

## Temporal variations in organic carbon species and fluxes from the Chena River, Alaska

Yihua Cai and Laodong Guo<sup>1</sup>

Department of Marine Science, University of Southern Mississippi, Stennis Space Center, Mississippi 39529

Thomas A. Douglas

U.S. Army Cold Regions Research and Engineering Laboratory, Fort Wainwright, Alaska 99703

### Abstract

Water samples were collected biweekly from the Chena River, Alaska, during 2005–2006 for analysis of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved carbohydrate (TCHO), including monosaccharide (MCHO) and polysaccharide (PCHO), particulate organic carbon (POC) and its isotopic compositions, and Si(OH)<sub>4</sub>. Carbon species exhibit strong temporal variations with elevated DOC, POC, and TCHO but depleted DIC and Si(OH)<sub>4</sub> during the spring freshet and decreased DOC, POC, and TCHO but elevated DIC and Si(OH)<sub>4</sub> concentrations under winter ice. Organic matter is mostly derived from surface soil leaching, whereas DIC and Si(OH)<sub>4</sub> are associated with groundwater and mineral layer leaching. On average, DIC was the predominant carbon species, accounting for  $77\% \pm 13\%$  of the total carbon pool, whereas DOC and POC comprised  $19\% \pm 10\%$  and  $4\% \pm 4\%$ , respectively. However, DOC became the dominant carbon species during the spring freshet. TCHO comprised  $15\% \pm 4\%$  of DOC with higher CHO:DOC ratios during spring runoff and summer. Within the TCHO pool, MCHO was the predominant CHO component ( $89\% \pm 10\%$ ), leaving  $11\% \pm 10\%$  as PCHO. The particulate organic matter source during the summer drought season was mostly autochthonous, with low POC:chlorophyll *a* and C:N but high POC:suspended particulate matter ratios and depleted  $\delta^{13}\text{C}$  values. The annual yields of DOC, DIC, and POC from the basin are  $133 \pm 8$ ,  $361 \pm 7$ , and  $27 \pm 4 \times 10^3$  mol C km<sup>-2</sup>, corresponding to an export flux of  $6.9 \pm 0.4$ ,  $18.8 \pm 0.4$ , and  $1.4 \pm 0.2 \times 10^8$  mol C yr<sup>-1</sup>, respectively. Anticipated changes in hydrological and biogeochemical cycles in high-latitude watersheds undergoing climate warming will likely be reflected in the chemical and phase speciation of carbon and other elements.

Carbon plays a fundamental role in Earth's climate and is a key component in the exchange between the biosphere, hydrosphere, and geosphere. A large pool of carbon is currently locked in permafrost in the form of organic carbon that is available for biogeochemical cycling if the permafrost melts (Guo et al. 2007). The introduction of this carbon to aquatic environments and the atmosphere through permafrost degradation could have major ramifications on the global carbon cycle and the climate system.

Northern rivers are major conduits for the transport and export of terrigenous organic carbon to the Arctic Ocean. Recent environmental changes and amplified warming in the Arctic have been shown to have a profound effect on northern watersheds, resulting in increasing river discharge (Peterson et al. 2002), permafrost degradation (Jorgenson et al. 2001), coastal erosion (Guo et al. 2004a; Stein and Macdonald 2004), and vegetation change (McGuire et al. 2006). However, the biogeochemical consequences of these ecosystem changes remain poorly understood. The response of riverine organic carbon composition and fluxes

to ongoing climate and environmental changes in the north is still a matter of debate (e.g., Frey and Smith 2005; Striegl et al. 2005). In addition, the composition and fluxes of riverine particulate organic carbon (POC) and dissolved inorganic carbon (DIC) have received little attention (Striegl et al. 2007), despite the fact that they may contribute substantially to the total C flux to the ocean (Stein and Macdonald 2004).

Recent studies have shown that dissolved organic carbon (DOC) from northern rivers is mostly contemporary and is thus derived from recently fixed terrestrial biomass (Benner et al. 2004; Guo and Macdonald 2006; Raymond et al. 2007; Striegl et al. 2007), whereas POC is old and is believed to be derived from deep soils and upper permafrost through river bank erosion (Guo and Macdonald 2006; Guo et al. 2007). Nevertheless, most studies on the carbon biogeochemistry of northern watersheds have focused, so far, on the summer growing season, with sparse sampling during the rest of the year due to remoteness and extreme weather conditions, especially during winter and snowmelt. The snapshot sampling strategy has been shown to miss important flow regimes in biogeochemical studies of northern watersheds. Furthermore, major river basins have large drainage areas and a variety of tributaries with distinctly different permafrost, hydrology, vegetation cover, land use, and water chemistry (Brabets et al. 2000). As a result, the information obtained is an ambiguous mixture of basin-wide signals, and specific processes in different watersheds cannot be revealed using the overall downstream signature. In contrast, small watersheds may exhibit more sensitivity to climate change and associated local

<sup>1</sup> Corresponding author (Laodong.Guo@usm.edu).

### Acknowledgments

We gratefully thank Mindy Juliana, Chuanhao Xu, and Laura Johnson for field sampling assistance and Associate Editor George Kling and two anonymous reviewers for constructive comments.

This work was supported in part by the National Science Foundation (EAR#0554781 and ARC#0436179), the International Arctic Research Center, the University of Southern Mississippi, and the U.S. Army Alaska.

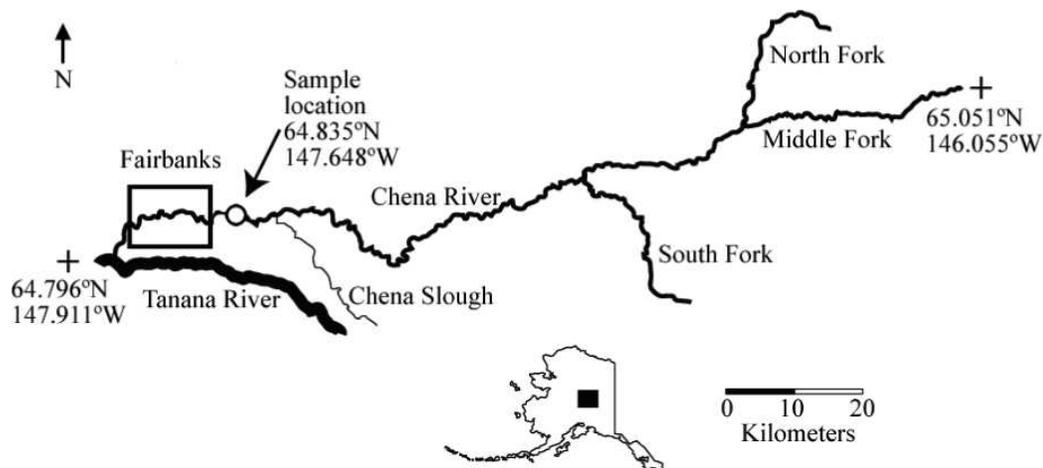


Fig. 1. Map of the Chena River basin and the sampling location at 64.835°N and 147.648°W (marked with a circle).

meteorological events such as rainfall and drought because of their smaller basin area and storage capacity.

Carbon dynamics and the seasonal controls on carbon export from watersheds are complicated processes. To address this aspect of northern high-latitude river biogeochemistry we conducted a yearlong investigation of the organic composition and water chemistry of a river underlain by discontinuous permafrost in the Alaskan interior. The goal was to identify specific controlling factors of carbon dynamics and fluxes and to gain a holistic understanding of the river basin.

Weekly to biweekly water samples were collected from the Chena River through a 12-month hydrological and seasonal cycle from March 2005 to February 2006 that covered the spring freshet and summer growing and winter frozen seasons. The chemical composition and export fluxes of organic carbon species, including DOC, colloidal organic carbon (COC), and POC, as well as carbohydrates (CHO), were quantified to provide a baseline data set to better understand the effects and biogeochemical consequences of climate and environmental change in northern terrestrial ecosystems.

## Materials and methods

**Site description**—The Chena River is a small watershed with an area of roughly 5,200 km<sup>2</sup> within the Yukon River basin (Fig. 1). The Chena River is a clear-water river fed by precipitation and subsurface flows. It contributes annually ~1.18 km<sup>3</sup> of water and significant amounts of carbon and nutrients to the Tanana River, the largest tributary of the Yukon River (Brabets et al. 2000).

Interior Alaska has a strong continental climate characterized by long cold winters and warm summers, with a short growing season (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. Day length also has an extreme variation, from less than 4 h in December to nearly 22 h in June. Annual precipitation in Fairbanks ranges from 142 to 478 mm, with 35% in the form of snow. Most of interior

Alaska is in the discontinuous permafrost zone (Brabets et al. 2000). Most of the north-facing slopes and some foot slopes and most toe slopes of south-facing hills are underlain by permafrost, whereas in the lowlands, permafrost is absent in Holocene-age terraces, alluvial fans, and the active floodplain along the Chena River.

The Chena River basin therefore provides a natural laboratory to examine the effects of climate and environmental changes on riverine carbon dynamics, transport, and biogeochemical processes. Our sampling site (64.835°N, 147.648°W) is located 23 km upstream of the confluence with the Tanana River and 6 km upstream of downtown Fairbanks to avoid potential human effects while representing the entire basin (Fig. 1).

**Sampling and analysis**—Weekly to biweekly water samples were collected from early March 2005 to February 2006 using a precleaned 3-liter high-density polyethylene (HDPE) bucket to scoop samples from a bridge spanning the Chena River. 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-liter acid-cleaned HDPE carboy to minimize the effects of river heterogeneity on sampling. During the winter frozen season with low water flow, 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 a prerinsed Memtrex cartridge (Osmoics, 0.45 μm) and the filtrates were sampled for the measurement of total dissolved nitrogen (TDN), DOC with acidification, total dissolved carbon (TDC) without acidification, CHO, and nutrients (Guo et al. 2004b; Guo and Macdonald 2006). Particulate samples were filtered on precombusted glass fiber filters (Whatman GF/F) for the determination of chlorophyll *a* (Chl *a*), POC, particulate nitrogen (PN), and their stable isotopic composition (δ<sup>13</sup>C and δ<sup>15</sup>N). An aliquot of sample was filtered on 0.45-μm polycarbonate filters (preweighed) to determine the concentration of suspended particulate matter (SPM).

Concentrations of TDC, DOC, and TDN were measured on a high-temperature combustion total organic carbon

(TOC) analyzer (Shimadzu TOC-V) interfaced with a nitrogen detector (TNM-1) (Guo and Macdonald 2006). The total DOC blank (including Milli-Q water, acid for sample acidification, and the instrument blank) was usually less than  $10 \mu\text{mol L}^{-1}$ . Precision is better than 2% and accuracy is within 1%, on the basis of DOC standards. Concentrations of DIC were calculated from the difference between TDC and DOC. Dissolved inorganic nitrogen (DIN, including  $\text{NO}_3$ ,  $\text{NO}_2$ , and  $\text{NH}_4$ ) and dissolved silicate ( $\text{Si}[\text{OH}]_4$ ) were analyzed using colorimetry on a Technicon AutoAnalyzer II. Concentrations of dissolved organic nitrogen (DON) were calculated from the difference between TDN and DIN concentrations (Guo et al. 2004b).

Dissolved carbohydrates, including total (TCHO), monosaccharide (MCHO), and polysaccharide (PCHO) dissolved carbohydrates, were analyzed using a 2,4,6-tripyrrolyl-*s*-triazine (TPTZ) method (Myklestad et al. 1997) modified by Hung et al. (2001). Briefly, for TCHO, river samples were hydrolyzed by  $1 \text{ mol L}^{-1}$  HCl at  $150^\circ\text{C}$  for 1 h. Then, 1 mL of hydrolysate, after neutralization with NaOH, was mixed with 1 mL of  $0.7 \text{ mmol L}^{-1}$  potassium ferricyanide and placed in a boiling water bath for 10 min. After that, 1 mL of  $2 \text{ mmol L}^{-1}$  ferric chloride solution and 2 mL of  $2.5 \text{ mmol L}^{-1}$  TPTZ (Sigma) solution were added to form a violet-colored complex. The absorbance was measured at 595 nm. The MCHO concentration in samples was directly measured without hydrolysis. The PCHO concentration in samples was calculated as the difference between TCHO and MCHO concentrations (all expressed as  $\mu\text{mol L}^{-1}$  C). Glucose was used as a standard. The precision of the method was <5% (1 SD) on the basis of multiple analyses of the glucose standard. The reagent blank in Milli-Q water was subtracted from samples' absorbance.

Background dissolved organic matter (DOM) and dissolved  $\text{Fe}^{2+}$  in river waters could have a potential effect on the analysis of TCHO. On the basis of our available absorbance data, background absorbance of DOM at 595 nm was estimated to have an average overestimation of <2% for MCHO. Unfortunately, concentrations of dissolved  $\text{Fe}^{2+}$  were not measured in our samples and few data are available for Alaska river waters. However,  $\text{Fe}^{2+}$  is thermodynamically unstable and most dissolved Fe is found in the form of  $\text{Fe}^{3+}$  in surface waters. Using unpublished dissolved Fe concentrations in Alaska river waters (Shiller pers. comm.), we estimated a potential overestimation for MCHO in the order of  $\sim 2 \mu\text{mol L}^{-1}$  C, which is  $\sim 4\%$  of the average MCHO concentration. In addition to the potential effect from  $\text{Fe}^{2+}$ , humic substances, which contain carbohydrate structures, may also cause overestimation of MCHO in river water samples (Hung et al. 2005), especially for samples with high DOC from the spring freshet. Regardless, the overall potential overestimation of MCHO seems minimal in our samples.

Concentrations of POC and PN as well as their  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values were measured by continuous-flow isotopic ratio mass spectrometry. Chl *a* concentrations were determined using a 90% acetone extraction procedure measured on a HP 8453 spectrophotometer without acidification.

On selected sample collection dates (05 May 2005, 20 September 2005, 07 November 2005, and 24 February 2006), large volumes of  $0.45\text{-}\mu\text{m}$  filtrate were collected for ultrafiltration. A spiral-wound 1-kDa cartridge (Amicon S10Y1) was used to isolate high-molecular-weight (HMW, >1 kDa) or COC from the low-molecular-weight (LMW, <1 kDa) DOC fraction. The abundance of LMW and COC was quantified using permeate time series sampling coupled with an ultrafiltration permeation model (Guo and Santschi 1996).

## Results and Discussion

*Hydrographic characteristics*—Discharge, water temperature, pH, conductivity, and concentrations of SPM, Chl *a*, and  $\text{Si}(\text{OH})_4$  are listed in Table 1. The discharge data are obtained from the U.S. Geological Survey (USGS) at <http://waterdata.usgs.gov/ak/nwis/uv?15514000> for the Chena River hydrological station (USGS 15514000). The Chena River has a typical arctic and subarctic river hydrological flow regime with low discharge during the frozen season followed by a spring freshet associated with snowmelt and ice breakup. During the ice-free season (May to October 2005), there were several high-flow events in response to precipitation, followed by an almost 2-month low flow period before the last high flow in late September and early October (Fig. 2). The water temperature was  $0.1^\circ\text{C}$  to  $0.4^\circ\text{C}$  during winter (March to April 2005 and October 2005 to February 2006), and rapidly increased to  $12^\circ\text{C}$  during a few weeks in May. The water temperature fluctuated between  $10^\circ\text{C}$  and  $12^\circ\text{C}$  from June to August 2005, and decreased in September and October to a consistent winter value of  $0.1^\circ\text{C}$ .

Water pH values varied from near neutral to slightly alkaline, with an average of 7.35 (Table 1). Before ice opening, the pH of the Chena River was slightly acidic in March, and then increased to a maximum value of 7.89 in late August 2005, but decreased again to <7 in January 2006. The temporal variation in pH may be related to different contributions from sources that include groundwater, snowmelt water, precipitation, and respiration under ice.

The SPM concentrations ranged from  $1.74$  to  $133 \text{ mg L}^{-1}$ , with the highest concentration measured during the spring freshet and the lowest concentration measured under the ice during the winter. In general, the SPM concentrations appear correlated with discharge. Chl *a* concentrations ranged from  $0.2$  to  $17.6 \mu\text{g L}^{-1}$ , with a mean value of  $4.1 \mu\text{g L}^{-1}$ . There were two Chl *a* concentration peaks. The first peak corresponded to the high discharge, high SPM concentrations, and low water temperatures during the spring freshet and the elevated Chl *a* was likely associated with ice algae growing under the ice before snowmelt as indicated by heavier  $\text{PO}^{13}\text{C}$  (Fig. 2). The second Chl *a* peak was observed in August and September 2005 during low discharge conditions, long day length, and intense radiation, which all favored phytoplankton growth.

Conductivity of river waters varied by a factor of two, with the lowest value of  $117 \mu\text{S cm}^{-1}$  during the spring freshet and the highest value of  $237 \mu\text{S cm}^{-1}$  during the winter of 2005, showing a significant inverse correlation

Table 1. Ancillary parameters, Chl *a*, dissolved silicate (Si(OH)<sub>4</sub>), and DIC concentrations.

Date	Discharge (m <sup>3</sup> s <sup>-1</sup> )	<i>T</i> (°C)	pH	Conductivity (μS cm <sup>-1</sup> )	SPM (mg L <sup>-1</sup> )	Chl <i>a</i> (μg L <sup>-1</sup> )	Si(OH) <sub>4</sub> (μmol L <sup>-1</sup> )	DIC (μmol L <sup>-1</sup> )
04 Mar 2005	7.65	0.2	6.85	226	4.06	1.2	218	2,165
16 Mar 2005	7.93	0.2	6.92	227	3.74	0.2	214	2,097
11 Apr 2005	9.91	0.3	7.27	220	3.66	1.7	203	1,932
21 Apr 2005	11.05	0.3	7.17	224	3.81	2.7	196	1,873
27 Apr 2005	76.47	0.4	7.29	117.3	133.1	16.2	96.5	963
05 May 2005	102.24	5.1	7.46	130.3	9.47	2.6	104	1,119
13 May 2005	65.99	9.3	7.43	155.2	11.5	3.8	128	1,273
27 May 2005	52.39	11.1	7.35	175.8	14.7	2.3	148	1,434
08 Jun 2005	75.33	12.3	7.30	158.1	9.51	1.1	134	903
27 Jun 2005	65.42	12.2	7.36	169.1	8.50	1.4	143	1,385
05 Jul 2005	101.67	11.7	7.68	140.2	7.35	2.2	125	1,015
19 Jul 2005	90.34	11.5	7.21	160.4	7.02	1.7	138	1,157
01 Aug 2005	59.47	10	7.19	175	4.49	2.2	143	1,307
10 Aug 2005	52.11	12.6	7.77	179.5	6.67	9.8	116	1,364
16 Aug 2005	45.03	12.3	7.65	185.6	6.15	17.6	107	1,425
29 Aug 2005	40.22	9.9	7.89	190.3	4.60	11.2	115	1,640
08 Sep 2005	40.22	8.8	7.75	192.8	4.60	10.5	124	1,664
20 Sep 2005	43.05	7.1	7.74	193.3	3.90	6.2	134	1,700
30 Sep 2005	92.61	3.5	7.75	167.6	8.20	5.0	147	1,352
13 Oct 2005	47.86	0.3	7.50	195.4	1.74	1.8	151	1,609
25 Oct 2005	33.98	0.1	7.68	204	1.83	1.2	178	1,637
07 Nov 2005	13.03	0.1	7.05	234	2.70	1.1	207	2,024
21 Nov 2005	15.29	0.1	7.32	213	2.67	1.8	197	1,817
02 Dec 2005	16.14	0.1	7.30	220	2.90	1.0	193	1,745
19 Dec 2005	15.01	0.1	6.85	210	2.80	0.2	209	1,759
06 Jan 2006	11.05	0.1	7.15	226	3.33	1.4	214	1,877
31 Jan 2006	7.36	0.1	6.90	237	-	1.4	-	2,175
24 Feb 2006	7.08	0.1	6.98	236	-	-	-	2,246
Average	44±31	5.0±5.3	7.35±0.31	192±33	10.50±25.21	4.1±4.8	157±40	1,595±382

with discharge (Fig. 3a). Concentrations of Si(OH)<sub>4</sub> had a seasonal variation similar to that of conductivity, with high concentrations (~210 μmol L<sup>-1</sup>) under the ice and low concentrations during the spring freshet. Relatively low Si(OH)<sub>4</sub> concentrations were also found in August 2005 (Fig. 3b) during low discharge and high Chl *a* concentrations, indicating biological uptake.

*Dissolved inorganic carbon*—Concentrations of DIC ranged from 963 μmol L<sup>-1</sup> during spring freshet to 2,246 μmol L<sup>-1</sup> under the ice, with an average of 1,595 μmol L<sup>-1</sup> (Table 1, Fig. 2a). Temporal variations in DIC concentrations are similar to conductivity and Si(OH)<sub>4</sub>, with elevated DIC concentrations in the winter, low concentrations during snowmelt, and intermediate values during the summer growing season (Fig. 2a). High DIC and Si(OH)<sub>4</sub> concentrations were measured during the late fall and winter, implying major sources of these species from the leaching of mineral layers transported by groundwater (Walwood and Striegl 2007), but a dilution of soil-leaching species during spring melt runoff. The DIC concentration was negatively correlated with discharge but positively correlated with conductivity (Fig. 3c), indicating that snowmelt waters dilute the DIC.

*Dissolved organic carbon and dissolved organic nitrogen*—Concentrations of DOC ranged from 207 to 1,187 μmol L<sup>-1</sup>,

with an average of 374 μmol L<sup>-1</sup> (Table 2, Fig. 2a). The lowest concentrations were measured under the ice and ranged from 207 to 237 μmol L<sup>-1</sup> (average 221 ± 12 μmol L<sup>-1</sup>), whereas the maximum value of 1,187 μmol L<sup>-1</sup> was measured during peak spring melt. After snowmelt, DOC concentrations decreased rapidly and fluctuated between 298 and 648 μmol L<sup>-1</sup> during the summer growing season, with DOC inputs linking to precipitation and storm events (Fig. 2).

Concentrations of DON varied systematically in the same manner as DOC, ranging from 2.6 to 32.7 μmol L<sup>-1</sup>, with an average of 9.9 μmol L<sup>-1</sup> (Table 2). The average DOC: DON molar ratio in the Chena River was 41 ± 13, ranging from 21 to 79 (Fig. 2b). Overall, these DOC: DON values are similar to those previously reported for Chena River (Guo et al. 2003) and Yukon River waters (Guéguen et al. 2006).

Radiocarbon data had suggested that DOM in the northern rivers are mostly derived from contemporary terrestrial sources (Guo et al. 2003; Benner et al. 2004; Guo and Macdonald 2006; Raymond et al. 2007; Striegl et al. 2007). In the Chena River, the DOC: DON ratio is generally higher than the POC: PN ratio except during the 2005–2006 winter (Fig. 2b), consistent with what has been previously reported for Alaskan rivers (Guo et al. 2003; Guo and Macdonald 2006; Striegl et al. 2007). In addition, a positive relationship existed between the DOC: DON ratio and the POC: PN ratio (not shown), implying a potential connection between DOM and POM

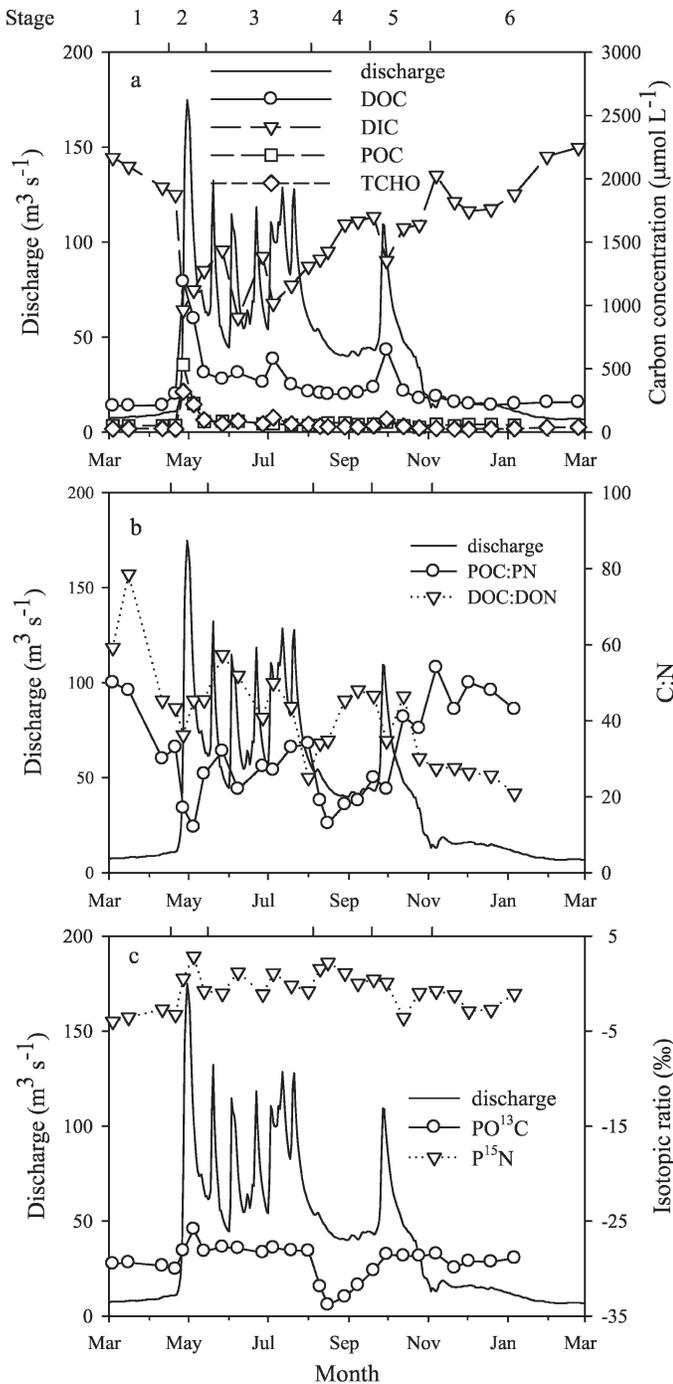


Fig. 2. Seasonal variations in the Chena River of (a) concentrations of DOC, DIC, POC, and TCHO; (b) C:N ratios of POM and DOM along with discharge and hydrological regimes; and (c) carbon and nitrogen isotopic composition of POM. The stages 1, 2, 3, 4, 5, and 6 denote the hydrological regimes of winter, spring melt, summer wet period, summer dry period, single major rain event, and freeze-up and winter, respectively.

cycling. However, the DOC:DON ratio during the 2005–2006 winter was lower than the POC:PN ratio, likely caused by higher DON concentrations under the ice (Fig. 2). Similarly, the DOC:DON ratio in the river ice

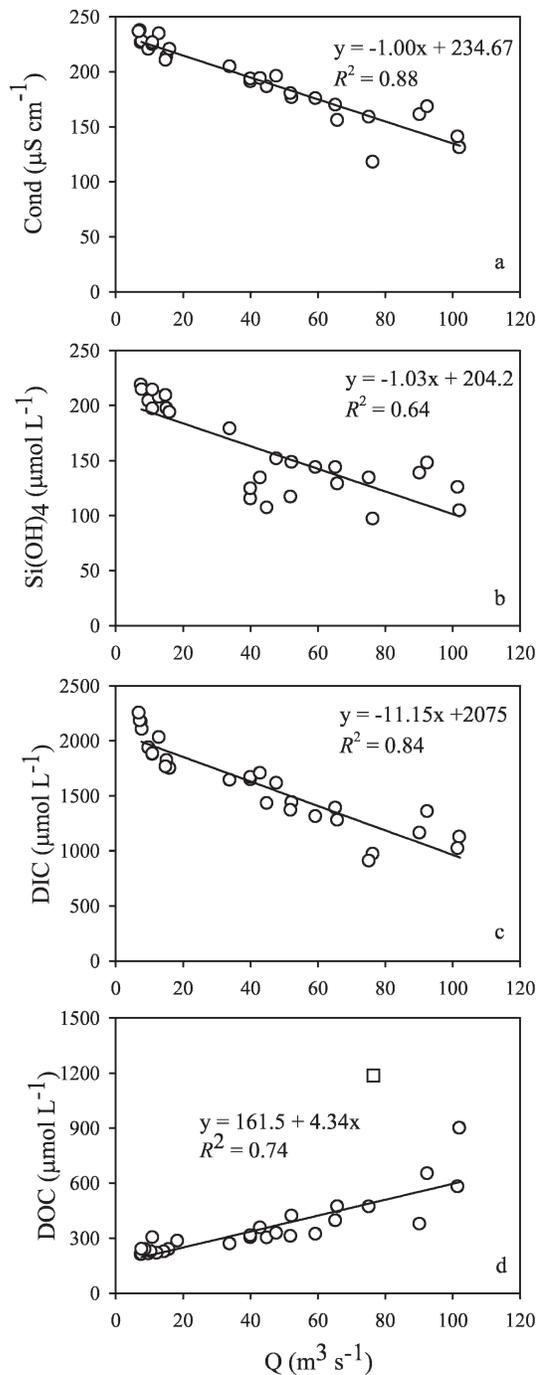


Fig. 3. Correlation between discharge ( $Q$ ) and (a) specific conductivity, (b) dissolved silicate, (c) DIC, and (d) DOC in the Chena River. Daily discharges are from the U.S. Geological Survey stream gage at Fairbanks, Alaska (no.15514000, www.usgs.gov). Note the open square in panel (d) represents the spring ice breakup when the DOC concentration was highly elevated from the common DOC- $Q$  relationship.

samples collected in December was much lower than in March (10 vs. 30). One possibility for this variation is the change in the proportion of hydrophobic and hydrophilic organic fractions with different C:N ratios (Aiken et al. 1992; Striegl et al. 2007).

Table 2. Concentrations of DOC, DON, and carbohydrate species in the Chena River.

Date	DOC ( $\mu\text{mol L}^{-1}$ )	DON ( $\mu\text{mol L}^{-1}$ )	C:N	TCHO ( $\mu\text{mol C L}^{-1}$ )	TCHO:DOC	MCHO ( $\mu\text{mol C L}^{-1}$ )	PCHO ( $\mu\text{mol C L}^{-1}$ )	MCHO%	PCHO%
04 Mar 2005	207	3.5	59	25.5	0.12	22.6	2.9	89	11
16 Mar 2005	208	2.6	79	26.1	0.13	23.1	3.0	88	12
11 Apr 2005	210	4.6	45	27.9	0.13	26.2	1.7	94	6
21 Apr 2005	300	6.9	43	24.9	0.08	24.6	0.3	99	1
27 Apr 2005	1,187	32.7	36	318.7	0.27	174.0	144.7	55	45
05 May 2005	896	19.8	45	218.0	0.24	170.4	47.6	78	22
13 May 2005	468	10.3	45	96.2	0.21	89.4	6.8	93	7
27 May 2005	417	7.3	57	65.9	0.16	65.0	0.9	99	1
08 Jun 2005	467	9.0	52	87.0	0.19	86.2	0.8	99	1
27 Jun 2005	392	9.6	41	64.8	0.17	62.2	2.6	96	4
05 Jul 2005	576	11.5	50	113.9	0.20	108.1	5.8	95	5
19 Jul 2005	373	8.5	44	62.5	0.17	53.1	9.4	85	15
01 Aug 2005	318	12.7	25	62.0	0.19	54.8	7.2	88	12
10 Aug 2005	306	9.0	34	47.2	0.15	37.9	9.3	80	20
16 Aug 2005	298	8.6	35	41.9	0.14	36.9	5.0	88	12
29 Aug 2005	298	6.6	45	41.3	0.14	40.7	0.6	98	2
08 Sep 2005	310	6.5	48	42.0	0.14	38.2	3.8	91	9
20 Sep 2005	352	7.6	47	50.5	0.14	49.4	1.1	98	2
30 Sep 2005	648	18.7	35	101.6	0.16	87.6	14.0	86	14
13 Oct 2005	323	7.0	46	45.4	0.14	37.4	8.0	82	18
25 Oct 2005	265	8.8	30	33.5	0.13	30.9	2.6	92	8
07 Nov 2005	281	10.2	27	29.7	0.11	27.4	2.3	92	8
21 Nov 2005	235	8.5	28	24.2	0.10	21.7	2.5	90	10
02 Dec 2005	222	8.4	26	22.2	0.10	22.2	0.07	99.7	0.3
19 Dec 2005	214	8.3	26	24.0	0.11	22.0	2.0	91	9
06 Jan 2006	223	10.7	21	27.0	0.12	26.5	0.5	98	2
31 Jan 2006	234	-	-	35.7	0.15	27.9	7.8	78	22
24 Feb 2006	236	-	-	39.1	0.17	26.3	12.8	67	33
Average	374 $\pm$ 222	9.9 $\pm$ 6.0	41 $\pm$ 13	64.2 $\pm$ 64.4	15 $\pm$ 4	53.3 $\pm$ 41.2	10.9 $\pm$ 27.7	89 $\pm$ 10	11 $\pm$ 10

The low DOC concentration in winter in the Chena River (Fig. 2a) is consistent with that in the Yukon River basin (Striegl et al 2007; Walvoord and Striegl 2007), suggesting a groundwater DOM source. A significant positive correlation between DOC concentrations and discharge (Fig. 3d) was observed, excluding the spring freshet data point, indicating an addition of DOM by surface and subsurface flow during the river open season and providing further evidence for the dominant allochthonous organic matter source. However, the concentrations of DOC during snowmelt were much higher than what would have been predicted from the relationship between DOC and discharge (Fig. 3d), which is consistent with what has been reported from other high-latitude watersheds (Guo and Macdonald 2006; Finlay et al. 2006). This abrupt shift in the DOM–discharge relationship likely indicates an accumulating soil leaching effect or a more efficient DOM leaching process from surface soils and overlying fresh plant litter during the spring freshet (Guo and Macdonald 2006). Although DOC is positively correlated with discharge, DIC and  $\text{Si}(\text{OH})_4$  are negatively correlated with discharge (Fig. 3). This contrasting correlation indicates different source terms and control mechanisms for organic and inorganic carbon species.

*Carbohydrates*—The average concentration of TCHO, including MCHO and PCHO, was  $64 \pm 64 \mu\text{mol L}^{-1} \text{C}$ ,

with a maximum concentration ( $318 \mu\text{mol L}^{-1} \text{C}$ ) during the spring freshet and a minimum concentration ( $22 \mu\text{mol L}^{-1} \text{C}$ ) under the ice (Table 2, Fig. 2a), comprising on average  $15\% \pm 4\%$  of the bulk DOC. Within the TCHO pool, MCHO was the predominant species, comprising on average 88% of the TCHO, whereas PCHO made up the rest of the TCHO (11%). However, during the spring freshet the percentage of PCHO in the TCHO was as high as 45%, and the percentage of MCHO was reduced to 55% (Table 2, Fig. 4a). The elevated PCHO fraction also occurred when DOC and TCHO concentrations were elevated during the summer growing season, indicating contributions from freshly photosynthesized aquatic organics. Polysaccharides during the spring freshet might be derived from autochthonous sources such as ice algae and allochthonous sources such as soil and plant litter. Several studies have demonstrated the production of PCHO by phytoplankton or bacteria in aquatic environments (Pakulski and Benner 1994; Wilkinson et al. 1997; Hung et al. 2001). There was a Chl *a* maximum during the spring freshet, hinting of the phytoplankton production, likely caused by ice algae released from the river ice (Horner and Schrader 1982). Indeed, biopolymers produced by ice algae are mostly polysaccharides (e.g., Krembs and Engel 2001). Thus, PCHO produced by the ice algae might influence the PCHO fraction in the river water during the spring freshet. Additional PCHO sources during spring freshet included

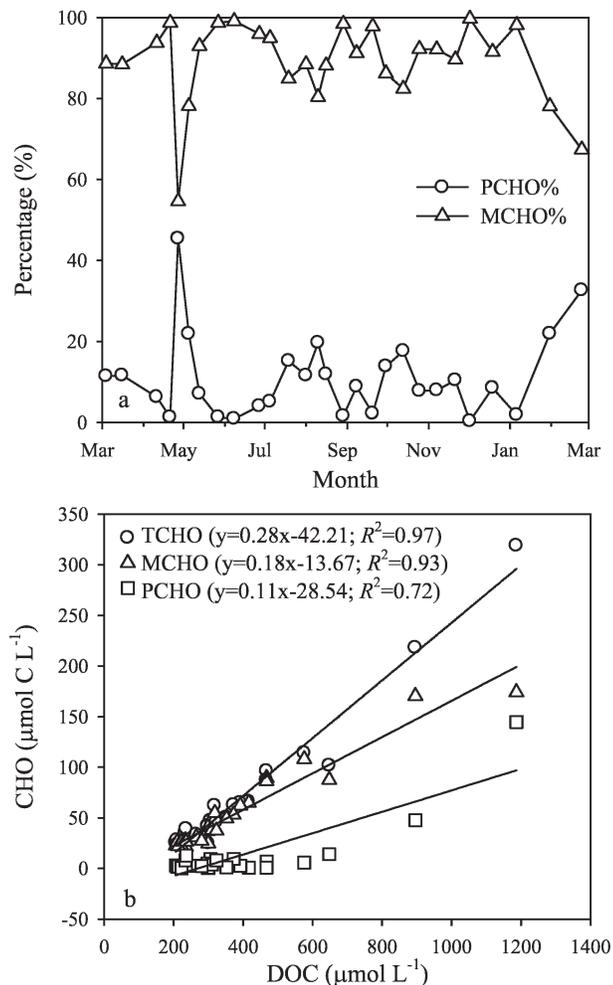


Fig. 4. (a) Seasonal variations of monosaccharide (MCHO) and polysaccharide (PCHO) in the Chena River; and (b) correlation between DOC and total carbohydrate (TCHO), MCHO, and PCHO in the Chena River.

allochthonous contribution from surface soils and overlying plant litters or polymers produced by microorganisms (Wilkinson et al. 1997). Furthermore, structural polysaccharides, including cellulose, hemicellulose, and pectin, are predominant in vascular plant tissues (Aspinall 1970), and the decomposition of plant litter would release polysaccharides, contributing to the higher percentage of PCHO

during the spring freshet (Fig. 4a). After spring freshet, the PCHO fraction dropped significantly and DOM seemed to undergo decomposition and transformation, resulting in a higher MCHO:TCHO ratio in river waters.

The percentage of TCHO in the DOC pool varied from 8% to 26%, with an average of  $15\% \pm 4\%$  (Table 2). This TCHO:DOC ratio is within the range reported for other rivers and aquatic environments (Wilkinson et al. 1997; Table 3). The highest TCHO:DOC ratio was observed during the spring freshet, followed by the summer growing season ( $\sim 0.14$ – $0.20$ ), and the lowest TCHO:DOC ratio was observed under the ice (usually  $< 0.15$ ). It seemed that riverine DOM exported during the spring freshet and summer growing season contained fresher and less degraded DOM components (higher PCHO:TCHO), whereas winter riverine DOM contained more degraded and older organic materials (lower PCHO:TCHO), consistent with the variation trend of  $\text{DO}^{14}\text{C}$  in Yukon River waters (Guo and Macdonald 2006). Although natural DOM seems to contain a similar fraction of TCHO (10–25%), the percentages of MCHO in the TCHO pool are distinctively different between river and salt waters,  $\sim 80\%$  in the freshwater and  $\sim 30\%$  in the seawater (Table 3), indicating different transformation pathways and mechanisms in the TCHO pool (Wilkinson et al. 1997; Hung et al. 2005). In marine systems, sources of TCHO are mostly from the in situ production of phytoplankton and bacteria metabolism with less decomposition and thus a higher PCHO fraction (Pakulski and Benner 1994), whereas in river systems, most TCHO comes from allochthonous sources and undergoes intensive decomposition and thus contains a lower PCHO fraction (Table 3; Hedges et al. 1994; Hung et al. 2005; Guéguen et al. 2006).

Concentrations of TCHO were significantly correlated with DOC (Fig. 4b), implying similar source terms for TCHO and DOC. However, the intercept value in the TCHO-DOC relationship plot is  $\sim 42 \mu\text{mol L}^{-1} \text{C}$ , likely representing the background level of non-CHO DOM. The nonlinear relationship between PCHO and DOC at low DOC concentration during the winter might be caused by the seasonal variation in DOC sources. Although both TCHO and DOC had a significant correlation with discharge and thus hydrological control, we didn't observe a negative correlation between the TCHO:DOC ratio and water temperature, as reported for the subtropical Trinity River (Hung et al. 2005). This difference may result from a

Table 3. A comparison of carbohydrate concentrations in different aquatic environments.

Sample location	MCHO ( $\mu\text{mol C L}^{-1}$ )	PCHO ( $\mu\text{mol C L}^{-1}$ )	TCHO ( $\mu\text{mol C L}^{-1}$ )	MCHO (%)	DOC ( $\mu\text{mol L}^{-1}$ )	TCHO:DOC	Reference
Chena River	53.3	10.9	64.2	83	374	0.17	This study
Yukon River	191	72.2	263	73	1,053	0.25	Guéguen et al. 2006
Trinity River	80.6	9.4	90.0	90	466	0.19	Hung et al. 2005
Trinity River	49.2	19.1	68.3	72	414	0.16	Hung et al. 2001
Galveston Bay	39.1	24.1	63.2	62	350	0.18	Hung et al. 2001
Western Arctic	4.0	7.7	11.7	34	67.2	0.17	Wang et al. 2006
Antarctic sea ice	38	15	53	72	254	0.21	Herborg et al. 2001

Table 4. Particulate organic matter and its elemental and isotopic compositions in the Chena River.

Date	POC ( $\mu\text{mol L}^{-1}$ )	PN ( $\mu\text{mol L}^{-1}$ )	C:N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	POC:Chl <i>a</i> ( $\text{g g}^{-1}$ )	POC:SPM ( $\text{mg g}^{-1}$ )	PN:SPM ( $\text{mg g}^{-1}$ )
04 Mar 2005	49.1	0.99	50	-29.51	-3.99	491	145	3.40
16 Mar 2005	51.1	1.07	48	-29.37	-3.56	3,068	164	4.01
11 Apr 2005	50.6	1.71	30	-29.73	-2.70	357	166	6.53
21 Apr 2005	52.7	1.60	33	-30.07	-3.27	234	166	5.88
27 Apr 2005	530.2	31.43	17	-28.13	0.53	393	47.8	3.31
05 May 2005	225.3	18.43	12	-25.87	2.84	1040	78.9	7.53
13 May 2005	82.5	3.15	26	-28.18	-0.79	261	105	4.66
27 May 2005	85.8	2.68	32	-27.76	-1.04	448	89.8	3.27
08 Jun 2005	85.8	3.93	22	-27.88	1.17	936	69.8	3.73
27 Jun 2005	65.5	2.36	28	-28.32	-1.13	561	82.6	3.48
05 Jul 2005	67.2	2.47	27	-27.83	1.07	366	94.8	4.07
19 Jul 2005	56.0	1.69	33	-28.10	-0.20	396	91.4	3.22
01 Aug 2005	52.1	1.53	34	-28.15	-0.81	284	89.0	3.05
10 Aug 2005	53.2	2.87	19	-31.91	1.52	65.2	142	8.96
16 Aug 2005	73.3	5.61	13	-33.82	2.19	50.0	132	11.79
29 Aug 2005	71.5	3.97	18	-32.97	1.09	76.6	187	12.10
08 Sep 2005	61.2	3.29	19	-31.75	0.01	69.9	160	10.00
20 Sep 2005	62.6	2.46	25	-30.21	0.42	121	193	8.82
30 Sep 2005	79.3	3.53	22	-28.52	0.07	190	116	6.02
13 Oct 2005	49.4	1.18	41	-28.67	-3.59	329	341	9.51
25 Oct 2005	38.3	1.01	38	-28.69	-0.97	383	251	7.76
07 Nov 2005	62.6	1.15	54	-28.47	-0.79	683	278	5.96
21 Nov 2005	49.5	1.15	43	-29.94	-1.21	330	222	6.03
02 Dec 2005	61.0	1.22	50	-29.24	-2.89	732	252	5.90
19 Dec 2005	59.2	1.24	48	-29.30	-2.76	3,554	254	6.20
06 Jan 2006	54.5	1.25	43	-28.91	-1.05	467	196	5.27
Average	85.7±96.9	3.96±6.55	32±12	-29.28±1.74	0.76±1.87	611±836	158±74	6.17±2.68

weak microbial and photochemical control on DOM in Chena River waters, likely due to the predominantly low water temperature in high-latitude watersheds.

*Colloidal organic carbon*—Concentrations of COC in Chena River waters ranged from 142 to 783  $\mu\text{mol L}^{-1}$ , with the highest concentration measured during the spring freshet (783  $\mu\text{mol L}^{-1}$ ) and the lowest during winter under the ice (142  $\mu\text{mol L}^{-1}$ ). Although COC concentrations were considerably different between sampling seasons the percentage of COC in the DOC pool was somewhat constant. On average, about 70% of the DOC partitioned in the colloidal or the >1-kDa HMW DOC fraction, and the other 30% was in the <1-kDa LMW DOC fraction. The consistently high COC fraction agrees well with high fractions of hydrophobic organic acids reported for Yukon River waters (Striegl et al. 2007). This is consistent with the dominating pedogenic organic matter source in arctic and subarctic river basins (Guéguen et al. 2006; Guo et al. 2007).

Within the TOC pool (TOC = POC + COC + LMW DOC), COC comprised, on average, ~56% of the TOC and the LMW DOC comprised 27%, leaving ~17% in the POC phase. High COC abundance in the TOC pool indicates that organic carbon transported in the Chena River is predominantly in the colloidal form, similar to what has been reported for the Yukon River (Guo and Macdonald 2006).

*Particulate organic matter*—The concentration of POC varied from 38  $\mu\text{mol L}^{-1}$  during October to 530  $\mu\text{mol L}^{-1}$

during the spring freshet, with an average of  $86 \pm 97 \mu\text{mol L}^{-1}$  (Table 4, Fig. 2c). The PN concentrations show a pattern of variation similar to POC, with the highest during the spring freshet (31  $\mu\text{mol L}^{-1}$ ) and low concentrations between 1 and 5  $\mu\text{mol L}^{-1}$  during other seasons (Table 4). Using an intensive property unit of milligrams of C per gram of particles for POC concentrations, however, they show a distinct seasonal variation with possibly the provenance of SPM. The POC:SPM ratio was 160  $\text{mg g}^{-1}$  under the ice before the 2005 ice breakup, but it decreased to 50  $\text{mg g}^{-1}$  during the spring freshet while the POC concentration was the highest. The POC:SPM ratio fluctuated between 90 and 160  $\text{mg g}^{-1}$  C throughout the summer growing season. When the river was frozen again, the POC:SPM ratio was elevated again and remained at ~200  $\text{mg g}^{-1}$  C (Table 4). Interestingly, both the Chena River and the Yukon River had roughly the same POC:SPM ratio (~160  $\text{mg g}^{-1}$ ) before the 2005 ice breakup (Guo unpubl.), implying that the Yukon and Chena rivers have similar DOM and POM sources under the ice. The PN:SPM ratio in the Chena River had a similar seasonal regime as the POC:SPM ratio, with a higher PN:SPM during the autumn drought, a lower value during the spring to summer transition, and a medium value under the ice (Table 4).

The POC:PN ratio in the Chena River ranged from 12 to 54, with an average of  $32 \pm 12$  and the highest value during the winter (base flow and groundwater dominated) and lowest during the spring freshet (high soil organic

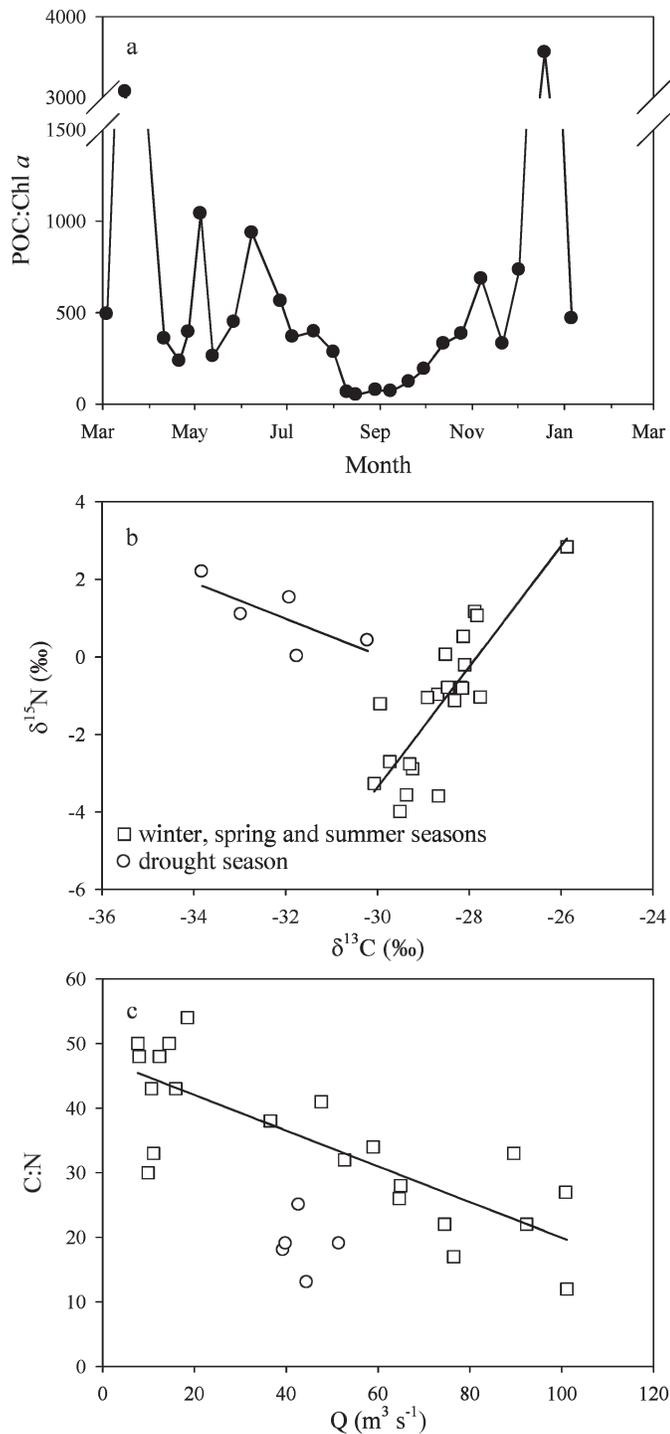


Fig. 5. (a) Seasonal variation of POC:Chl *a* ratio in the Chena River; (b) correlation between  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of POM; (c) correlation between particulate C:N ratio and discharge ( $Q$ ).

matter) and late summer drought season (high aquatic biomass; Table 4, Fig. 2b). Accompanying the lower POC:PN ratios were relatively higher Chl *a* concentrations and lower POC:Chl *a* ratios (Tables 1 and 4). However, the POC:Chl *a* weight ratio in the Chena River was highly variable, ranging from 50 to 3,500, with an average of  $611 \pm 836$  (Table 4, Fig. 5a). The low POC:Chl *a* ratio did not

always match the lower POC:PN ratio because of the complicated hydrological regime and organic source terms.

There was a Chl *a* maximum during the spring freshet (Table 1). Ice algae that had been growing before the river opened could be a source of river POM under the ice and during the spring freshet. However, the high POC:Chl *a* ratio indicates that most of the POC was not produced by autochthonous processes during the winter, although heavier  $\text{PO}^{13}\text{C}$  values during ice opening support the ice algae as a POM source during the spring freshet (Fig. 2). The late summer to fall drought season is a typical hydrological event for boreal streams and small rivers that is characterized by low discharge and low SPM concentrations. These conditions favor algae growth. In the Chena River, there was an elevated Chl *a* during the drought season, with significantly higher POC:SPM and PN:SPM ratios. The POC:Chl *a* ratio during the drought season was as low as 50 (Table 4, Fig. 5a), similar to that for a typical phytoplankton community (Sun et al. 1993), suggesting that most of river POM during the drought season was derived from aquatic organisms, as shown by the fatty acid composition in the Yukon River (Zou et al. 2006).

**Carbon and nitrogen isotope composition**—The isotopic composition of POM in the Chena River is given in Table 4. Values of  $\delta^{13}\text{C}$  ranged from  $-33.82\text{‰}$  to  $-25.87\text{‰}$  (mean  $-29.3\text{‰}$ ), and values of  $\delta^{15}\text{N}$  ranged from  $-3.99\text{‰}$  to  $+2.84\text{‰}$  (mean  $-0.76\text{‰}$ ). Although values of  $\delta^{13}\text{C}$  varied between  $-30\text{‰}$  and  $-28\text{‰}$  during most of the sampling period, there were two time periods with distinct  $\delta^{13}\text{C}$  values, one with the heaviest  $\delta^{13}\text{C}$  during spring freshet ( $-25.87\text{‰}$ ) and the other with the lowest  $\delta^{13}\text{C}$  values ( $-33.82\text{‰}$ ) during the drought season with high Chl *a* concentrations. Values of  $\delta^{15}\text{N}$ , on the other hand, were lower under the ice during winter and higher during the summer growing season (Fig. 2c). The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  exhibited their yearly highest values during the spring freshet. The heavier  $\delta^{13}\text{C}$  during spring freshet likely resulted from POM contribution from ice algae (McRoy et al. unpubl.). Accompanying the lowest  $\delta^{13}\text{C}$  values during August and September were the relatively heavier  $\delta^{15}\text{N}$  values, indicating different POM sources between the spring freshet and the drought season. Water temperatures decreased throughout the drought period from late July to late September (Table 1). Highly depleted  $\delta^{13}\text{C}$  values during the drought season likely resulted from higher fatty acids produced by freshwater algae (Zou et al. 2006), especially in arctic river waters, as supported by the high Chl *a* concentration during the drought season (Table 4, Fig. 2c). Goñi et al (2005) also found that the fatty acids in POM had a highly depleted  $\delta^{13}\text{C}$  composition ( $-36\text{‰}$  to  $-40\text{‰}$ ), most likely derived from freshwater algae in the Mackenzie River. Different mixing lines in the  $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$  and C:N ratio discharge plots during drought season suggest the introduction of a new POM source, which is most likely derived from the freshwater algae since this end member has a highly depleted  $\delta^{13}\text{C}$ , low C:N ratio, and emerges simultaneously with the Chl *a* peak (Fig. 5), although a different allochthonous POM source with depleted  $\delta^{13}\text{C}$  and low C:N cannot be excluded. Our

POM isotope compositions are both within the range of  $C_3$  vascular plants and are in good agreement with those reported previously for the Chena and Yukon rivers (Guo et al. 2003; Guo and Macdonald 2006).

Overall, POM showed significant seasonal variations, with distinctly different POC:Chl *a*, POC:PN, and POC:SPM ratios between the winter and summer growing seasons. Sources of POM in the late fall and early winter were likely from the active layer in areas underlain by permafrost, and from groundwater inputs. The POM sources shifted to surface soils and overlying plant litter during the spring freshet (Fig. 5). During the summer season in nondrought conditions, these two sources mixed conservatively and constitute the riverine POM. The POM source during the drought season was mostly autochthonous, as indicated by the Chl *a* maximum, low POC:Chl *a* and C:N ratios, the high POC:SPM ratios, and the more depleted  $\delta^{13}C$  composition.

*Partitioning of carbon species*—In general, DIC is the predominant carbon species in the Chena River, accounting for  $77\% \pm 13\%$  of the total carbon pool (DIC + DOC + POC), whereas DOC and POC only comprise  $19\% \pm 10\%$  and  $4\% \pm 4\%$ , respectively (Fig. 6). However, during the spring freshet, the DOC and POC fractions increased dramatically, with DOC being the predominant C species, while the DIC fraction decreased. This feature of the yearly flow regimes could not have been revealed without intensive time series sampling. Figure 6 presents a ternary diagram of the three carbon pools and the different flow regimes that yield unique carbon signatures. In general, most of the carbon in the Chena River is DOC and DIC, with less than 20% of the carbon coming from POC at the most. Spring melt yields the greatest POC and DOC concentrations compared with DIC. Flows during summer precipitation events and summer droughts yield more of a DIC fraction compared with POC and DOC. Winter flows are almost completely dominated by DIC, with minor DOC and POC.

The average DOC:POC ratio in the Chena River is  $5.2 \pm 1.5$ , which is higher than in the Yukon River (1.3 at upper reach and 2.1 at lower reach) and the Tanana River (0.91), but similar to the Porcupine River (4.6) (Striegl et al. 2007). The Yukon River receives water, solutes, and sediments from tributaries that can be generally categorized as glacial-fed rivers (such as the Tanana River), blackwater rivers (such as the Porcupine River), and clear-water rivers (such as the Chena River). Overall, the clear-water and blackwater rivers seem to have higher DOC:POC ratios, whereas glacial-fed rivers have lower DOC:POC ratios. The Yukon River has a median value (Striegl et al. 2007), reflecting the relative contribution of these different tributary types.

*Carbon yields and riverine export fluxes*—The seasonal and annual C yields were calculated with the USGS LOADEST program (<http://water.usgs.gov/software/loadest/>). The annual yields of DOC, DIC, and POC from the Chena River basin were  $133 \pm 8$ ,  $361 \pm 7$ , and  $27 \pm 4 \times 10^3$  mol  $km^{-2}$ , respectively. These yields correspond to an

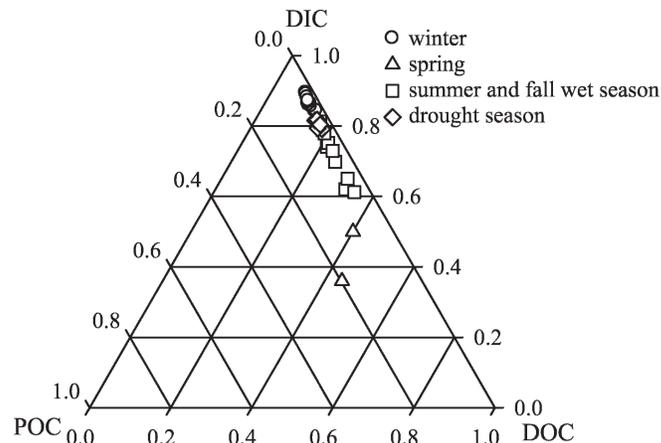


Fig. 6. Ternary plot of DOC, DIC, and POC fractions in the Chena River.

annual riverine export flux of  $6.9 \pm 0.4$ ,  $18.8 \pm 0.4$ , and  $1.4 \pm 0.2 \times 10^8$  mol  $yr^{-1}$  C for DOC, DIC and POC, respectively.

Carbon yields in the Yukon River basin have been reported (Striegl et al 2007). However, studies with time series sampling in small northern watersheds are still scarce. Whereas large rivers integrate different processes from the entire basin, small watersheds may have more specific and direct responses to climate and environmental changes, and are thus highly complementary to previous studies of larger watersheds.

The yields of all three carbon species decreased from the spring flood season to the open water season to the drought season and finally to the winter season (Table 5), consistent with the water yield variation among these seasons. A linear relationship exists between carbon yields and water yields (plots not shown), though the slopes are different among DOC, DIC, and POC, with a steep slope for DOC and flat one for POC. As shown in Table 5, the spring freshet, representing only 4.4% of the time in a year (16 d), contributed up to 22% of the annual DOC flux, ~8% of the annual DIC flux, and 24% of the annual POC flux, whereas the winter frozen season, which lasted for 171 d (~47% of the year) during 2005–2006, contributed only 6%, 19%, and 7% of the annual fluxes for DOC, DIC, and POC, respectively. Clearly, the spring freshet is the most important event for the DOC and POC fluxes, whereas the winter season is important for DIC export. The strong seasonality in carbon yields and export fluxes between the spring freshet, the open water season, and the winter season, and between DOC, DIC, and POC is unique for northern high-latitude watersheds, and can only be revealed by intensive time series sampling.

Compared with different tributaries within the Yukon Basin (Striegl et al. 2007), DOC in the Chena River fits in the general relationship for annual water yields but DIC and POC deviate far downward from the relationship, causing the lower total C yields in the Chena River. As a clear-water stream in the Yukon River basin, the Chena River is expected to have lower loads of suspended

Table 5. Water yield (mm d<sup>-1</sup>) and carbon yield (mol C d<sup>-1</sup> km<sup>-2</sup>) and flux (10<sup>6</sup> mol C yr<sup>-1</sup>) in the Chena River.

Species	Days	Water	DOC	DIC	POC
Annual yield (flux)	365	0.67	365 (694)	989 (1876)	75 (142)
Winter yield (flux)	171	0.18	48.1 (42.8)	392 (349)	11.8 (10.5)
Spring freshet yield (flux)	16	1.85	1,800 (150)	1,827 (152)	417 (34.9)
Drought season yield (flux)	51	0.80	256 (67.8)	1,254 (332)	44.2 (11.7)
Other open season yield (flux)	127	1.12	656 (433)	1,580 (1042)	128 (84.5)
Ratio of winter flux : annual flux	171/365	0.13	0.06	0.19	0.07
Ratio of spring freshet flux : annual flux	16/365	0.12	0.22	0.08	0.24

sediments, POC, and particulate inorganic carbon (PIC), which was not measured in this study. Lower sediment and PIC yields may partially account for the lower DIC yield. Other factors, such as organic carbon respiration and CO<sub>2</sub> degassing (e.g., Kling et al. 1991), water yields and flow paths, and soil–water interactions (Striegl et al 2005, 2007), could also lead to the low C load in the Chena River.

Arctic warming is more pronounced during the winter months. Consequently, increasing arctic river winter discharge rates have been observed (Peterson et al. 2002). Responses of carbon and other biogeochemical cycles to warming will likely be manifested in changes in organic composition, chemical and phase speciation, and carbon yields from river basins (Guo et al. 2007). Frey and Smith (2005) proposed an amplified carbon release in west Siberian watersheds under a future warming climate. In contrast, Striegl et al. (2005) predicted decreasing DOC export and increasing DIC export in the Yukon River basin if annual flow remains stable. The effects of climatic warming on carbon export from northern watersheds are complicated and largely unknown. Changes in hydrology, vegetation, and microbial activities as well as permafrost dynamics likely all play an important role (e.g., Judd and Kling 2002). So far, there is no baseline or long-term carbon data for trend analysis in the Chena River. The winter flow had increased 59% and the annual flow increased 15% in the Chena River between 1968 and 2005 (Walvoord and Striegl 2007). On the basis of the relationship between carbon and water yields in the Chena River, the carbon flux could have increased during the last several decades and may continue to increase with continuous warming, especially during winters. The winter carbon yields in small rivers could provide a window for examining the effects of climate warming on terrestrial carbon export across the land–ocean interface. Therefore, the winter monitoring of carbon species, which is often ignored by most previous studies, is important for a complete understanding of the response of the carbon cycle to a changing climate. Specific seasonal events representing winter low flows, spring melt peak flows, summer drought periods, and summer rainstorms drive unique flow regimes that are likely missed by sporadic sampling campaigns, thus potentially affecting conclusions derived from field observations. These different flow regimes have unique biogeochemical characteristics that should be incorporated into future investigations of northern river systems for a better understanding of the warming impacts at large basin scales.

## References

- AIKEN, G. R., D. M. MCKNIGHT, K. A. THORN, AND E. M. THURMAN. 1992. Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org. Geochem.* **18**: 567–573.
- ASPINALL, G. O. 1970. *Polysaccharides*. Pergamon.
- BENNER, R., B. BENITEZ-NELSON, K. KAISER, AND R. M. W. AMON. 2004. Export of young terrigenous dissolved organic carbon from rivers to the Arctic Ocean. *Geophys. Res. Lett.* **31**: L05305, doi:10.1029/2003GL019251.
- BRABETS, T. P., B. WANG, AND R. H. MEADE. 2000. Environmental and hydrological overview of the Yukon River Basin, Alaska and Canada. *Water Resour. Invest. Rep.* 99-4204. USGS.
- 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. *Geophys. Res. Lett.* **33**: L10401, doi:10.1029/2006GL025754.
- FREY, K. E., AND L. C. SMITH. 2005. Amplified carbon release from vast west Siberian peatlands by 2100. *Geophys. Res. Lett.* **32**: L09401, doi:10.1029/2004GL022025.
- GOŃI, M. A., M. B. YUNKER, R. W. MACDONALD, AND T. I. EGLINTON. 2005. The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort shelf of the Arctic Ocean. *Mar. Chem.* **93**: 53–73.
- GUÉGUEN, C., L. D. GUO, D. WANG, N. TANAKA, AND C.-C. HUNG. 2006. Chemical characteristics and origin of dissolved organic matter in the Yukon River. *Biogeochemistry* **77**: 139–155.
- GUO, L. D., J. K. LEHNER, D. M. WHITE, AND D. S. GARLAND. 2003. Heterogeneity of natural organic matter from the Chena River, Alaska. *Water Res.* **37**: 1015–1022.
- , AND R. W. MACDONALD. 2006. Sources and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope (<sup>13</sup>C, <sup>14</sup>C and <sup>15</sup>N) composition of dissolved, colloidal and particulate phases. *Global Biogeochem. Cycles* **20**: GB2011, doi:10.1029/2005GB002593.
- , C. L. PING, AND R. W. MACDONALD. 2007. Mobilization pathways of organic carbon from permafrost to arctic rivers in a changing climate. *Geophys. Res. Lett.* **34**: L13603, doi:10.1029/2007GL030689.
- , AND P. H. SANTSCHI. 1996. A critical evaluation of the cross-flow ultrafiltration technique for sampling colloidal organic carbon in seawater. *Mar. Chem.* **55**: 113–127.
- , I. SEMILETOV, O. GUSTAFSSON, J. INGRI, P. ANDERSSON, O. DUDAREV, AND D. WHITE. 2004a. Characterization of Siberian Arctic estuarine sediments: Implications for terrestrial organic carbon export. *Global Biogeochem. Cycles* **18**: GB1036, doi:10.1029/2003GB002087.
- , J. Z. ZHANG, AND C. GUÉGUEN. 2004b. Speciation and fluxes of nutrients (N, P, Si) from the upper Yukon River. *Global Biogeochem. Cycles* **18**: GB1038, doi:10.1029/2003GB2152.

- HEDGES, J. I., G. L. COWIE, J. E. RICHEY, P. D. QUAY, R. BENNER, M. STROM, AND B. R. FORSBERG. 1994. Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. *Limnol. Oceanogr.* **39**: 743–761.
- HERBORG, L.-M., D. N. THOMAS, H. KENNEDY, C. HAAS, AND G. S. DIECKMANN. 2001. Dissolved carbohydrates in Antarctic sea ice. *Antarctic Sci.* **13**: 119–125.
- HORNER, R., AND G. C. SCHRADER. 1982. Relative contributions of ice algae, phytoplankton, and benthic microalgae to primary production in nearshore regions of the Beaufort Sea. *Arctic* **36**: 485–503.
- HUNG, C.-C., D. TANG, K. WARNKEN, AND P. H. SANTSCHI. 2001. Distributions carbohydrates, including uronic acids, in estuarine waters of Galveston Bay. *Mar. Chem.* **73**: 305–318.
- , K. W. WARNKEN, AND P. H. SANTSCHI. 2005. A seasonal survey of carbohydrates and uronic acids in the Trinity River, Texas. *Org. Geochem.* **36**: 463–474.
- JORGENSEN, M. T., C. H. RACINE, J. C. WALTERS, AND T. E. OSTERKAMP. 2001. Permafrost degradation and ecological changes associated with a warming climate in central Alaska. *Clim. Change* **48**: 551–579.
- JUDD, K. E., AND G. W. KLING. 2002. Production and export of dissolved C in arctic tundra mesocosms: The roles of vegetation and water flow. *Biogeochemistry* **60**: 213–234.
- 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.
- KREMBS, C., AND A. ENGEL. 2001. Abundance and variability of microorganisms and transparent exopolymer particles across the ice–water interface of melting first-year sea ice in the Laptev Sea (Arctic). *Mar. Biol.* **138**: 173–185.
- MCGUIRE, A. D., F. S. CHAPIN III, J. E. WALSH, AND C. WIRTH. 2006. Integrated regional changes in arctic climate feedbacks: Implications for the global climate system. *Annu. Rev. Env. Resour.* **31**: 61–91.
- MYKLESTAD, S. M., E. SKANOY, AND S. HESTAMANN. 1997. A sensitive and rapid method for analysis of dissolved mono- and polysaccharides in seawater. *Mar. Chem.* **56**: 279–286.
- PAKULSKI, J. D., AND R. BENNER. 1994. Abundance and distribution of carbohydrates in the ocean. *Limnol. Oceanogr.* **39**: 930–940.
- PETERSON, B. J., AND OTHERS. 2002. Increasing river discharge to the Arctic Ocean. *Science* **298**: 2171–2173.
- RAYMOND, P. A., AND OTHERS. 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. *Global Biogeochem. Cycles* **21**: GB4011, doi:10.1029/2007GB002934.
- STEIN, R., AND R. W. MACDONALD. 2004. The organic carbon cycle in the Arctic Ocean., Springer.
- STRIEGL, R., 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. *Geophys. Res. Lett.* **32**: L21413, doi:10.1029/2005GL024413.
- 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 Resour. Res.* **43**: W02411, doi:10.1029/2006WR005201.
- SUN, M.-Y., R. C. ALLER, AND C. LEE. 1993. Spatial and temporal distributions of sedimentary chloropigments as indicators of benthic processes in Long Island Sound. *J. Mar. Res.* **52**: 149–176.
- WALWOOD, 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., **34**: L12402, doi:10.1029/2007GL030216.
- WANG, D., S. M. HENRICHs, AND L. D. GUO. 2006. Distributions of nutrients, dissolved organic carbon and carbohydrates in the western Arctic Ocean. *Cont. Shelf Res.* **26**: 1654–1667.
- WILKINSON, K. J., A. JOZ-ROLAND, AND J. BUFFLE. 1997. Different roles of pedogenic fulvic acids and aquagenic biopolymers on colloid aggregation and stability in freshwaters. *Limnol. Oceanogr.* **42**: 1714–1724.
- ZOU, L., M.-Y. SUN, AND L. GUO. 2006. Temporal variations of organic carbon inputs into the upper Yukon River: Evidence from fatty acids and their stable carbon isotopic compositions in dissolved, colloidal and particulate phases. *Org. Geochem.* **37**: 944–956.

Received: 14 May 2007  
Accepted: 13 February 2008  
Amended: 3 March 2008