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# Seasonal Variations In Nutrient Concentrations and Speciation in the Chena River, Alaska

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[1] To better understand the seasonal controls on nutrient abundances, speciation, and fluxes in a watershed underlain by discontinuous permafrost, we collected water samples biweekly from the Chena River during 2005–2006 to measure inorganic and organic N, P, and Si in dissolved and particulate phases. Nitrate concentrations were low (8–14 $\mu$M) during the winter and summer dry seasons but were elevated during the spring freshet (15–24 $\mu$M). Ammonium varied from 8 to 13 $\mu$M during the winter but dropped dramatically during the ice-open season to 0.1–3 $\mu$M. Phosphate was very low throughout the year (ranging from 0.03 to 0.3 $\mu$M), reflecting the pristine condition of the watershed. Dissolved silica was high in the winter and reached its minimum during the spring freshet. DIN was the dominant species in the total N pool (60%), followed by DON (30%) and PN (10%). Most of the phosphorous was present in the particulate phase (74%), with phosphate and DOP only comprising 19% and 7%, respectively. Seasonal variations in nutrient concentrations and speciation were mostly controlled by the hydrological flow regime and biological activity in the river. Annual nutrient export fluxes from the Chena River during 2005–2006 were 51.1 $\times$ $10^6$ mole-N, 1.4 $\times$ $10^6$ mole-P, and 197 $\times$ $10^6$ mole-Si, corresponding to an annual yield of 9.8 $\times$ $10^3$ mol-N $km^{-2}$, 0.28 $\times$ $10^3$ mol-P $km^{-2}$, and 37.9 $\times$ $10^3$ mol-Si $km^{-2}$, respectively. Within the annual export fluxes, the spring freshet contributed about 18% of TN, 27% of TP, and 10% of Si, while the winter season contributed 11% of TN, 12% of TP, and 20% of Si. Continued climatic warming in northern watersheds will likely increase the export of nutrient species from watersheds.

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## 1. Introduction

[2] High latitude regions have warmed dramatically in recent decades and this has resulted in permafrost thawing and increased river discharge and material fluxes into the Arctic Ocean [*Peterson et al.*, 2002; *Jorgenson et al.*, 2006; *Guo et al.*, 2007]. With continued warming, higher export fluxes can be expected for chemical species, including carbon, nutrients, and major/trace elements, from tundra and permafrost terrains to streams, rivers and the ocean [e.g., *Guo et al.*, 2004; *Petrone et al.*, 2006; *Frey et al.*, 2007; *Walvoord and Striegl*, 2007]. However, nutrient biogeochemical cycling in arctic river basins and the impact and biogeochemical consequences of arctic warming are poorly understood. Little is known about the response of individual watersheds to climate warming and permafrost thawing in the Arctic, especially for small rivers. Therefore, baseline data sets and time series measurements are critical for trend analysis and a better understanding of the links between arctic biogeochemical cycles and climate change.

[3] The riverine nutrient flux entering the Arctic Ocean is an integrated basin scale biogeochemical signal [*Holmes et al.*, 2001]. Individual headwater watersheds, even in the same river basin, may differ from each other in their nutrient concentrations, speciation, cycling and exports due to different physical, geological and environmental settings [e.g., *Dornblaser and Striegl*, 2007; *Striegl et al.*, 2007]. However, systematic investigations of the nutrient biogeochemistry in small arctic and boreal watersheds remain sparse [*Tockner et al.*, 2002; *Hodson et al.*, 2005; *Petrone et al.*, 2006].

[4] Interior Alaska is underlain by warm (−2 to −3°C) discontinuous permafrost which is susceptible to climate warming. If this permafrost thaws, degradation and subsidence are expected [*Osterkamp and Romanovsky*, 1999; *Hinzman et al.*, 2006a; *Jorgenson et al.*, 2006]. This will have major impacts on watershed hydrology and nutrient fluxes by increasing the groundwater contribution, creating deeper and longer water flow paths, and weakening spring snowmelt events [*Hinzman et al.*, 2006b; *Walvoord and*

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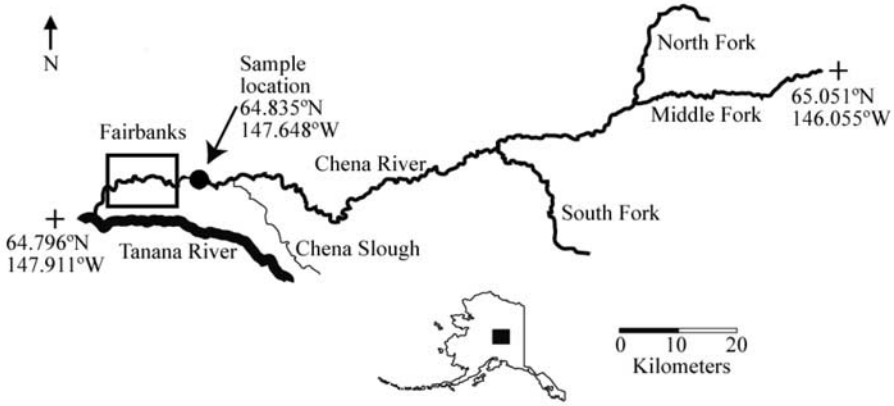


**Figure 1.** A map of the Chena River basin and the sampling location at 64.835°N and 147.648°W (marked with a solid circle).

*Striegl*, 2007]. Permafrost degradation will also expose previously frozen mineral and organic surfaces to weathering processes. How watershed biogeochemistry responds to climate warming and associated hydrological changes are complicated processes that may sometimes induce opposing consequences. For example, enhanced groundwater yield tends to export more soil solutes while longer groundwater residence times in deep soil horizons may promote the adsorption and microbial decomposition of dissolved organic matter and some other solutes [*Striegl et al.*, 2005; *Petrone et al.*, 2006; *Walvoord and Striegl*, 2007]. Other factors, including changes in vegetation distribution and forest fire prevalence would also affect terrestrial ecosystem biogeochemistry and the export of chemical species from watersheds.

[5] The objectives of this study were to determine nutrient abundance, speciation and fluxes and their relationship to hydrological conditions in the Chena River and to provide a baseline data set (including nutrient concentrations, speciation, and fluxes) for evaluating the responses of nutrient biogeochemistry to arctic warming and environmental changes in northern watersheds. River water samples were collected biweekly from the Chena River during 2005–2006. Chemical forms of nutrients (N, P, and Si) reported in this study include nitrate plus nitrite (referred hereafter as nitrate), ammonium, dissolved inorganic phosphate (DIP), and dissolved silicate ($Si(OH)_4$), dissolved organic nitrogen (DON), dissolved organic phosphorous (DOP), particulate nitrogen (PN), and particulate phosphorous (PP).

## 2. Materials and Methods

### 2.1. Site Description

[6] The Chena River is a clear water river that drains a watershed of roughly 5,200 $km^2$ (Figure 1). It contributes annually ~1.18 $km^3$ of water to the Tanana River, the largest tributary of the Yukon River. Most of interior Alaska is in the discontinuous permafrost zone [*Brabets et al.*, 2000; *Ping et al.*, 2006]. Interior Alaska has a strong continental climate characterized by long cold winters and warm summers with a short growing season (from early May to mid-September). Temperature for the Fairbanks area has extreme seasonal variations, from −50°C in winter to 33°C in summer, with an annual mean of −3.1°C [*Hinzman et al.*, 2006a]. Sunlight also has an extreme variation from less than 4 h in December to nearly 22 h in June. Annual precipitation in Fairbanks, 35% as snow, ranges from 142 mm to 478 mm, with a 50-year average of 387 mm.

[7] Our sampling site is located upstream of downtown Fairbanks (64.835°N; 147.648°W) near the USGS hydrological station (1 km downstream of the sampling site) and above the urban center to avoid potential human impacts while representing the entire basin.

### 2.2. Sample Collection

[8] Water samples were collected weekly to bi-weekly from March, 2005 through February, 2006 (Table S1, available as auxiliary material) using a precleaned 3 L high density polyethylene (HDPE) bucket to scoop samples from a bridge spanning the Chena River.[1] During the open water season, water samples were collected from the south, center, and north sides of the river and were mixed together in a 10 L acid cleaned HDPE carboy to minimize the effects of river heterogeneity on sampling. The river wasn't sampled at different depths since it is generally a shallow river with low water gage (<1 m) during most of the open season (http://waterdata.usgs.gov/ak/nwis/uv?15514000). During the winter frozen season water samples were collected from the main channel under the ice through a hole drilled with a SIPRE style auger. Water samples were filtered through 0.4 $\mu$m Millipore HTTP filters. Filtrates were collected and stored frozen for nutrient analysis, which included total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN), phosphate or dissolved inorganic phosphorus (DIP), DOP, and $Si(OH)_4$. Filter samples were freeze-dried for the analysis of suspended particulate matter (SPM) and PP. For particulate organic carbon (POC) and PN analysis, water samples were filtered through pre-combusted 0.7 $\mu$m GF/F filters. Filters were freeze-dried and acid fumed for POC and PN analysis.

### 2.3. Nutrient Measurements

[9] Concentrations of nitrate ($NO_3$ plus $NO_2$), ammonium ($NH_4$), and $Si(OH)_4$ were analyzed using colorimetry on a

[1]Auxiliary materials are available in the HTML. doi:10.1029/2008JG000733.

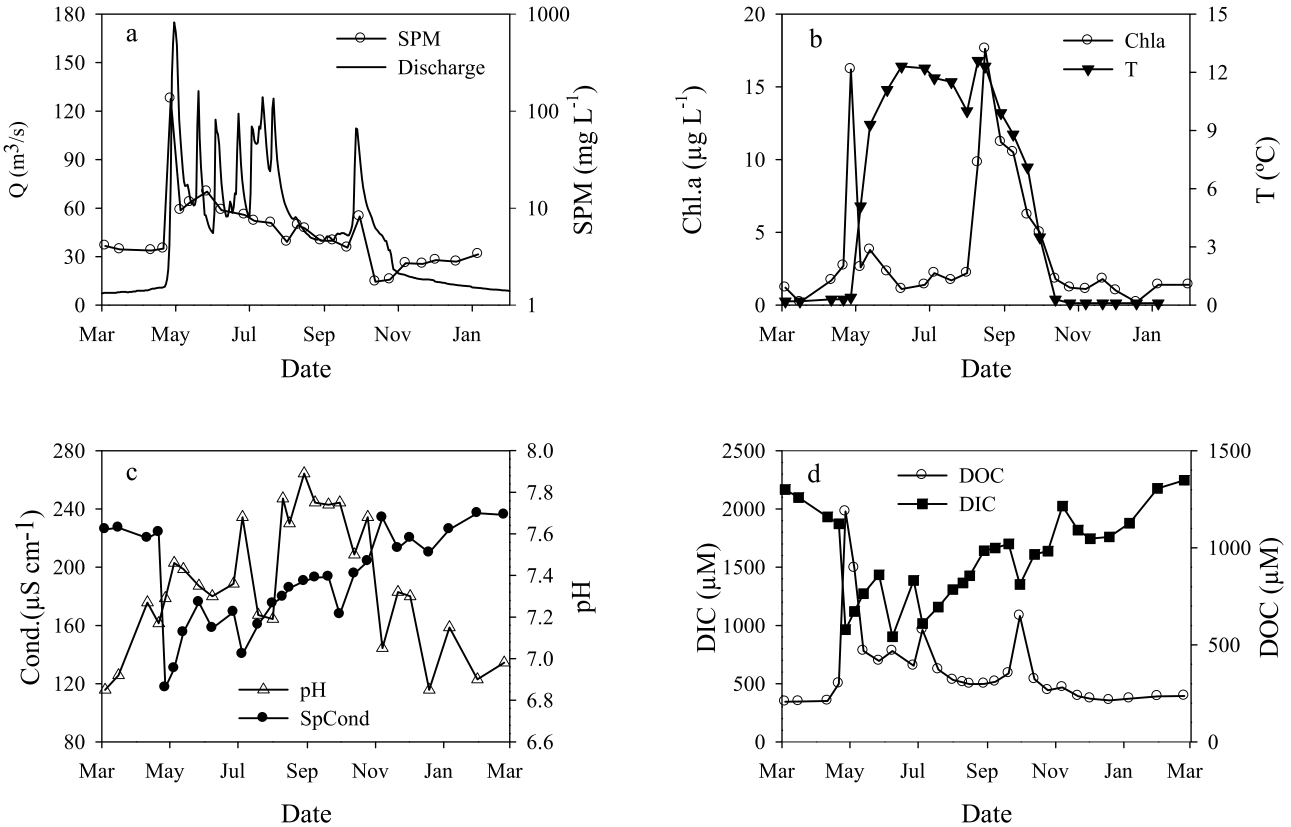


**Figure 2.** Seasonal variation in hydrographical parameters and water chemistry in the Chena River. (a) Suspended particulate matter (SPM) concentration and discharge (Q); (b) chlorophyll a concentration and water temperature; (c) pH and specific conductance; (d) DOC and DIC concentrations.

Technicon AutoAnalyzer II [*Whitledge et al.*, 1981; *Guo et al.*, 2004]. The accuracy for silicate, nitrate and ammonium measurements was 0.05 $\mu$M, 0.01 $\mu$M and 0.03 $\mu$M, respectively. The precision of the measurements was approximately half of the above accuracy levels. Concentrations of DIN were calculated as the sum of concentrations of $NO_3$ + $NO_2$ + $NH_4$. Concentrations of PN were measured by an elemental analyzer.

[10] Concentrations of dissolved organic carbon (DOC), total dissolved carbon (TDC), and TDN were measured on a Shimadzu TOC analyzer (TOC-V) interfaced with a nitrogen detector (TNM-1). The precision and accuracy for both C and N analyses were better than 2% based on measurements of inserted standards. Dissolved inorganic carbon (DIC) concentrations were calculated as the difference between TDC and DOC while concentrations of DON were calculated from the difference between TDN and DIN concentrations [*Guo et al.*, 2004; *Guo and Macdonald*, 2006].

[11] Phosphate concentrations in the Chena River are close to or lower than the detection limit (~50 nM) of the traditional autoanalyzer. Therefore, phosphate concentrations were measured on a HP 8453 spectrophotometer with a 5 cm cuvette to improve the detection limit. Total dissolved phosphorus (TDP) concentrations were measured by autoclave-assisted persulfate oxidation of the DOP at boiling temperature, followed by the standard phosphomolybdenum blue method. Concentrations of DOP were calculated from the difference between TDP and DIP. Concentrations of PP were determined by wetting filter samples with $Mg(NO_3)_2$ solution and ashing the samples at 550°C for 2 h to decompose organic phosphorus compounds, followed by extraction with 1 M HCl for 16 h at room temperature. Orthophosphate concentrations in the extracts were determined by the standard antimonyphosphomolybdate colorimetric method using an HP 8453 spectrophotometer. Precision and accuracy for the analysis of P were better than 1%.

## 3. Results

### 3.1. Hydrological Data

[12] Discharge, water temperature, pH, conductivity, and concentrations of SPM, Chl-a, DIC, and DOC are shown in Table S1 and depicted in Figure 2. Based on variations in hydrographic parameters, four unique hydrological seasons can be identified during our sampling period of 2005–2006: (1) winter base flow (March to April, 2005 and October 2005 to February 2006), (2) spring runoff event dominated by snowmelt (April to May, 2005), (3) summer and fall open water (including fall flood; May to mid-August, and late September to October, 2005), and (4) late summer drought (mid-August to late September, 2005).

[13] During 2005–2006 there was a prominent summer drought event from mid-August to late September 2005 characterized by low discharge (40 $m^3$ $s^{-1}$), high water temperatures (12°C), low SPM concentrations (4–7 mg $L^{-1}$), and high Chl-a concentrations (Figure 2).

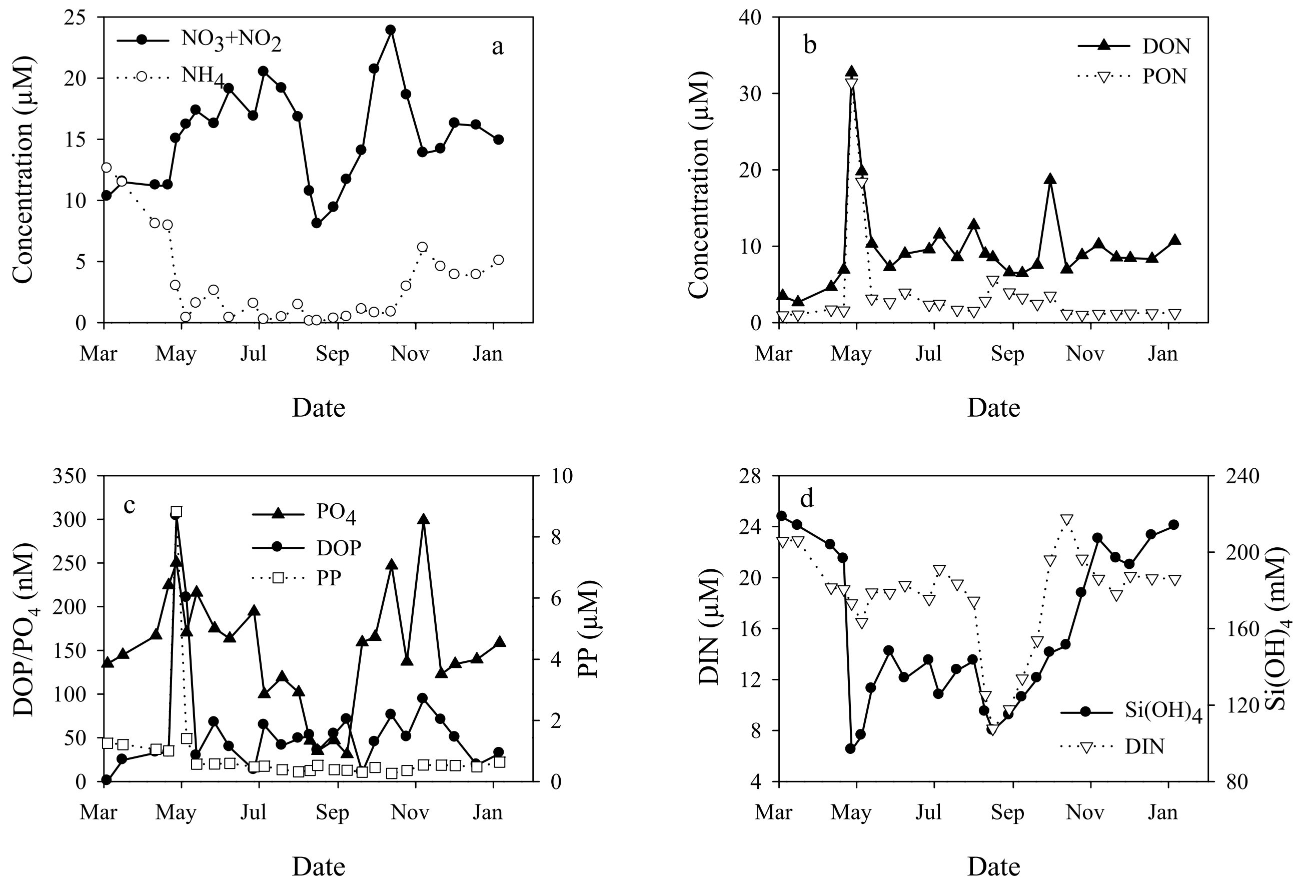


**Figure 3.** Seasonal variation in nutrient concentrations in the Chena River. (a) Nitrate and ammonium; (b) DON and PN; (c) phosphate, DOP, and PP; (d) dissolved silicate and DIN.

### 3.2. Seasonal Variations in Nutrient Concentrations

[14] Variations of nutrient concentrations are shown in Table S2 and Figure 3. Ammonium remained at very low concentrations (0.1–2.6 $\mu$M) during the river open water season but increased dramatically in the winter. However, ammonium was about 5.6 $\mu$M lower in the winter of 2005–2006 than in the winter of 2004–2005, coincident with higher discharge during 2005–2006 (Table S1). Generally, nitrate had the highest concentrations during the summer and fall open water seasons and the lowest concentrations during the winter. The nitrate concentration minimum occurred during the summer drought season when Chl-a concentrations were elevated (Figure 3). Winter nitrate concentrations during 2005–2006 were about 4 $\mu$M higher than during 2004–2005, compensating for about 75% of the ammonium loss during the winter of 2005–2006. The DIN concentration was somewhat stable throughout the year, ranging from 16.6 to 22.9 $\mu$M except during the summer drought when the DIN concentration dropped to as low as 8.1 $\mu$M. The DON and PON concentrations were low during the winter but increased dramatically during the spring freshet. There were several DON concentration peaks during the open water season accompanying the high flow events. Similar to ammonium, the winter DON concentration during 2005–2006 was higher than during 2004–2005 due to the higher river discharge. The PN concentration was similarly low (1.2 $\mu$M on average) during both winters and increased roughly 30 times during the spring freshet. The PN concentration was also elevated during the summer drought season when the river discharge was low and the Chl-a concentration was high.

[15] The phosphate (DIP) concentration in the Chena River ranged from 0.03 to 0.30 $\mu$M during the year. The maximum DIP concentration occurred during the spring freshet and early November during river ice formation. Maximum concentrations of major ions as well as conductivity were also observed during ice formation (T. A. Douglas, unpublished data) and are likely due to the decreased flows and exclusion of solutes during river ice formation. Lower DIP concentrations were measured during the summer drought season which is similar to DIN. Concentrations of DOP were even lower than DIP, with a yearly average of 0.060 ± 0.063 $\mu$M. However, during the spring freshet the DOP concentration was comparable to the DIP concentration. The PP concentration was fairly constant throughout the year except during the spring freshet. The average PP concentration was 0.6 ± 0.3 $\mu$M excluding data points from the spring freshet during which it increased dramatically to 8.8 $\mu$M along with the SPM maximum (Figure 3).

[16] The $Si(OH)_4$ concentration was high during the winter with an average of 203 ± 12 $\mu$M. It dropped to about half of the winter value, about 100 $\mu$M, during the spring freshet and summer drought seasons. During the open water season the $Si(OH)_4$ concentration was somewhat stable, fluctuating within a small range of 125–150 $\mu$M.

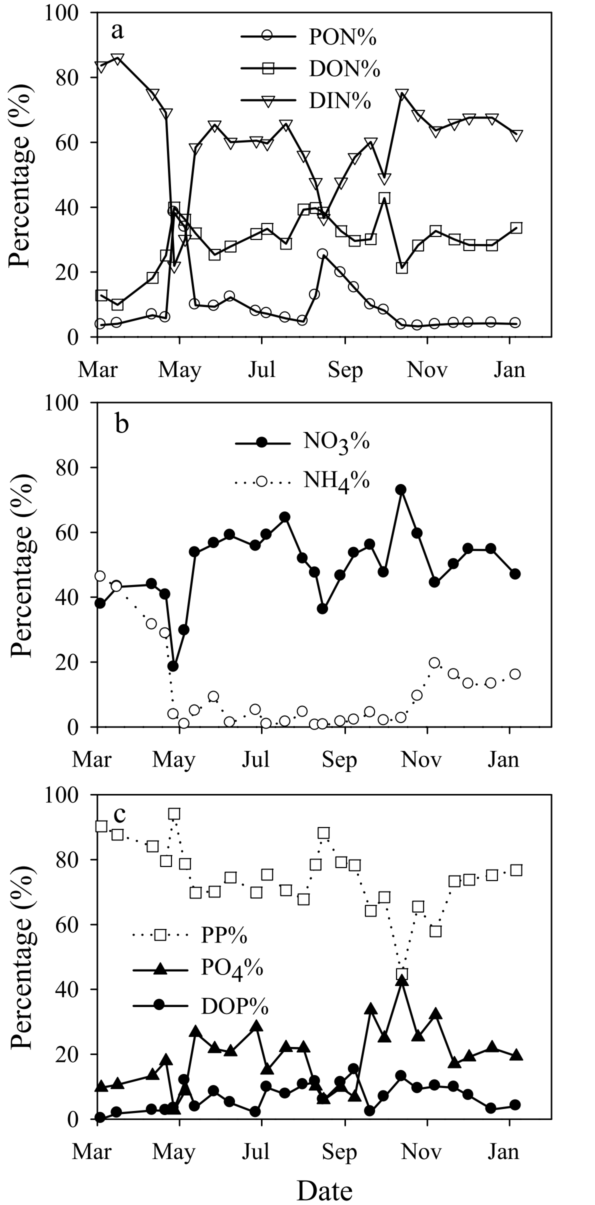


**Figure 4.** Seasonal variation in nutrient species in the Chena River. (a) PN%, DON%, and DIN%; (b) $NO_3$% and $NH_4$%; (c) PP%, $PO_4$%, and DOP%.

### 3.3. Seasonal Variations in Nutrient Speciation

[17] DIN was the dominant N species in the Chena River watershed but its percentage in the total N pool decreased during discrete events that included the spring freshet, the summer drought and the fall rain event (Table S3 and Figure 4). During the spring freshet the %DIN decreased to as low as 20% while the %PN and the %DON increased to 40% and 38%, respectively. The high surface flows associated with the fall precipitation flushed large amounts of soil DON into the river and increased DON to 43% of the N pool and decreased DIN to 49% of the total N pool. The DIN% was relatively low (37%) during the summer drought season due to biological uptake while the DON% and PN% were 38% and 25%, respectively. Nitrate was a dominant DIN species during most of the year except during the end of the 2005 winter when the ammonium concentration was higher than nitrate (Table S2). Overall, DIN accounted for 60 ± 15% of the total N in the Chena River while DON and PN comprised 30 ± 8 and 10 ± 9%, respectively.

[18] Most of the P was present in the particulate form, comprising 74 ± 10% of the total P in the Chena River while DIP and DOP comprised 19 ± 9% and 7 ± 4% of the total P. The phase partitioning of P showed a seasonal variation similar to that of N. The PP percentage increased to 94% and 88% during the spring freshet and summer drought season, respectively. Meanwhile, DIP concentrations were at their minimum value during these two seasons (Table S3 and Figure 4).

## 4. Discussion

### 4.1. Controlling Factors for Nutrient Concentrations

#### 4.1.1. Hydrological Cycles

[19] Conductivity, SPM and all nutrient species, except DIN and DIP, exhibit a hydrological control, but with different impacts (Figure 5). Concentrations of $Si(OH)_4$, DIC and conductivity in the Chena River were significantly inversely correlated ($P < 0.0001$) with discharge although a few data points from the summer drought season lie under the correlation line. Combined with the oxygen and hydrogen stable isotopic composition (T. A. Douglas, unpublished data), these correlations clearly demonstrate the mixing between groundwater with high $Si(OH)_4$ and DIC concentrations and flow from snowmelt/precipitation lacking in both species [*Guo et al.*, 2004; *Guo and Macdonald*, 2006; *Cai et al.*, 2008]. In contrast, dissolved organic nutrients and POC and PN positively correlated with discharge ($P < 0.05$), indicating a dominant allochthonous source for DOM and POM [*Spitzy and Leenheer*, 1991; *Guo et al.*, 2003; *Cai et al.*, 2008]. Particulate P in the Chena River, which might contain a certain amount of inorganic P [*Tiessen*, 1996], showed a different relationship with discharge than POC, PN and SPM. During winter low flow conditions the PP concentration was elevated but decreased significantly with increasing discharge to a background value of 0.3 to 0.6 $\mu$M. The PP values remained in the range of 0.3 to 0.6 $\mu$M during most of the open water season.

#### 4.1.2. Sources of Nutrients

[20] DIN and DIP concentrations had a small variability throughout the year, in the range of 15–25 $\mu$M and 0.10–0.30 $\mu$M, respectively, except during the summer drought season (Figure 5). The DIN concentration in the Chena River was within the range of interior Alaska watersheds underlain by discontinued permafrost [*Jones et al.*, 2005; *Petrone et al.*, 2006] but higher than most Alaskan and Siberian Arctic rivers that exhibit greater permafrost coverage (<15 $\mu$M [*Cauwet and Sidorov*, 1996; *Holmes et al.*, 2001; *Guo et al.*, 2004; *Dornblaser and Striegl*, 2007]) and southern boreal streams with less permafrost coverage (<6.8 $\mu$M [*Ford and Naiman*, 1989; *Stottlemyer*, 1992; *Cooke and Prepas*, 1998]). Surprisingly, the speciation and phase partitioning of N in the Chena River are significantly different from the upper Yukon River in which DON is the dominant N species, making up 67% of the total N pool while PN and DIN made up 25% and 7%, respectively [*Guo et al.*, 2004]. Similarly, the DIP concentration in the

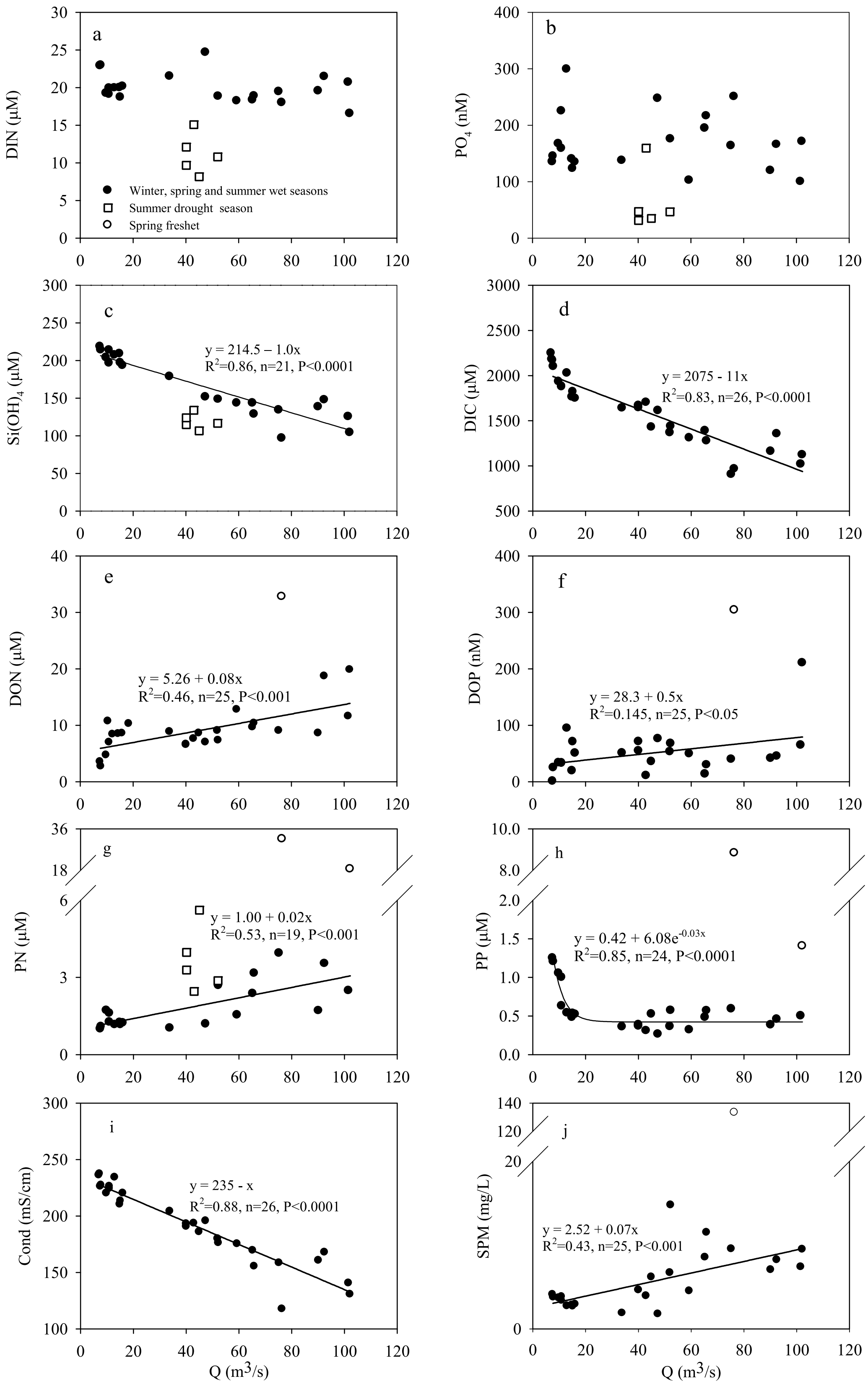


**Figure 5.** Relationships between nutrient concentrations and discharge (Q). Only the solid symbols in the figures are used in the regressions. (a) DIN; (b) $PO_4$; (c) $Si(OH)_4$; (d) DIC; (e) DON; (f) DOP; (g) PN; (h) PP; (i) conductivity; (j) SPM.

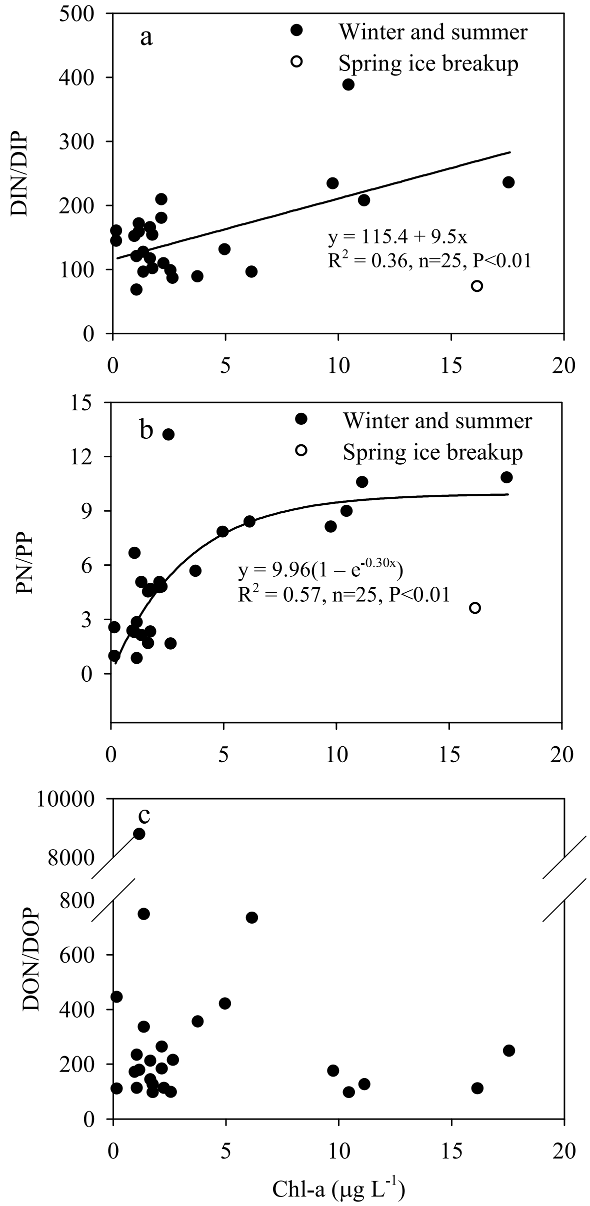


**Figure 6.** Relationships between the chlorophyll-a concentration and ratios of (a) DIN/DIP, (b) PN/PP, and (c) DON/DOP.

Chena River is about two times higher than in the upper Yukon River [*Guo et al.*, 2004]. The elevated DIN and DIP concentrations may suggest extra input from intense degradation of warm discontinued permafrost and weathering of deeper active and mineral layers and intensive nitrogen fixation for DIN [*MacLean et al.*, 1999; *DeLuca et al.*, 2002; *Jones et al.*, 2005; *Petrone et al.*, 2006].

#### 4.1.3. Spring Freshet

[21] Spring freshet is a distinct major hydrological event for arctic and subarctic rivers which delivers disproportionately high amounts of DOM and suspended particles to the rivers [*Dittmar and Kattner*, 2003; *Rember and Trefry*, 2004; *Finlay et al.*, 2006; *Guo and Macdonald*, 2006; *Cai et al.*, 2008] and requires more intensive sampling. Apparently, all dissolved organic and particulate nutrients in the Chena River showed annual maximum concentrations and deviated far above the nutrients-discharge relationship in response to the spring ice breakup and flooding (Figure 5).

#### 4.1.4. In Situ Biological Uptake

[22] Summer drought in the Chena River was characterized by the annual Chl-a maximum, indicating the river algae growth enhanced during low turbidity, long water resident time, and greater solar irradiance. Large amounts of dissolved inorganic nutrients were assimilated during this algae bloom and converted into autochthonous particulate nutrients. This in situ process undoubtedly accounted for the decrease in dissolved inorganic nutrient concentrations and the increase in the PN concentration (Figure 5).

### 4.2. N/P Ratio of Dissolved and Particulate Phases

[23] The DIN/DIP molar ratio in the Chena River was in the range of 67 to 387, with an annual average value of 147 ± 68. This ratio is almost 10 times the Redfield ratio (N/P = 16) and among the highest ratios in world rivers (usually less than 100 [*Lara et al.*, 1998; *Liu et al.*, 2003; *Turner et al.*, 2003; *Guo et al.*, 2004]). The high N/P ratio indicates a strong P-limitation in the Chena River basin. The yearly average DON/DOP molar ratio in the Chena River is even greater at 566 ± 1679. This is close to the value measured for the upper Yukon River (716 ± 812 [*Guo et al.*, 2004]) and is significantly higher than what has been reported for subtropical and temperate rivers such as the Changjiang (∼337 [*Liu et al.*, 2003]), Loire (∼64 [*Meybeck et al.*, 1988]) and Morlaix rivers (∼97 [*Wafar et al.*, 1989]). Differences in the DON/DOP ratio between northern watersheds and other world rivers reflect distinct characteristics of terrestrial DOM sources in pristine basins underlain by permafrost. In contrast to the high DIN/DIP and DON/DOP ratios in dissolved phase, the particulate N/P molar ratio (0.8–13) in the Chena River was significantly lower than the Redfield ratio. This low yearly range in the PN/PP ratio is identical to the upper Yukon River [*Guo et al.*, 2004] and reflects particulate sources derived from old and highly degraded soils [*Ping et al.*, 1998; *Guo and Macdonald*, 2006; *Guo et al.*, 2007; *Cai et al.*, 2008]. Interestingly, the Changjiang River and its tributaries, even though they experience widespread anthropogenic influences, also have PN/PP ratios less than the Redfield ratio [*Liu et al.*, 2003]. These low PN/PP ratios indicate that human activities may have little or no direct effect on the composition of riverine particulate nutrients despite the fact that dissolved nutrient loads have been shown to be greatly influenced by anthropogenic factors [*Turner et al.*, 2003].

[24] Our observation that N/P ratios of dissolved inorganic and particulate nutrients are correlated with Chl-a concentrations in the Chena River (n = 25, $P < 0.01$; Figure 6) supports the notion that aquatic biological activity could play a role in controlling nutrient cycling and transformation, especially during the summer growing season when water turbidity is low. DIN and DIP are likely utilized by aquatic organisms in a ratio similar to the Redfield ratio. Due to the disproportionately high DIN and low DIP concentrations in the Chena River, any biological uptake of dissolved inorganic nutrients should greatly increase the DIN/DIP ratio in the remaining dissolved inorganic nutrient pool. Meanwhile, aquatic biogenic particles with a C/N ratio similar to the Redfield ratio will contribute to the particulate

**Table 1.** Annual Yield of Nutrient and Water and Flux of Nutrient and Water From the Chena River[a]

| Species | Days | Water | DIN | DON | PN | DIP | DOP | PP | $Si(OH)_4$ |
|---|---|---|---|---|---|---|---|---|---|
| Annual yield | 365 | 0.67 | 5.2 | 3.3 | 1.3 | 0.05 | 0.02 | 0.21 | 37.9 |
| Annual flux | 365 | 1.27 | 26,893 | 17,290 | 6,935 | 237 | 113 | 1,099 | 197,100 |
| Winter flux | 171 | 0.16 | 3,827 | 1,458 | 267 | 27.4 | 8.0 | 132 | 39,330 |
| Spring freshet flux | 16 | 0.16 | 4,320 | 3,200 | 1,760 | 63.2 | 21.4 | 305 | 19,680 |
| Drought season flux | 51 | 0.21 | 3,172 | 1,806 | 513 | 17.3 | 9.2 | 77.3 | 30,090 |
| Other open season flux | 127 | 0.74 | 15,574 | 10,826 | 4,395 | 129 | 74.4 | 585 | 108,000 |
| Ratio of winter flux/annual flux | 171/365 | 0.13 | 0.14 | 0.08 | 0.04 | 0.12 | 0.07 | 0.12 | 0.20 |
| Ratio of spring freshet flux/annual flux | 16/365 | 0.13 | 0.16 | 0.19 | 0.25 | 0.27 | 0.19 | 0.28 | 0.10 |

[a]Units of measure are $10^3$ mol km$^{-2}$ a$^{-1}$ (annual yield of nutrient), mm d$^{-1}$ (annual yield of water), $10^3$ mol a$^{-1}$ (flux of nutrient), and km$^3$ (flux of water).

nutrient pool during the summer growing season. Indeed, during the high primary production season, autochthonous POM sources prevailed over terrestrial POM sources in the Chena River [*Cai et al.*, 2008]. Similar cases have been observed for other Northern high latitude rivers [*Goñi et al.*, 2005; *Zou et al.*, 2006]. The addition of autochthonous POM likely increases the nutrient stoichiometry of suspended particles to values that are close to the Redfield ratio in the Chena River. An exception to the relationship between the stoichiometry of dissolved inorganic nutrients, particulate nutrients and Chl-a concentrations occurred during the spring freshet (Figures 6a and 6b). High Chl-a concentrations during the spring freshet most likely resulted from ice algae dissociated from the bottom of river ice [*Cai et al.*, 2008] and benthic algae flushed from organic coated riverbed surfaces. However, these autochthonous particles only made up a small fraction of the river suspended particle pool due to the massive addition of surface soils and plant litter during snowmelt and its associated peak flow event [*Guo and Macdonald*, 2006; *Zou et al.*, 2006]. Therefore, the dissolved inorganic nutrient and particulate nutrient pools still exhibited typical terrestrial characteristics under low Chl-a concentrations.

[25] Unlike the dissolved inorganic nutrients and the particulate nutrients the organic N/P ratio in the dissolved phase did not show a significant correlation with Chl-a concentrations (Figure 6c). Thus, river algae could not be a major source of DOM to the Chena River, even during the summer algal bloom. Instead, terrestrial DOM is the dominant source to the Chena River [*Guo et al.*, 2003; *Cai et al.*, 2008]. This supports results from the upper Yukon River that are inferred from the isotopic and molecular composition of DOM [*Guéguen et al.*, 2006; *Guo and Macdonald*, 2006].

### 4.3. Yields and Fluxes of Nutrients From the Chena River

[26] Annual nutrient export fluxes from the Chena River are estimated with the LOADEST program from U.S. Geological Survey at 51.1 × $10^6$ mol-N, 1.4 × $10^6$ mol-P and 197 × $10^6$ mol-Si, corresponding to an annual yield of 9.8 × $10^3$ mol-N km$^{-2}$, 0.28 × $10^3$ mol-P km$^{-2}$, and 37.9 × $10^3$ mol-Si km$^{-2}$, respectively, while water yields and flow volume are calculated with data provided by the U.S. Geological Survey (http://waterdata.usgs.gov/ak/nwis/uv?15514000; Table 1). Within the annual total N flux, DIN accounted for 53%, followed by DON (34%) and PN (13%). For phosphorus, PP accounted for 76% of the total P flux, and DIP and DOP accounted for 16% and 8%, respectively. Overall, DIN and PP are the dominant nutrient forms responsible for N and P losses, similar to those reported for other interior Alaskan watersheds [*Guo et al.*, 2004; *Jones et al.*, 2005; *Petrone et al.*, 2006]. In addition to TDP, riverine PP has been demonstrated to be an important reactive P source to global oceans [e.g., *Berner and Rao*, 1994; *Delaney*, 1998; *Mayer et al.*, 1998; *Suluta et al.*, 2004]. However, very few PP data are available compared to DIP or TDP in arctic and subarctic rivers [e.g., *Lara et al.*, 1998; *Brabets et al.*, 2000; *Holmes et al.*, 2000; *Petrone et al.*, 2006].

[27] Yields of DON and TDP in the Chena River are similar to those from other Yukon River tributaries [*Dornblaser and Striegl*, 2007]. However, yields of PN and PP are about one third of other Yukon tributaries, reflecting the fact that the Chena River is a clear water river with low suspended sediment load and corresponding particulate nutrient loads. In addition, due to the high DIN abundance, the water yield normalized DIN yield and thus TN yields in the Chena River are much higher than those of the Yukon River and other tributaries even though the Chena River has the lower normalized PN yield.

[28] It has been shown that dissolved silicate yields decrease in general from low latitude to high latitude river basins reflecting a temperature dependence on natural weathering rates [*Guo et al.*, 2004]. The dissolved silicate yield from the Chena River is 33 × $10^3$ mol km$^{-2}$ a$^{-1}$ which is higher than other arctic and subarctic rivers and is close to the value reported for subtropical rivers [*Guo et al.*, 2004, and references therein]. The higher dissolved silicate yield from the Chena River indicates a higher weathering rate or perhaps the presence of other dissolved silicate sources, most likely from hot springs in the Chena River basin which also provide a possible DIN source to the Chena River [*Petrone et al.*, 2006].

[29] Arctic and subarctic rivers show a pronounced seasonal pattern of exporting a majority of their dissolved organic and particulate chemical species during the spring freshet [*Guo et al.*, 2004; *Rember and Trefry*, 2004; *Finlay et al.*, 2006; *Guo and Macdonald*, 2006]. However, glacial-fed rivers have a weaker spring freshet event and their peak flow usually occurs during the summer when glaciers melt in response to high air temperatures [*Hinzman et al.*, 2006b]. So far, only a few studies have included winter sampling events to examine the importance of winter solute fluxes from northern rivers [*Petrone et al.*, 2006; *Cai et al.*, 2008]. In the Chena River, more than a quarter of the particulate nutrient species (PN and PP) were exported during the spring freshet (Table 1) indicating the dominance

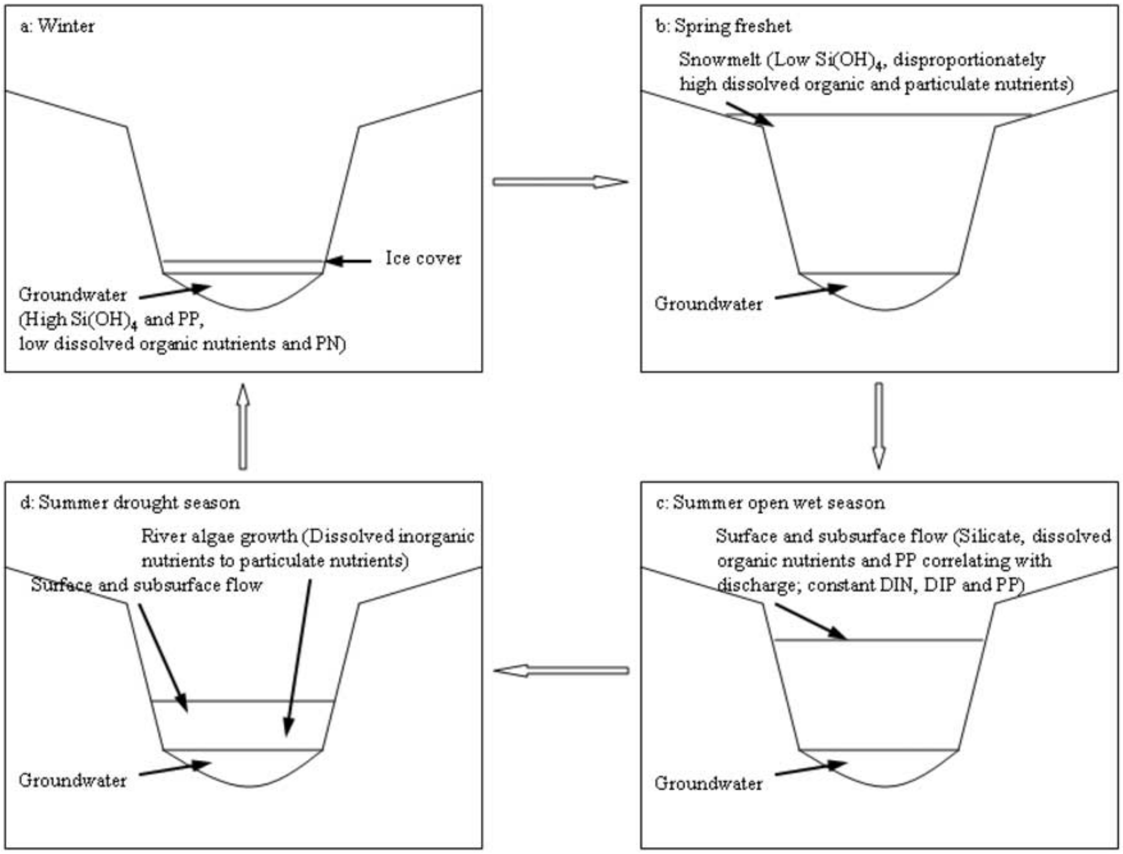


**Figure 7.** A conceptual model of nutrient dynamics in the Chena River. (a) Winter; (b) spring freshet; (c) summer open wet season; (d) summer drought season.

of spring snowmelt runoff in exporting suspended sediment and associated nutrients. The spring freshet also exported a variable but substantial portion of the dissolved nutrients (10–27%, depending on individual species), with water flux (13%) that equals to the portion exported during winter. The spring freshet is a flash flood event with less than 2 weeks duration but with disproportionately high discharge and material fluxes. Therefore, even with biweekly sampling and the U.S. Geological Survey LOADEST method, nutrient fluxes could still be underestimated. On the other hand, up to 20% of nutrients were exported from the Chena River during the winter (Table 1), even though very low discharge occurred. Thus, the transport mechanisms are different between nutrients and DOC, and between inorganic and organic chemical species [*Cai et al.*, 2008]. Long-term observations are needed to better understand the response of nutrient species to climate and environmental changes in northern high latitude watersheds.

### 4.4. Nutrient Dynamics and the Response to Environmental Change

[30] Nutrient concentrations and speciation in the Chena River exhibited a distinct seasonal variation in response to different hydrographical flow regimes and biological activities. During the winter, river base flow mainly consists of groundwater [*Walvoord and Striegl*, 2007], which also transported high $Si(OH)_4$ and DIN concentrations but low dissolved organic nutrients and PN from mineral layers (Figure 7a). Major snowmelt events flush disproportionately elevated dissolved organic and particulate nutrients from surface soils to the river and this dilutes the $Si(OH)_4$ accompanying the annual peak flow (Figure 7b). After the spring freshet phases out the soil active layer begins to thaw and contribute nutrients to the river as air and water temperatures increase gradually and surface and subsurface flows flush through watershed soils (Figure 7c). When the summer drought commences, primary production in the river is very high. River algae growth utilizes large amounts of dissolved inorganic nutrients that are greater than the supply by the surface and subsurface flow and this induces the significant decrease in these nutrient species. On the other hand, the river algal bloom produces autochthonous particulate nutrients and causes elevated PN and PP concentrations (Figure 7d).

[31] Climate warming in the Arctic has been observed for several decades and is predicted to continue [*ACIA*, 2004]. The major impacts of this amplified warming in interior Alaska are expected to include increased river discharge [*Peterson et al.*, 2002], changes in the surface vegetative cover [*Sturm et al.*, 2005; *McGuire et al.*, 2006], and, most importantly for soil and water biogeochemistry, the warming and subsequent degradation of permafrost [*Jorgenson et al.*, 2006]. Permafrost degradation will gradually open pathways between surface water and groundwater and therefore could enhance dissolved inorganic nutrient fluxes from northern watersheds [*Petrone et al.*, 2006; *Frey et al.*,

2007; *Walvoord and Striegl*, 2007]. The summer growing season is sensitive to climate warming. However, the potential increase in nutrient exports are likely to be more significant during the winter due to the more prominent warming trend in the winter [*Serreze et al.*, 2000] and the fact that winter base flows are associated with the lowest yearly discharge. Further, warming will likely shorten the winter season in northern watersheds and this, in turn, could increase river water yields compared to current winter flows [*Lammers et al.*, 2001; *Peterson et al.*, 2002]. Both processes will undoubtedly alter the composition of nutrients and their export fluxes.

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