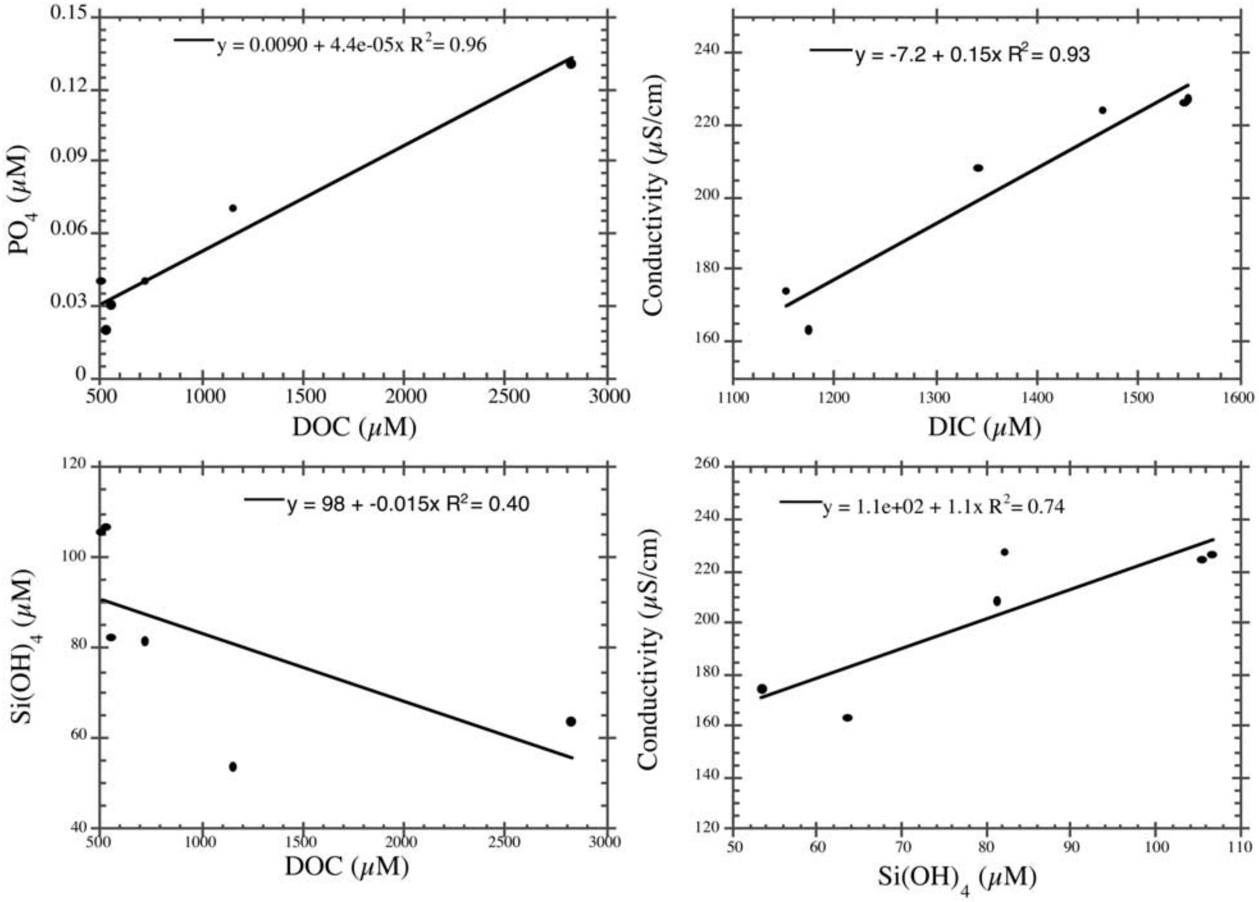

Figure 4. Relationship between nutrients (P and Si), DOC (dissolved organic carbon), DIC (dissolved inorganic carbon), and conductivity. Note that the relationships here were used mainly to show the contrasting behaviors of PO$_4$ and Si(OH)$_4$.

[21] Variations of N and P partitioning from May to September are shown in Figure 5. In general, the percentage of DIN in the total N pool increased from ~3% in May to 15% in September. Other variation features in the N partitioning include a highest particulate N percentage in late May when the freshwater discharge was at its peak during the year and a highest DON percentage in early May when the leaching of soil organic matter was most intensive (Guéguen et al., submitted manuscript, 2004). The average percentage of DIP in the total P pool was only less than 2% (Figure 6), decreasing from ~4% in May to <2% between June and September. Similar to both DOC and DON, DOP had its highest percentage (up to 12% of the total P) in May during snowmelt. As discussed in the previous section, high DOP during the snowmelt was largely derived from the intensive leaching of soil organic matter, likely stored in the upper soil horizons that are the first to leach organic fractions upon initiation of spring melt (Guo et al., manuscript in preparation, 2004).

[22] Within the total N pool, dissolved inorganic N comprised, on average, only ~7 ± 4% of the total N and particulate N made up 25 ± 10% of the total N, with DON being the dominant N species (with an average of 67 ± 10%) (Figure 6). While N was predominantly present in DON phase, P was predominantly partitioned in the particulate phase (with an average of 94 ± 6% of the total P), leaving 4 ± 5% of the total P in the DOP and ~2 ± 1% in the DIP phases (Figure 6). The dominance of PP in the total P pool could be partly due to the sorption of DIP and DOP onto suspended particles [e.g., *Mayer and Gloss*, 1980].

[23] Overall, the partitioning of N and P indicated that DON and particulate phosphorus (PP) were the dominant N and P species transported by the Yukon River and exported to the Bering Sea and the Arctic Ocean. Therefore DON and PP may play a critical role in the biogeochemical cycling of N and P and in the transformation of nutrients between dissolved/particulate and inorganic/organic species in the river system and the coastal regions of the Yukon Delta.

3.3. Discharge of Nutrients

[24] As shown in Figure 2, Arctic rivers have a distinct streamflow pattern with most freshwater discharge occurring in the summer months. Therefore the ice open season in Arctic rivers should contribute most of the riverine fluxes of nutrients to the ocean. Instantaneous nutrient fluxes can be calculated using the river discharge data and measured

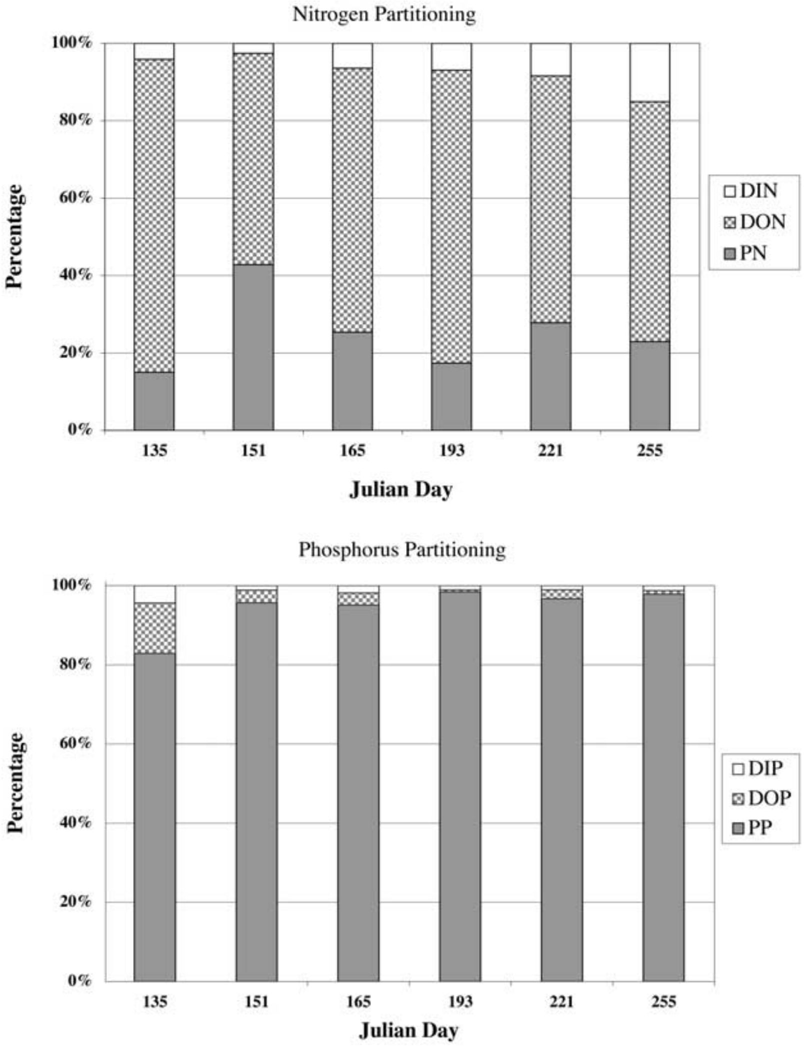

Figure 5. Variations of N and P partitioning between dissolved, particulate, and organic phases in the Yukon River from May to September 2002. DIN, dissolved inorganic nitrogen (NO_3 + NO_2); DON, dissolved organic nitrogen; PN, particulate nitrogen; DIP, dissolved inorganic P (PO_4); DOP, dissolved organic phosphorus; PP, particulate phosphorus.

nutrient concentrations (Table 3). For dissolved inorganic nutrients, the average instantaneous flux at the Stevens Village station was 12.6 ± 5.5 mole-N/s for DIN (ranging from 2.95 in early May to 19.2 mole-N/s in June), 0.26 ± 0.23 mole-P/s for DIP (ranging from 0.11 in September to 0.71 mole-P/s in late May), and 455 ± 195 mole-Si/s for dissolved silica (ranging from 63 in early May to 576 mole-Si/s in June), respectively (Table 3).

[25] In addition to the fluxes of dissolved inorganic nutrients, instantaneous fluxes of organic and particulate N and P can also be calculated using the available concentrations measured along with those dissolved inorganic nutrient species. For example, the instantaneous flux of DON ranged from 576 mole-N/s in early May to the highest (2997 mole-N/s) in late May, with an average flux of 1410 ± 949 mole-N/s. Flux of PN was 68.9 ± 84.2 mole-N/s, ranging from 11 to 235 mole-N/s. Instantaneous fluxes of dissolved organic and particulate N are considerably higher than those of NO_3 (Table 3), indicating that, in addition to dissolved inorganic N species, DON and PN can contribute considerably to the overall N flux to the ocean through rivers [*Mayer et al.*, 1998]. Similar to N fluxes, instantaneous fluxes of DOP and PP were also significantly higher than those of DIP (Table 3). Together, these results all point to the significance of both organic and particulate nutrient species in Yukon River waters.

[26] The Yukon River differs from those rivers that are heavily influenced by human activities, where DIN and DIP are usually the dominant nutrient species [*Meybeck*, 1982; *Mayer et al.*, 1998; *Liu et al.*, 2003]. However, our results are consistent with features in other unpolluted and pristine rivers where DON and PP dominate riverine N and P fluxes [e.g., *Brunskill et al.*, 1975; *Meybeck*, 1982; *Humborg et al.*, 2003].

[27] Since nutrient concentrations showed a considerable temporary variability (Figure 3), fluxes of nutrients are not

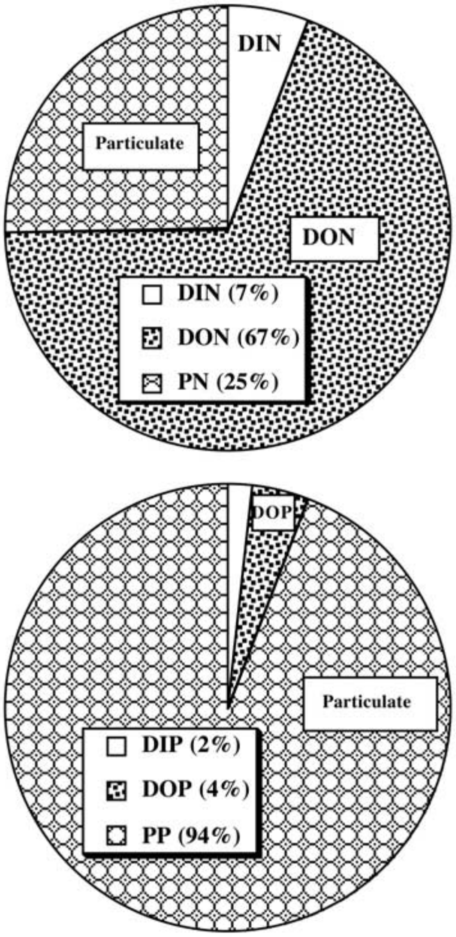

Figure 6. Average phase partitioning of N and P in Yukon River waters. DIN, DON, and PN denote dissolved inorganic, dissolved organic, and particulate nitrogen, respectively, while DIP, DOP, and PP represent dissolved inorganic, dissolved organic, and particulate phosphorus, respectively.

directly proportional to fresh water discharge. As shown in Table 3, there was a marked temporary variation in the calculated instantaneous nutrient fluxes. Differences in the instantaneous fluxes can be up to 6 to 9 times for a given nutrient species. Therefore it is difficult to obtain an integrated annual nutrient flux by snapshot sampling in a river basin. In addition, annual nutrient fluxes cannot be accurately quantified for Arctic rivers without knowledge of nutrient concentrations and chemical speciation during the frozen season even though the overall water discharge is low in winter (Figure 2). As the first approximation, however, the annual nutrient fluxes at the sampling station can be estimated using winter river discharge and interpolated nutrient concentration before freezing assuming there is little nutrient fractionation during ice formation [*Granskog and Virkanen*, 2001] and little variations in nutrient concentrations during the frozen season. As listed in Table 3, the integrated annual nutrient flux was relative low for NO_3 and PO_4, 241×10^6 mole-N/yr and 3.4×10^6 mole-P/yr, respectively, but significantly higher for $Si(OH)_4$, 8670×10^6 mole-Si/yr, compared to the DIN and DIP fluxes. Annual fluxes of DON and DOP, on the other hand, were much higher, $20{,}390 \times 10^6$ moles-N/yr and 5.8×10^6 moles-P/yr, respectively (Table 3). While DOP flux was comparable to that of PO_4, annual DON flux was about 2 orders of magnitude higher than that of DIN, showing a typical characteristic of pristine rivers. Similarly, particulate N and P also had much higher annual fluxes relative to those of dissolved inorganic N and P, 877×10^6 mole-N/yr for PN and 246×10^6 mole-P/yr for PP (Table 3). Considerably higher DON and PP annual fluxes suggest again that DON and PP were important nutrient species in the Yukon River and may contribute significantly to the overall supply of nutrients to the ocean. Therefore it is essential that organic and particulate nutrient species be examined along with the conventional dissolved inorganic N and P in evaluating riverine annual nutrient fluxes, as also suggested by *Mayer et al.* [1998].

[28] Nutrient fluxes in the Yukon River were dominated by instantaneous nutrient fluxes during the river ice open season. For example, nutrient fluxes during river open season (May to September) accounted for 73% to 95% of the annual fluxes depending on specific nutrient species (Table 3). On average, the instantaneous nutrient flux during river ice open season contributed 73% of the annual flux for DIN, 87% for DON, 89% for PN, 87% for DIP, 95% for DOP, 87% for PP, and 74% for $Si(OH)_4$, respectively.

[29] The nutrient fluxes listed in Table 3 are likely a lower limit for the export fluxes of the Yukon River Basin, since our sampling site is not from the most downstream station, even though there is little difference in nutrient concentrations between the most downstream station and our sampling station (see also Table 2). Accurate estimation of annual nutrient fluxes will require concurrent measurements of nutrients and discharge data throughout the year and knowledge of partitioning of nutrient between underlying water and overlying ice. Our annual nutrient fluxes from the Yukon River were lower than those calculated using historical data, as given by *Holmes et al.* [2000], likely owing to the relative low freshwater discharge in 2002, as shown in Figure 2. Future studies are needed to extend the sampling and measurements of nutrient species to winter season to reliably evaluate the annual nutrient fluxes and to establish a baseline for future environmental monitoring and for determination of biogeochemical consequences of climate and hydrological change in the Arctic region.

3.4. Comparisons of Normalized Nutrient Fluxes

[30] When the nutrient flux is normalized to the drainage area, a specific flux of nutrients can be obtained. As listed in Table 4, average nutrient specific fluxes from the Yukon River Basin are 0.57 mmol/m^2/yr for NO_3, 0.012 mmol/m^2/yr for PO_4, and 19 mmol/m^2/yr for $Si(OH)_4$, respectively. For comparison, nutrient specific fluxes calculated from available literature data for other Arctic rivers and major world rivers in the Northern Hemisphere are also listed in Table 4. It is clear that both NO_3 and PO_4 specific fluxes of the Yukon River Basin are considerably lower than those of rivers in tropical/subtropical and temperate regions. However, they

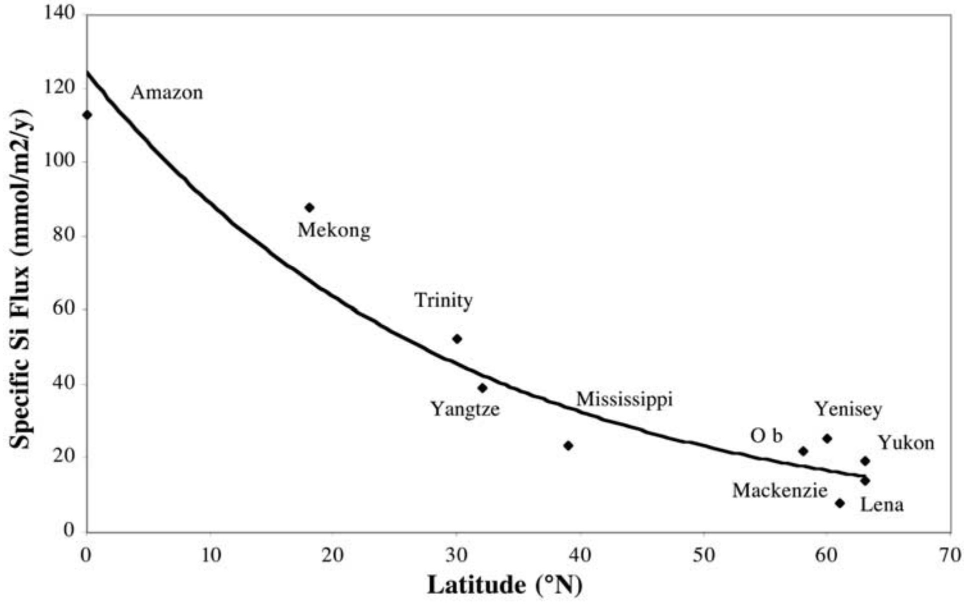

Figure 7. Variation of Si(OH)$_4$ specific flux (mmole/m^2/yr) normalized to basin's drainage area with mean latitude of drainage basin in Northern Hemisphere major rivers.

are similar to those of the Mackenzie River (Table 4). Normalized fluxes from both the Yukon River and the Mackenzie River are also lower than most Siberian Arctic rivers, even though the Arctic rivers, in general, have lower specific fluxes of NO$_3$ and PO$_4$ compared to other major world rivers. Since both NO$_3$ and PO$_4$ could be profoundly influenced by human activities, such as damming and agricultural and industrial developments, variations of nutrient specific flux between rivers could be largely the result of human impacts [e.g., *Meybeck*, 1982; *Turner et al.*, 2003]. For example, the Yangtze River has the highest NO$_3$ specific flux (28 mmlo/m^2/yr), while the Mississippi River has the highest PO$_4$ specific flux (1.4 mmole/m^2/yr) (Table 4).

[31] Concentrations of Si(OH)$_4$ in river waters, on the other hand, are mainly derived from the weathering of silicate minerals [*Millot et al.*, 2002; *Suchet et al.*, 2003]. Therefore the Si(OH)$_4$ specific flux should mostly reflect the rate of natural weathering in a given river basin. Indeed, while differences in nutrient specific flux can be up to 50-fold for NO$_3$ and over 100-fold for PO$_4$, specific fluxes for Si(OH)$_4$ were more comparable (~10-fold difference) between rivers ranging from the tropical (such as the Amazon Basin) to the Arctic region (such as the Mackenzie and Yukon River Basins) (Table 4). These results suggest that specific fluxes for Si(OH)$_4$ are less influenced by human activities than chemical weathering and geology in each river basin. When the Si specific flux is plotted against the mean latitude of each river basin, there is a general trend showing an increase in Si specific flux with decreasing latitude in the Northern Hemisphere (Figure 7). In other words, normalized Si annual flux decreases from tropical/subtropical, temperate river basins to Arctic river basins. Lower Si specific flux in

Table 3. Instantaneous (moles/s) and Integrated Annual Fluxes (10^6 moles/yr) of Nutrient Species (Dissolved, Particulate, Inorganic, and Organic Forms) From the Upper Yukon River Near the USGS Stevens Village Station[a]

	N-NO$_3$	N-DON	N-PN	P-PO$_4$	P-DOP	P-PP	Si-Si(OH)$_4$
Julian Day							
135	2.95	576	10.7	0.13	0.36	2.38	63
151	14.1	2997	234.8	0.71	1.88	56.8	553
165	19.2	2028	75.4	0.28	0.43	13.8	576
193	12.6	1365	31.4	0.14	0.057	12.6	470
221	11.3	856	37.3	0.18	0.36	15.6	526
255	15.5	638	23.6	0.11	0.071	7.9	544
Type of flux							
Average instantaneous flux, moles/s	12.6 ± 5.5	1410 ± 949	68.9 ± 84.2	0.256 ± 0.23	0.528 ± 0.682	18.2 ± 19.5	455 ± 195
2002 flux (10^6 moles/yr)[b]	241	20390	877	3.41	5.80	246	8670
Fraction of open season flux to annual flux	0.73	0.87	0.89	0.87	0.95	0.87	0.74

[a] DON, dissolved organic nitrogen; PN, particulate nitrogen; DOP, dissolved organic phosphorus; PP, particulate phosphorus.

[b] Annual nutrient flux (10^6 moles/yr) was the integrated flux using measured nutrient concentrations and corresponding river water discharge at the Stevens Station. Nutrient concentrations of the frozen season were based on the interpolated nutrient concentrations from autumn sampling points assuming little changes in nutrient concentrations during ice formation. Since the sampling station is not from the most downstream station, nutrient fluxes here are the lower limit of export fluxes to the Bering Sea.

Table 4. Comparison of Nutrient Specific Flux (mmole/m^2/yr) Between Rivers, Calculated From the Nutrient Concentrations Listed in Table 2 and Discharge and Drainage Area Listed Here

River	Mean Latitude (basin wide)	Discharge, km^3/yr	Drainage Area, 10^9 m^2	NO_3, mmol/m^2/yr	PO_4, mmol/m^2/yr	$Si(OH)_4$, mmol/m^2/yr
Amazon	0° (~20°S–7°N)	6938	7050	9.8	0.69	113
Mekong[a]	18°N (8°N–28°N)	473	795	-	-	88
Changjiang (Yangtze)	30° (24°N–36°N)	925	1800	28	0.26	42
Trinity	32°N (30°N–34°N)	22	46	19	0.88	39
Mississippi	38°N (~29°N–48°N)	600	3250	21	1.4	23
Ob	58°N (~48°N–68°N)	404	2990	7.6	0.31	22
Yenisey	60°N (~47°N–73°N)	580	2440	6.2	0.095	25
Mackenzie	62° (~54°N–70°N)	281	1680	0.40	0.017	8
Lena	63°N (~53°N–73°N)	525	2430	1.3	0.099	14
Yukon[b]	64° (~59°N–69°N)	200	855	0.57	0.012	19

[a] Data of dissolved silicate concentration in Mekong River are taken from *Berner and Berner* [1996].

[b] As the first approximation, specific fluxes for Yukon River Basin were estimated from our nutrient data assuming similar nutrient concentrations between our sampling station and the most downstream station. Therefore nutrient fluxes here could be the lower limit of export fluxes of Yukon River to the Bering Sea.

Arctic river basins suggests that temperature may be an important factor in controlling $Si(OH)_4$ fluxes in river basins. Surely, the geologic framework and presence of silicates verse carbonate substrate can control $Si(OH)_4$ fluxes. In addition, the presence of permafrost in northern rivers may play a role. Our conclusions here are consistent with the effect of temperature on silicate weathering rates for river basins in a cold climate [*Edmond and Huh*, 1997; *Millot et al.*, 2003].

4. Summary and Conclusions

[32] Concentrations of nutrients (N, P, Si) in dissolved, particulate, inorganic, and organic phases were measured in Yukon River waters from snowmelt in mid-May to ice opening in late May/June and continued to September. Concentrations of NO_3 and PO_4 measured in the Yukon River were significantly lower than those of tropical/subtropical and temperate rivers, indicating a near-pristine nature of the Yukon River Basin. Concentrations of $Si(OH)_4$, on the other hand, were more comparable to those observed in other rivers. Even though inorganic nutrient concentrations were low in Yukon River waters, concentrations of DON and DOP were relatively high, and N and P were mostly partitioned in dissolved organic and particulate phases, respectively. Contrasting variation patterns between PO_4 and $Si(OH)_4$ and their different correlations with freshwater discharge, conductivity, and DOC concentration suggest that PO_4 and $Si(OH)_4$ are derived from different biogeochemical processes in the Yukon River basin.

[33] Integrated annual nutrient flux at the Steven Village station in 2002 was 2.4×10^8 mole-N/yr for NO_3, 203×10^8 mole-N/yr for DON, 8.8×10^8 mole-N/yr for PN, 0.034×10^8 mole-P/yr for PO_4, 0.058×10^8 mole-P/yr for DOP, 2.5×10^8 mole-P/yr for PP, and 87×10^8 mole-Si/yr for $Si(OH)_4$, respectively. The instantaneous fluxes during the river ice open season contributed substantially to their annual fluxes, accounting 73% of the annual flux for NO_3, 87% for DON, 89% for PN, 87% for PO_4, 95% for DOP, 87% for PP, and 74% for $Si(OH)_4$, respectively. Nutrient specific fluxes normalized to drainage area in the Yukon River Basin were 0.57 mmole/m^2/yr for NO_3, 0.012 mmole/m^2/yr for PO_4, and ~19 mmole/m^2/yr for $Si(OH)_4$, respectively. These relatively low specific fluxes of N and P in the Yukon River Basin reflect its pristine status with little anthropogenic influence, whereas cold climate in the Arctic/subarctic region may result in its lower Si specific flux. Globally, NO_3 and PO_4 specific fluxes in rivers are generally related to anthropogenic inputs, with the highest values found in most populated river basins, whereas $Si(OH)_4$ specific flux demonstrated a general increase with decreasing latitude of each river basin. The increase in $Si(OH)_4$ specific flux with decreasing latitude indicates a climatic control on $Si(OH)_4$ concentration in river waters and therefore its export flux to the ocean.

[34] Our results support a model whereby early summer Yukon River flows are dominated by snowmelt runoff and late summer flows contain a distinct signal of active layer biogeochemistry. A changing (warming) climate in the Yukon River watershed is likely to enhance the riverine fluxes of nutrients into the Bering Sea.

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