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Sources and export fluxes of inorganic and organic carbon and nutrient species from the seasonally ice-covered Yukon River

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Abstract Climate and environmental changes are having profound impacts on Arctic river basins, but the biogeochemical response remains poorly understood. To examine the effect of ice formation on temporal variations in composition and fluxes of carbon and nutrient species, monthly water and particulate samples collected from the lower Yukon River between July 2004 and September 2005 were measured for concentrations of organic and inorganic C, N, and P, dissolved silicate ($Si(OH)_4$), and stable isotope composition (δD and $\delta^{18}O$). All organic carbon and nutrient species had the highest concentration during spring freshet and the lowest during the winter season under the ice, indicating dominant sources from snowmelt and flushing of soils in the drainage basin. In contrast, inorganic species such as dissolved inorganic carbon (DIC) and $Si(OH)_4$ had the highest concentrations in winter and the lowest during spring freshet, suggesting dilution during snowmelt and sources from groundwater and leaching/weathering of mineral layer. The contrasting relation with discharge between organic, such as dissolved organic carbon (DOC), and inorganic, such as DIC and $Si(OH)_4$, indicates hydrological control of solute concentration but different sources and transport mechanisms for organic and inorganic carbon and nutrient species. Concentration of DOC also shows an inter-annual variability with higher DOC in 2005 (higher stream flow) than 2004 (lower stream flow). Average inorganic N/P molar ratio was 110 ± 124, with up to 442 under the ice and 38–70 during the ice-open season. While dissolved organic matter had a higher C/N ratio under the ice (45–62), the particulate C/N ratio was lower during winter (21–26) and spring freshet (19). Apparent fractionation factors of C, N, P, Si and δD and $\delta^{18}O$ between ice and river water varied considerably, with high values for inorganic species such as DIC and $Si(OH)_4$ (45 and 9550, respectively) but lower values for DOC (4.7). River ice formation may result in fractionation of inorganic and organic solutes and the repartitioning of seasonal flux of carbon and nutrient species. Annual export flux from the Yukon River basin was 1.6×10^{12} g-DOC, 4.4×10^{12} g-DIC, and 0.89×10^{12} g-POC during 2004–2005. Flux

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estimation without spring freshet sampling results in considerable underestimation for organic species but significant overestimation for inorganic species regardless of the flux estimation methods used. Without time-series sampling that includes frozen season, an over- or under-estimation in carbon and nutrient fluxes will occur depending on chemical species. Large differences in carbon export fluxes between studies and sampling years indicate that intensive sampling together with long-term observations are needed to determine the response of the Yukon River to a changing climate.

Keywords Dissolved organic matter · Particulate organic matter · Dissolved inorganic carbon · Nutrients · River ice formation · Export fluxes · Yukon River · Arctic river

Introduction

River export of carbon and nutrients to the ocean plays an important role in biogeochemical cycling, especially in the Arctic Ocean, which receives a disproportionately large amount of global runoff (Aagaard and Carmack 1989). Quantitative determination of export fluxes of nutrients (N, P, and Si) and carbon species such as dissolved organic carbon (DOC), particulate organic carbon (POC) and dissolved inorganic carbon (DIC) by Arctic rivers is required to constrain nutrient and carbon budgets in the Arctic Ocean, and to anticipate likely changes in the biogeochemical cycling consequent to climate and environmental change in northern drainage basins. Over the past two decades, the arctic climate has warmed appreciably but the impacts on arctic ecosystems and biogeochemical cycling remain poorly understood (Serreze et al. 2003; Hinzman et al. 2005; McGuire et al. 2009). Although hydrological changes in the Arctic region, such as increasing freshwater discharge (Peterson et al. 2002), permafrost thawing (Jorgenson et al. 2006), and landscape change (Smith et al. 2005), are likely to alter export fluxes of organic carbon and nutrient species (Guo et al. 2004a; Rember and Trefry 2004; Finlay et al. 2006; Balcarczyk et al. 2009; Frey and McClelland 2009), it remains a matter of debate exactly what the changes are likely to be (Frey and Smith 2005; Striegl et al. 2005).

The Yukon River, one of the largest rivers in North America, drains Arctic and subarctic regions with continuous and discontinuous permafrost in northwestern Canada and central Alaska (Brabets et al. 2000). The Yukon River basin, which drains from east to west, has a mean latitude of ~64°N. This uniformly high latitude, which represents an important difference compared to most other large Arctic rivers that drain from south to north, makes the Yukon particularly sensitive to cryospheric change (Schuster 2003; Jorgenson et al. 2006). As a result, increasing attention is being paid to the response of this river's geochemistry to ongoing climate change (Schuster 2003; Guo et al. 2004a, 2007; Striegl et al. 2005, 2007; Guéguen et al. 2006; Guo and Macdonald 2006; Petrone et al. 2006; Dornblaser and Striegl 2007; Raymond et al. 2007; Walvoord and Striegl 2007; Cai et al. 2008a, b; McClelland et al. 2008; Spencer et al. 2008, 2009). Nevertheless, there are few published studies that examine both organic carbon and nutrient species, and none that compare or contrast the response of different biogeochemical components to change.

Since the Yukon River has an ice cover for about half a year, knowledge of the composition and transport of carbon and nutrients in water flowing under the ice is essential not only for quantitative constraint of river export fluxes, but also for fundamental understanding of river geochemical cycling and, especially, its sensitivity to climate change. However, interactions between ice, water, and substances carried by the river have scarcely been studied. Little is known about the fractionation of carbon and nutrient species during river ice formation, the sources and transport of solutes during winter season and biogeochemical cycling of these solutes under the ice in Arctic rivers. It is likely that ice formation could result in an enrichment of carbon and nutrients in the water beneath the ice (Belzile et al. 2002), and thus acts to enhance riverine export flux to the ocean during winter.

To examine the temporal variation in composition and fluxes of carbon and nutrients from the Yukon River basin, monthly or bimonthly samples were collected from the lower Yukon River at Pilot Station, Alaska, from July 2004 to September 2005 and analyzed for the concentration of organic and inorganic C, N, and P in both dissolved and particulate phases, including DOC, POC, DIC, dissolved organic nitrogen (DON), particulate nitrogen (PN), dissolved inorganic nitrogen (DIN), dissolved organic phosphorus (DOP), dissolved inorganic phosphorus (DIP), particulate phosphorus (PP), and $Si(OH)_4$. River ice core samples were also measured to determine the fractionation of organic carbon and nutrients between ice and river water.

Methods

Study area

The Yukon River has an average annual discharge of more than 202 km^3 and $\sim 60 \times 10^6$ tons of suspended sediment into the Bering Sea and Arctic Ocean (Brabets et al. 2000; Holmes et al. 2002). Along its length of about 3,340 km, the Yukon River drains 853,300 km^2 of Arctic and subarctic regions in northwestern Canada and central Alaska (Fig. 1). Major tributaries, like the Koyukuk, Tanana, and Yukon, supply waters with varied geochemical characteristics (Schuster 2003; Dornblaser and Striegl 2007; Striegl et al. 2007; Spencer et al. 2008). Our previous studies, which have been conducted at an upstream station in the Yukon River (Guo et al. 2004a; Guéguen et al. 2006; Guo and Macdonald 2006), did not incorporate water draining from the Tanana and Koyukuk Rivers. Pilot Station, Alaska, which was sampled for this study, is located just above the influence of seawater from the Bering Sea (Fig. 1), and, therefore, provides the best representation of water characteristics and fluxes that are products of the entire basin and its biogeochemical processes.

Sampling

Sampling was conducted monthly when the river was ice free and bimonthly during winter under the ice at a well mixed section near Pilot Station Alaska in the downstream reach of the Yukon River (Lat 61.94°N Lon 162.87°W) from July 2004 to September 2005. Large-volume grab samples ($\sim$20 cm below surface) were collected from midstream while the boat was maintained against stream flow. Winter samples were collected under the ice in midstream. Following collection, about 40 L of water were filtered immediately through a pre-rinsed 0.45 μm polycarbonate cartridge (Osmonics). The first 5–10 L of filtrate were discarded and about 20 L of filtrate were collected in an acid-cleaned polyethylene container. Aliquots of filtrate were sampled for the determination of DOC, DIC and nutrients (Guo and Macdonald 2006). Nutrients (N, P, Si) and DOC samples were collected in acid-cleaned polyethylene bottles, which were kept frozen until analysis. DIC samples were collected in an acid-cleaned 60 mL amber bottle preserved with 20 μL of saturated $HgCl_2$ solution. Samples for POC and PN were filtered on precombusted GF/F glass fiber filters and kept frozen until analysis. Samples for total suspended solids (TSS) were filtered on pre-weighed nucleopore filters (Guo et al. 2004a) and saved for measurements of particulate phosphorus. Although the river seems vertically well mixed at the Pilot Station sampling site, near-surface grab samples may underestimate concentrations of particulate species.

Two ice cores were collected from the Yukon River in mid-channel during the April 5, 2005 sampling trip using an ice corer. These 98 and 105 cm-thick ice cores were cut into top ice (white ice), middle ice and bottom ice sections. Each section of the two ice cores was combined for thawing and filtration through 0.4 μm filters (Millipore Isopore). Filtrates were sampled for measurements of carbon and nutrient (N, P, and Si) species.

Measurements of DOC, TDN, POC, PN and DIC

Concentrations of DOC were determined on a Shimadzu TOC-V analyzer as described in Guo et al. (1995). DOC samples were acidified to a pH of ≤ 2 and sparged for 5 min using ultra-pure air to remove DIC before analysis. Concentrations of total dissolved carbon (TDC, including DOC and DIC) and total dissolved nitrogen (TDN, including DON and DIN) were determined on the same TOC analyzer interfaced with a nitrogen detector. For TDC and TDN measurements, samples were directly injected without acidification and sparging. Concentrations of DIC were calculated as the difference between TDC and DOC, while DON was calculated from the difference between TDN and DIN (see next).

Concentrations of POC and PN are determined by an elemental analyzer interfaced with continuous flow isotope ratio mass spectrometry. POC/PN filter

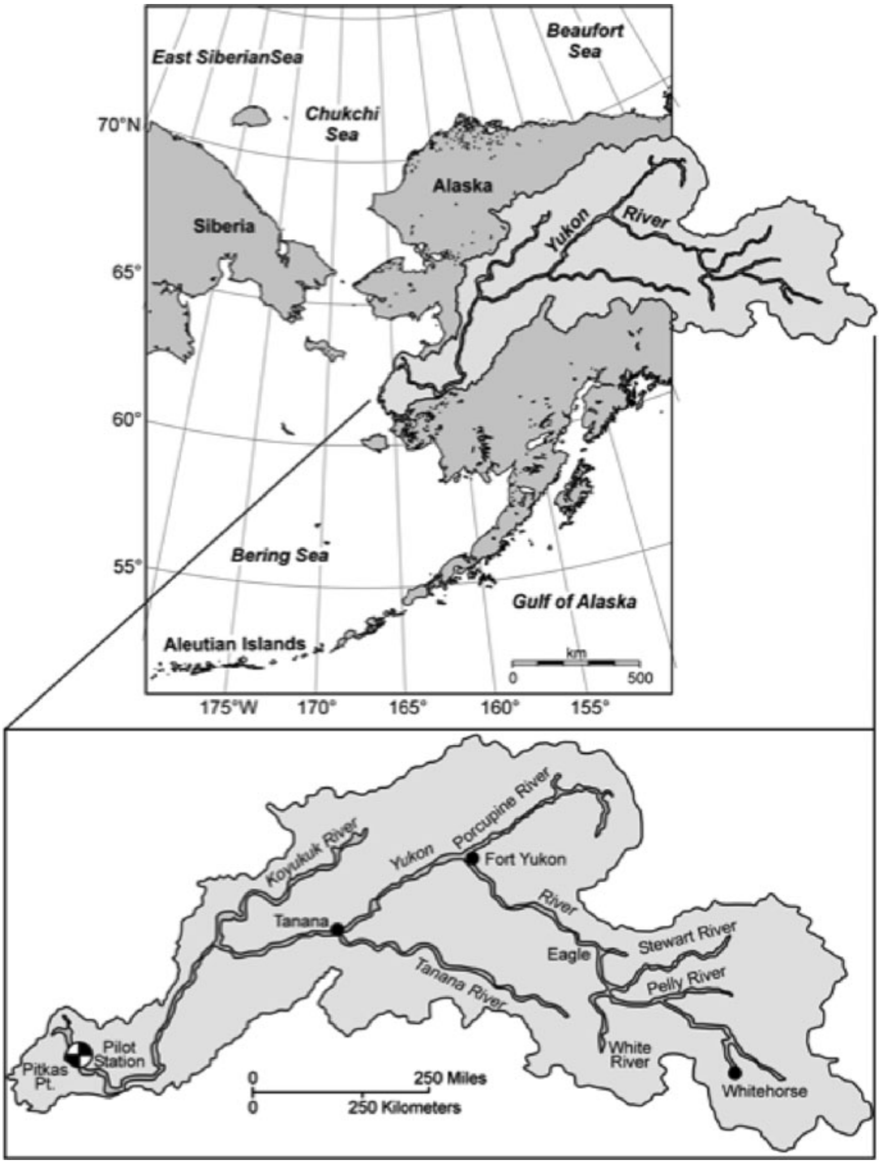

Fig. 1 Map of the Yukon River basin and the sampling location at Pilot Station, Alaska (61.94°N, 162.87°W)

samples were treated with HCl acid fumes for 24 h before analysis.

Measurements of nutrients (N, P, and Si)

Nitrate and nitrite ($NO_3 + NO_2$), ammonium (NH_4), and dissolved silicate ($Si(OH)_4$) were analyzed using the colorimetric methods on an autoanalyzer (Grasshoff et al. 1999; Guo et al. 2004a). The concentration of DIN was calculated as the sum of the concentrations of NO_3^-, NO_2^-, and NH_4^+. Phosphate or DIP concentrations in Arctic river waters are generally low and normally measured as total dissolved phosphorus (TDP) in previous studies (e.g. Dornblaser and Striegl 2007; McClelland et al. 2008; Frey and McClelland 2009). Therefore, phosphate concentration was measured on a HP 8453 spectrophotometer with a 5 cm cuvette (Cai et al. 2008b). Concentrations of TDP (=DIP plus DOP) were measured after autoclave-assisted persulfate oxidation of DOP at boiling temperature, followed by the standard phosphomolybdenum blue method as described in Cai and Guo (2009). Concentrations of DOP were calculated from the difference between TDP and DIP. Concentrations of particulate phosphorus (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 1 M HCl extraction for 16 h at room temperature. Orthophosphate concentrations in the extracts were determined by the standard antimonyphosphomolybdate colorimetric method (Solorzano and Sharp 1980) using an HP 8453 spectrophotometer. The detection limits were generally 10 nmol/L with precision better than 2% for both DIP and TDP.

Measurements of stable isotopes (δD and δ^{18}O) and other parameters

Stable oxygen and hydrogen isotope composition of river waters were measured on an isotope ratio mass spectrometer at the Alaska Stable Isotope Facility, University of Alaska Fairbanks. The hydrogen isotope ratio (in terms of δD) and oxygen isotope ratio (δ^{18}O), relative to the VSMOW standard water, was reported with the conventional delta notation (‰).

Chl-*a* concentrations were determined using a 90% acetone extraction procedure measured on a HP 8453 spectrophotometer without acidification. Concentrations of TSS were determined by sample volume and filter weight difference before and after sampling after freeze drying to a constant weight. The DOM absorption coefficient at 370 nm, $\alpha_g(370)$, was measured on a HP 8453 UV–vis spectrophotometer (Belzile and Guo 2006). Specific conductivity and pH were determined using a salinometer and a DigiSense pH meter, respectively, both in situ and in the laboratory. In situ water temperature, conductivity, dissolved oxygen and pH were determined using Hydrolab sensors (Hach Environmental).

Results and discussion

Hydrographic features

Hydrographic parameters (Table 1) include fresh water discharge, water temperature, pH, conductivity, concentration of total suspended solids (TSS), and stable isotopic composition of hydrogen (δD) and oxygen (δ^{18}O). Based on the USGS National Water Information System (http://waterdata.usgs.gov/ak/nwis), the Yukon River freshwater discharge (stream-flow) at Pilot Station during 2005 spring freshet peaked at 33,428 m^3/s on May 17, which is almost double to the maximum discharge measured in 2004 (18,272 m^3/s on June 12, 2004). Higher fresh water discharge during 2005 would likely affect concentration and flux of solutes from the Yukon River. Water temperature varied from −0.18°C during winter to 19°C during summer (Table 1) although the air temperature between December and February sometimes dipped below −40°C. River water pH was lowest under the ice in April (7.16) and highest between July and September, with an average of 7.7 ± 0.4. As shown in Table 1, pH values during the ice-open season in 2005 were generally higher than those in 2004, indicating a difference in water chemistry, likely influenced by discharge and sources and composition of DOM, and a difference in primary production. Specific conductivity in Yukon River waters varied from 103 μS/cm in July 2004 to 341 μS/cm under the ice in February 2005, with an average of 242 ± 75 μS/cm, showing a clear dilution effect on the specific conductivity during spring freshet. The concentration of TSS was very low under the ice, between 5 and 10 mg/L, compared to 105–475 mg/L during open water season. Therefore, TSS was predominately transported during the openwater period, especially during the spring freshet (Table 1).

On April 5 2005, both water temperature and specific conductivity demonstrated a homogeneous water column below the ice (Fig. 2), indicating that winter sampling from the upper water column was representative of the whole water column for dissolved species. The vertical profiles of dissolved oxygen and pH show a slight decrease towards the bottom (Fig. 2), likely reflecting a stagnant layer near the riverbed–water interface.

Stable isotope composition (δD and δ^{18}O) showed similar variations. Average δD and δ^{18}O values were −149.4 ± 8.6‰ and −18.4 ± 0.5‰ (Table 1). Our δ^{18}O values reported here are similar to the flow-weighed average value (−18.8‰) reported for the six largest Arctic rivers (Cooper et al. 2008). Values of δD and δ^{18}O were higher in winter waters under the ice, consistent with higher ground water contribution during winter (Walvoord and Striegl 2007). However, both δD and δ^{18}O values during the ice-open season were consistently lower in 2005 compared to 2004, indicating a higher contribution from precipitation

Table 1 Hydrographic parameters, stable isotope composition of river water, and concentrations of dissolved inorganic carbon (DIC), dissolved inorganic nitrogen (DIN, including NO_3^-, NO_2^- and NH_4^+), dissolved inorganic phosphorus (DIP), dissolved silicate ($Si(OH)_4$), and absorption coefficient ($\alpha_g(370)$) in Yukon River waters at Pilot Station, Alaska (61.94°N and 162.87°W) during 2004–2005

Sampling date	Q (m^3/s)	Water temp (°C)	pH	Conductivity (µS/cm)	TSS (mg/L)	$\delta^{18}O$ (‰)	δD (‰)	DIC (µM)	DIN (µM)	DIP (µM)	$Si(OH)_4$ (µM)	N/P (at ratio)	$\alpha_g(370)$ (m^{-1})
7/15/04	10765	nd	7.72	103	–	−18.9 ± 0.08	−149 ± 0.5	1269	5.67	0.147	105	39	5.00
8/25/04	8924	19	7.78	233	427	−17.1 ± 0.17	−146 ± 0.1	1656	6.32	0.139	108	46	3.22
9/30/04	8068	4	7.63	275	134	−17.6 ± 0.12	−145 ± 0.2	1607	9.09	0.128	127	71	2.88
11/10/04	4093	0	7.24	226	9.9	−17.7 ± 0.03	−135 ± 0.4	1483	13.20	0.209	167	63	8.79
12/15/04	2152	0	7.17	324	6.0	−17.9 ± 0.02	−141 ± 0.4	1982	20.38	0.136	200	149	6.33
2/9/05	1536	−0.18	7.46	341	5.0	−16.9 ± 0.12	−146 ± 0.5	2087	19.49	0.131	180	149	1.90
4/5/05	1293	−0.18	7.16	320	5.1	−16.0 ± 0.09	−144 ± 0.7	2128	21.09	0.048	196	442	1.86
5/17/05	33428	4	7.90	150	475	−19.4 ± 0.02	−158 ± 0.4	1178	11.01	0.169	77	65	21.59
6/14/05	19858	14	8.00	180	105	−20.0 ± 0.01	−160 ± 0.9	1178	6.04	0.159	92	38	11.08
7/19/05	11955	19	8.20	245	387	−20.2 ± 0.08	−159 ± 0.8	1430	7.09	0.181	108	39	6.32
9/7/05	8414	12	8.40	263	362	−20.9 ± 0.09	−159 ± 0.8	1916	2.99	nd	119	nd	8.28
Average ± SD	–	–	7.7 ±0.4	242 ± 75	192 ± 197	−18.4 ± 0.56	−149.4 ± 8.6	1629 ± 356	11.12 ± 1.5	0.145 ± 0.042	134 ± 43	110 ± 124	7.02 ± 5.68

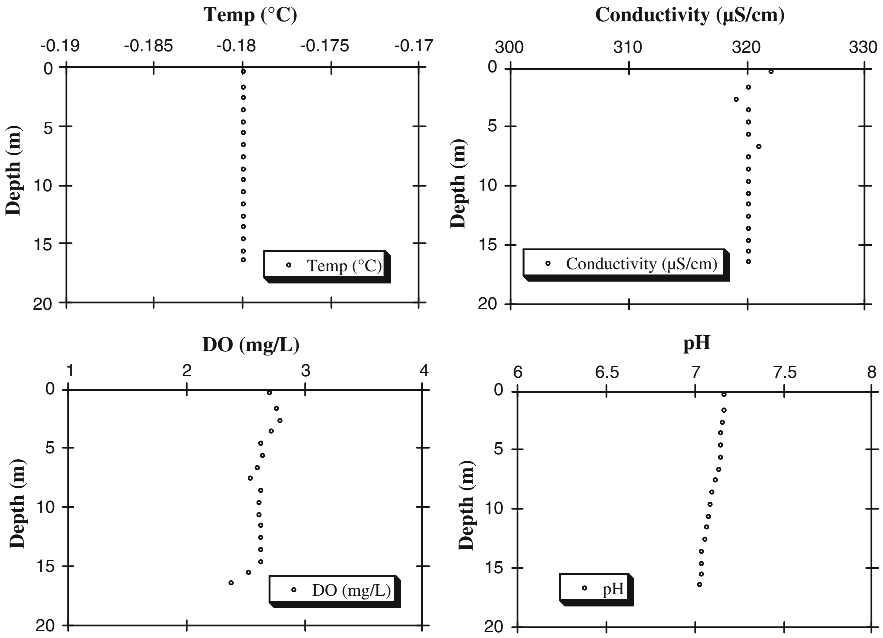

Fig. 2 Vertical profiles of water temperature (°C), conductivity (μS/cm), dissolved oxygen (DO, mg/L) and pH in the water column under the ice in the Yukon River near Pilot Station. The total water depth under the ice at this station is 16.5 m

(snow and rainwater) during 2005. In addition, the average $\delta^{18}O$ value during 2004–2005 is slightly higher than that reported for the upper Yukon River at Stevens Village during 2002 (Guo and Macdonald 2006), reflecting different contributions of precipitation between tributaries and years. Indeed, lower δD and $\delta^{18}O$ values in 2005 coincided with a higher freshwater discharge compared to 2004. When plotted against water temperature (Fig. 3), both δD and $\delta^{18}O$ show a convex distribution with a relatively higher δD and $\delta^{18}O$ value indicating ground water source when water temperature is low, a relatively lower δD and $\delta^{18}O$ value indicating snowmelt water, and a higher δD and $\delta^{18}O$ value again when water temperature is high, likely from thawed active layer and proportionally increased ground water input in late summer and fall.

Seasonal variations of carbon and nutrient species

Concentrations of inorganic and organic carbon and nutrient species, including DIC, DOC, POC, DIN, DON, PN, DIP, DOP, POP, and $Si(OH)_4$ are listed in Tables 1 and 2. Concentrations of nutrient and carbon species in the Yukon River show a strong seasonality. As depicted in Fig. 4, there is a considerable difference in carbon and nutrient concentrations between ice covered conditions, spring freshet, and summer seasons.

Concentrations of DOC jumped from 182 μM below the ice in April 2005 to 1,682 μM in May 2005 right after ice breakup, a difference of almost a factor of 10 (Table 4). In general, DOC concentration was highest during ice breakup, decreased rapidly towards fall and winter, and consistently decreased more slowly between November 2004 and April 2005 (Fig. 4). DOC also showed a significant rise in October and November coincident with freeze up, likely due to exclusion of DOC during ice formation (see discussion below; and Belzile et al. 2002), a feature not previously reported. The fall increase could also be partly due to other inputs from the land, for example, DOC excluded from riverbank soils, which were also freezing, may have contributed to the temporary rise in river DOC concentration.

The concentration of DOC positively correlated with the adsorption coefficient, $\alpha_g(370)$, of DOM ($DOC = 0.0121 \times a_g(370) + 1.665$, $R^2 = 0.89$, $P < 0.001$). Nevertheless, the DOC-specific $a_g(370)$, an index of DOM molecular weight and aromaticity (Belzile and Guo 2006 and references therein), showed relatively large seasonal variations (with a factor of 3) and an inverse correlation with the DOC/DON ratio (not shown), but showed no clear relationship with river discharge.

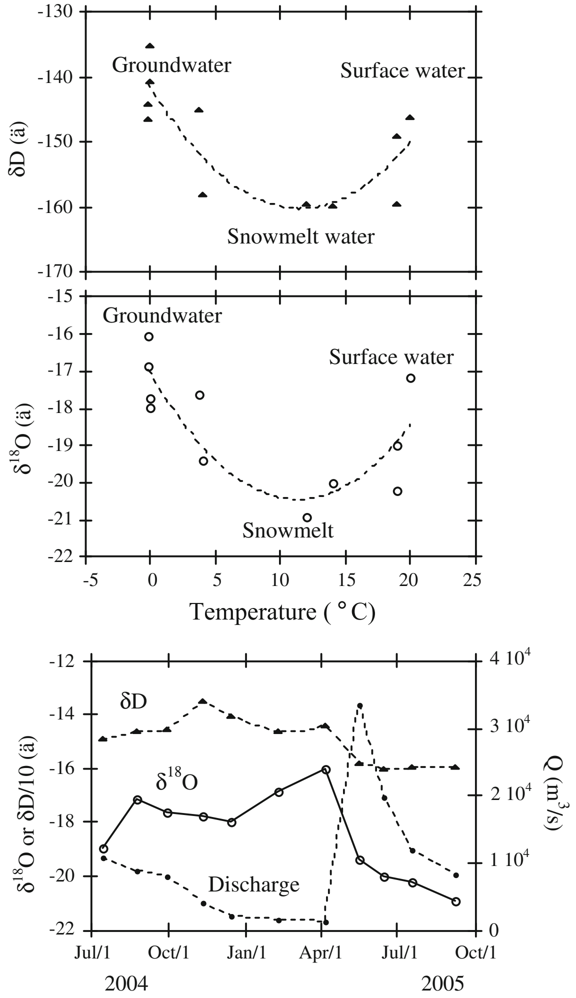

Fig. 3 Relationship between stable isotope composition (δD and δ^{18}O) and water temperature or discharge (m^3/s) in the Yukon River

Concentrations of POC varied from 65–76 μM when the river was frozen to 557–667 μM during and after ice break up, with an average of 317 ± 292 μM (Table 1). The average POC concentration is slightly higher than the 2001–2005 average (266 μM) reported by Striegl et al. (2007), showing large seasonal and annual variability. Overall, the POC concentrations are within the range reported for total particulate carbon in Yukon River waters (Schuster 2003), indicating that particulate inorganic carbon (PIC) is not a significant component compared to POC (Schuster 2003) although PIC concentration could be significant in other Yukon tributaries such as the Tanana River (Striegl et al. 2007). POC concentration is also comparable to that of DOC in Yukon River waters, with an average POC/DOC ratio of 1.05 ± 1.28. However, the POC/DOC ratio varied considerably (0.18–4.3) exhibiting the lowest values when the river was frozen over and suspended loads were low. The average POC/DOC ratio was lower than that of the Mackenzie River (1.4), but much higher than ratios of the large Siberian rivers (0.03–0.17) (Stein and Macdonald 2004). Specific POC concentration or the carbon content of suspended particles ranged from 0.8 to 16%, with an average value of 1.6 ± 0.6% during summer and 13.5 ± 2.9% during winter, indicating different particle types and POC sources. High specific POC content below the ice was likely derived from microbial biomass (see also discussion in next section). Summer POC/TSS ratios in the Yukon River are similar to those in Siberian rivers (Lobbes et al. 2000).

DIC concentrations ranged from 1,178 μM during ice breakup to 2,128 μM during the end of the frozen season, with an average of 1,629 ± 356 μM. These values were considerably higher than those of POC and DOC except during ice break-up in May when DOC concentration was the highest (Table 1). Average DIC/DOC ratio was 5.8 ± 3.2, with the highest ratio (11.7) in April 2005 and lowest ratio (0.7) in May 2005. The averaged and open season DIC/DOC ratios in the Yukon River are similar to those reported for the Chena River, Alaska (5.5 ± 2.8, Cai et al. 2008a). Although alkalinity is given in the PARTNERS data file, DIC data are not directly available for comparison. Our average DIC/DOC ratio is higher than that calculated from 2001 to 2005 averaged DIC and DOC concentrations in the Yukon (3.13, Striegl et al. 2007). The strong seasonality and significant difference in DIC/DOC ratio between tributaries suggest that changes in DIC/DOC ratio may be used as a complementary indicator for climate and environmental change in river basins.

For inorganic nutrient species, the average concentrations were 11.1 ± 1.5 μM for DIN, 0.14 ± 0.04 μM for DIP and 134 ± 43 μM for Si(OH)$_4$. Similar to DIC, all inorganic nutrient species had elevated concentrations during the winter season and lower concentrations during the ice-open season (Table 1), except for DIP. For organic nutrient species, average DON concentration was 10.8 ± 10.5 μM, ranging from lowest of 2.91 μM

Table 2 Concentrations of dissolved organic carbon (DOC), nitrogen (DON), phosphorus (DOP), particulate organic carbon (POC), nitrogen (PN), and phosphorus (PP) in Yukon River waters at Pilot Station, Alaska (61.94°N, 162.87°W) during 2004–2005

Sampling date	DOC (µM)	DON (µM)	DOP (µM)	DOC/DON (at ratio)	POC (µM)	PN (µM)	PP (µM)	POC/PN (at ratio)	POC (mg-C/g)	Chl-a (µg/L)	POC/Chl-a (µmol/µg)
7/15/04	269	6.54	0.084	41	456	10.4	nd	44	–	nd	–
8/25/04	218	6.33	0.031	34	642	15.3	nd	42	18.0	nd	–
9/30/04	225	5.98	0.055	38	201	8.3	4.46	24	18.0	2.0	101
11/10/04	428	9.37	0.143	46	76	2.9	0.79	26	92.6	1.8	42
12/15/04	352	7.90	0.034	45	70	2.8	0.74	25	141	0.8	88
2/9/05	213	4.22	0.067	50	65	3.1	0.73	21	156	0.6	108
4/5/05	182	2.91	0.024	62	68	2.6	0.76	26	160	1.3	52
5/17/05	1683	41.14	0.273	41	557	29.9	17.25	19	14.1	4.7	119
6/14/05	529	12.54	0.155	42	195	7.6	3.38	26	22.2	3.9	50
7/19/05	316	8.62	0.033	37	411	18.5	12.07	22	12.7	4.4	93
9/7/05	297	13.62	nd	22	242	10.0	nd	24	8.0	nd	–
Average ± SD	428 ± 429	10.8 ± 10.5	0.113 ± 0.108	42 ± 10	317 ± 292	9.9 ± 8.6	5.85 ± 6.36	27 ± 8	64.2 ± 65.5	2.4 ± 1.6	82 ± 29

under the ice to the highest of 41.1 µM during spring freshet (Table 2). The concentration of DOP varied from 0.024 µM under the ice to 0.273 µM during spring freshet, with an average concentration of 0.113 ± 0.108 µM. Similar to POC, both PN and PP also had the highest concentrations during spring freshet and the lowest under the ice, with an average of 9.9 ± 8.6 µM for PN and 5.85 ± 6.36 µM for PP (Table 2).

Overall, concentrations of organic C, N, and P species in both dissolved and particulate phases were highest during spring freshet and lowest in winter under the ice. In contrast, concentrations of inorganic C, N, and P species and $Si(OH)_4$ were the lowest during spring freshet and highest in the winter frozen season. These contrasting temporal variations (Fig. 4) indicate distinctly different interactions between the sources (and sinks) of organic and inorganic components and the hydrological supply of water to the Yukon River.

Sources of carbon and nutrient species

Molar ratios of DIN/DIP ranged from 38 during the ice-open season to 442 in winter under the ice. These ratios, which are considerably higher than the Redfield ratio (16:1) that characterizes most oceanic environments (Broecker and Peng 1982), together with the low DIP concentration, indicate a P-limiting ecosystem in the Yukon River. The high N/P ratio of up to 442 under the ice was likely caused by phosphorus uptake by microorganisms, or by different source waters. Unlike all other inorganic carbon and nutrient species, DIP concentration decreased from November 2004 to April 2005 (Fig. 4). Low DIP concentration under the ice may have been a result of coprecipitation of phosphate with Fe oxide-hydroxides (e.g. Mayer and Jarrell 1995), microbial utilization of DIP and the dominance of groundwater sources. Concentrations of DIP were not measured during the USGS and PARTNERS program (Dornblaser and Striegl 2007; McClelland et al. 2008), preventing a direct comparison of DIN/DIP ratio. However, based on their available data, the average TDN/TDP ratio was 115 ± 102, indicating also an overall high N/P ratio ecosystem.

Average DOC/DON molar ratio was 41.6 ± 10.1, and showed a general decrease from spring freshet to the late summer in 2005, suggesting an increase in contribution from autochthonous fresh DOM components or the highly degraded soil DOM inputs (both with lower C/N ratio). The highest DOC/DON ratio was not observed in the spring freshet when DOM is mostly derived from surface plant litter and soil organic matter (Guo and Macdonald 2006), but in late winter and early spring before ice breakup (Table 2). Furthermore, the winter DOC/DON ratio increased from December 2004 to April 2005, indicating

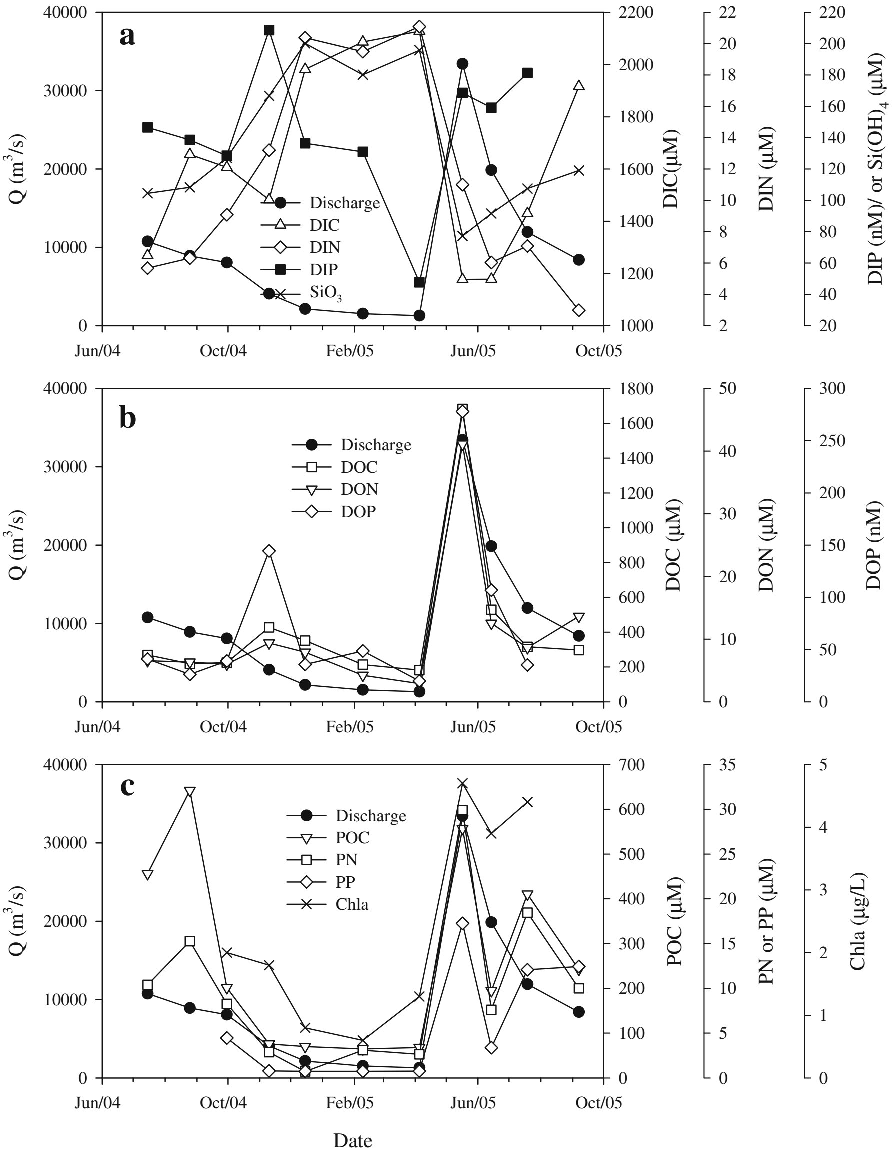

Fig. 4 Temporary variations of water discharge (Q) and organic and inorganic carbon and nutrients (N, P, and Si) in the Yukon River from July 2004 to September 2005 (Pilot Station, Alaska, 61.94°N and 162.87°W). The river was ice covered from early October to early May. Data of river discharge are from USGS (www.usgs.gov)

preferential decomposition of N-containing DOM by microbial activity and an increase in the reworked DOM component under the ice. Our average DOC/DON ratio was slightly higher than that measured by the PARTNERS program (McClelland et al. 2008) for the Yukon during 2004–2006 (37 ± 7), likely due to more winter sampling points in our study.

Changes in DOC/DON ratio with season suggest a DOM source shifting from mostly terrestrial DOM during spring freshet to a mixed aquagenic-terrestrial DOM during the ice-open season to a microbially modified or reworked DOM in winter under the ice (Zou et al. 2006). Our results are consistent with changes in DOM optical properties, such as CDOM absorption spectral slope and SUVA$_{254}$ values, between spring freshet and under the ice (Spencer et al. 2008). For example, higher spectral slope and lower SUVA values under the ice (April 05, 2005, the same river water sample collected by us for USGS) both indicate the presence of less aromatic DOM with higher fraction of low molecular weight DOM components.

DOC concentration during the ice-open season was higher in 2005 than 2004 (306 vs. 243 μM), as

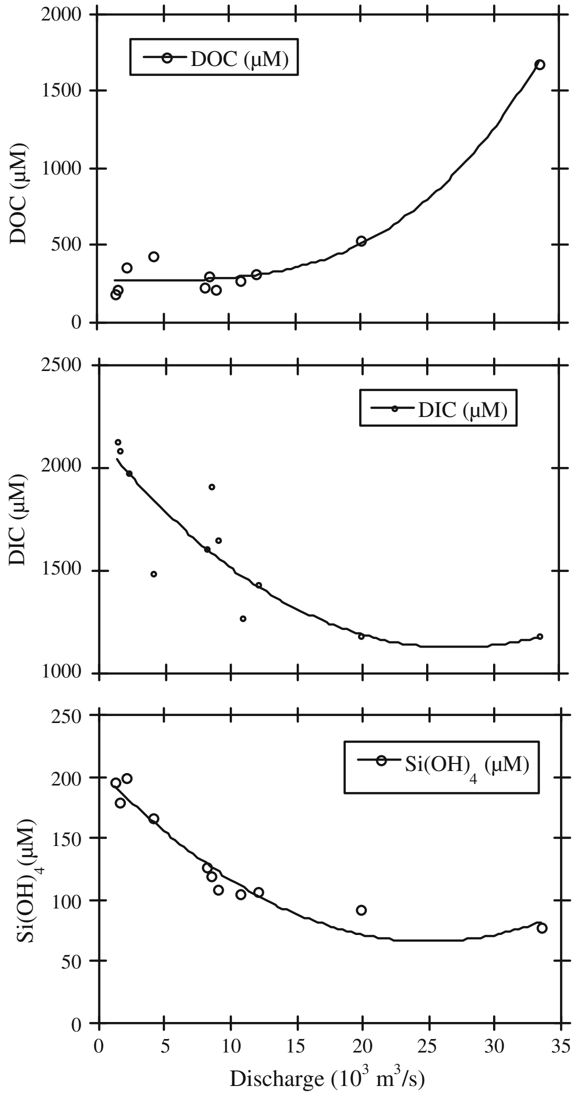

Fig. 5 Relationship between discharge (m^3/s) and DOC, DIC and dissolved silicate concentrations (μM) in the Yukon River

was the discharge. Indeed, DOC concentration shows a monotonic increase with increasing discharge (Fig. 5), indicating hydrological control of the wash-out of DOC from allochthonous sources, as also reported for other river systems (Hope et al. 1994; Warnken and Santschi 2004). Considering the vast amount of soil OC stored in Arctic regions (Michaelson et al. 1996; Ping et al. 2008) and amplified warming in the Arctic, the resultant degradation of permafrost and peatlands could potentially release large amounts of POC and DOC to Arctic rivers (Guo et al. 2004b; Xu et al. 2009). However, the young ^{14}C age of DOC observed in Arctic rivers argues that, for the present, modern sources supply the bulk of the DOC to rivers (Benner et al. 2004; Guo and Macdonald 2006; Raymond et al. 2007). Based on radiocarbon data, Guo and Macdonald (2006) inferred that DOC in the upper Yukon River is derived mostly from modern terrestrial biomass and not from old soil OC. The lack of co-variation between DOC and POC concentrations (Guo et al. 2007) implies a different response to discharge and, therefore, a different source and turnover time for DOC and POC in the Yukon River basin.

The quality and sources of POC are reflected by intensive properties such as particulate C/N ratio, POC content (in mg-C/g), and POC/Chl-a ratio. As listed in Table 2, the average POC/PN ratio was 27 ± 8, which is much lower than the average DOC/DON ratio (41.6 ± 10.1), with a general decrease from July 2004 to winter. Interestingly, the lowest POC/PN ratio was measured during spring freshet, suggesting that recently produced organic matter and highly degraded old soil organic matter, both with lower POC/PN ratio, were entering with snowmelt (Table 2). POC content within particles was lowest during spring freshet (14.1 mg-C/g) but highest in winter under the ice (160 mg-C/g). The lower POC/TSS ratio during spring and the summer season implies a general soil source, while higher POC/TSS ratio in winter suggests a different POC source below the ice, likely from bacterial biomass and other organic-rich fine particulate materials. Concentration of Chl-a was generally low in winter and elevated in summer (Table 2). The average POC/Chl-a ratio was 82 ± 29 (μmol-C/μg-Chl-a), with lower values in November (after ice formation), April (before ice break) and June (after ice break), but highest during the spring freshet. The highest Chl-a concentration was measured during spring freshet, implying a terrestrial vegetation source of POC.

In contrast to DOC and other organic species, DIC concentration monotonically decreased with increasing discharge, as did dissolved silicate concentration (Fig. 5), suggesting dilution to be important. The negative correlation between DIC and discharge implies that DIC derives mostly from leaching and weathering of inorganic minerals through ground waters, consistent with observations in the upper Yukon River (Guo et al. 2004a; Guo and Macdonald 2006). DIC under the ice could also be derived from the decomposition of dissolved and particulate organic matter within the water, but this source cannot be quantitatively evaluated here without other measurements.

Partitioning of C, N and P between inorganic, organic, dissolved, and particulate phases

The partitioning of C, N, and P between dissolved inorganic and organic and particulate phases in the Yukon River during the 2004–2005 is summarized efficiently using a ternary diagram (Fig. 6). Among the DIC, DOC, and POC components transported in the Yukon River, DIC was predominant, contributing on average 71 ± 16% of the total carbon (DOC + POC + DIC), followed by DOC (17 ± 12%) and POC (12 ± 11%) with the caveat that POC might be underestimated in our surface-water samples. During the winter season, DIC comprised up to 89% of the total C. During the spring freshet, however, DOC became the dominant C species, contributing up to 50% of the total C. The dynamic partitioning and changes in C species are unique features in seasonally ice-covered rivers in the north. Our results here are similar to those reported by Striegl et al. (2007) for the Yukon River between 2001 and 2005.

The three N species, DIN, DON and PN, were of almost equal importance, with an average of 38 ± 25, 31 ± 14 and 31 ± 15%, respectively. However, DIN in the winter season was clearly the dominant N species transported in the Yukon River (Fig. 6). Both DON and PN were the dominant species during spring freshet and the summer season. In contrast to C and N, particulate P predominated, contributing up to 88 ± 11% of the total P pool in the Yukon River, followed by DIP (8 ± 7%) and DOP (4 ± 4%). Overall, DIC and PP are the predominant species transported in the Yukon River, while N was more dynamically partitioned among DIN, DON and PN pools. The partitioning of C, N, and P between dissolved, particulate, inorganic and organic phases all had a strong seasonal variation. This is the first complete dataset for phase partitioning of N and P although there have been measurements and flux estimation for nutrients in the Yukon River basin and other Arctic rivers (Schuster 2003; Dornblaser and Striegl 2007; McClelland et al. 2008; Frey and McClelland 2009).

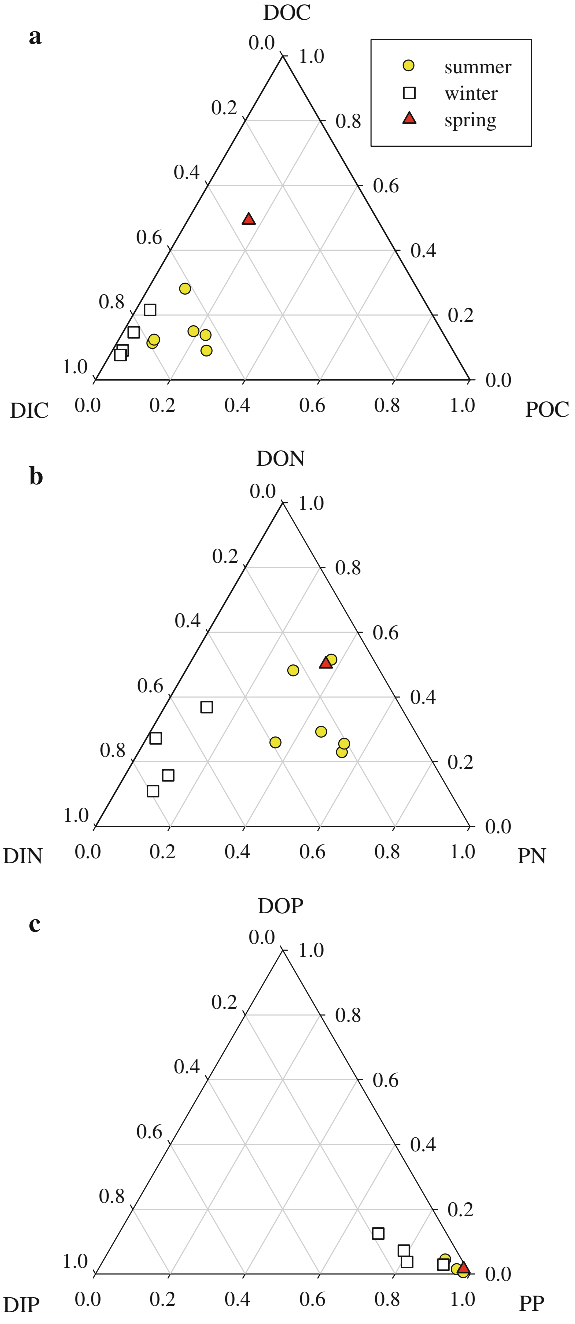

Fig. 6 Ternary plots showing the partitioning of C, N and P among dissolved organic, dissolved inorganic and particulate phases in Yukon River waters. *Triangular data points* are from the winter season (below the ice) and the *circles* correspond to the ice open season (summer and fall)

Fractionation of carbon and nutrient species and stable isotopes (δD and δ^{18}O) between river water and ice

Arctic rivers are completely ice covered during winter. The freezing and thawing processes, characteristic of northern high latitude rivers and their drainage basins, likely have significant influence on the partitioning, transformation and transport of organic and inorganic carbon and nutrients as well as other trace elements in Arctic aquatic environments. However, quantitatively these processes remain poorly understood in Arctic rivers.

Concentrations of DOC, DIC, total dissolved nitrogen (TDN), and $Si(OH)_4$ and stable isotope composition (δD and δ^{18}O) of the ice and underlying water are listed in Table 3. To examine the fractionation of solutes during ice formation, a fractionation factor was operationally defined here as the concentration ratio of a specific chemical species between water and ice. As shown in Table 3, the estimated fractionation factor of DOC between river water and ice was about 3.0–6.7 depending on the concentration of solute used for representing river waters, while for DIC the fractionation factor was 37–54. Total dissolved nitrogen (TDN), including DIN and DON, had a fractionation factor of 110–162, which is much higher than DOC and DIC (Table 3). The concentration of $Si(OH)_4$ in ice samples was near the detection limit, resulting in a fractionation factor of 9,300–9,800, which is much higher than those of DOC and TDN, but lower than the fractionation factor for specific conductivity (41,000–53,000). Overall, inorganic species exhibit a higher fractionation factor than organic species during ice formation in the Yukon River, suggesting that the two components can become somewhat decoupled in transport.

The ratio of δD or δ^{18}O values between winter river water and average ice was about 1.14–1.18 for δD and 1.14–1.51 for δ^{18}O (Table 3). Winter δD and δ^{18}O values in river waters were significantly lower than those measured for the overlying river ice, with an average enrichment of 17‰ for δD and 3.2‰ for δ^{18}O (Table 3). This enrichment is similar to isotopic fractionation of δ^{18}O ($\sim$2.5‰) associated with the production of ice in the Mackenzie River (Macdonald et al. 1995), which favors isotopically heavier ice and lighter water.

Since river water below the ice is constantly replaced by upstream water, the solutes excluded during ice formation will be carried away. Thus, fractionation factors between ice and river water reported in Table 3 for carbon and nutrient species are apparent values. Because inorganic carbon and many nutrient species increased in concentration from fall to winter (Fig. 4), the fractionation factors for inorganic species are likely to be the higher limits or overestimates. On the other hand, the apparent fractionation factors for organic species are likely to be underestimates.

Table 3 Concentration of carbon and nutrients and stable isotope composition of river ice and water samples and their apparent fractionation factors between river water and ice in the Yukon River

Ice or river water	Cond. (μS/cm)	DOC (μM)	DIC (μM)	TDN (μM)	$Si(OH)_4$ (μM)	δD (‰)	δ^{18}O (‰)
Top ice	0.011	31	43	0.093	0.02	−123	−15.2
Mid ice	0.005	41	24	0.145	0.02	−128	−15.4
Bottom ice	0.006	60	52	0.219	0.02	−122	−11.3
Average ice	0.007	44	39	0.152	0.02	−124	−14.0
Water below ice	320	182	2128	24.0	196	−144	−16.0
Average winter water	303	293	1920	24.6	186	−141	−17.2
Fractionation factor between river water and bottom ice[a]							
April 2005 water	53333	3.0	41	110	9800	1.18	1.41
Average winter water	50500	4.8	37	112	9300	1.15	1.51
Fractionation factor between river water and average ice							
April 2005 water	45714	4.1	54	158	9800	1.16	1.14
Average winter water	43285	6.7	49	162	9300	1.14	1.23

[a] Fractionation factor was operationally defined as the concentration ratio of a given species between river water and ice

A previous study has shown a significant fractionation of DOC, colored dissolved organic matter (CDOM), and ions between ice and water in northern lakes (Belzile et al. 2002); fractionation of oxygen isotopes during the formation of river ice also occurs (Macdonald et al. 1995). For example, exclusion factors in lake ice were reported for DOC (2.6–4.3), CDOM (1.4–114, with an average of 32), and specific conductivity (typically higher than those of CDOM) (Belzile et al. 2002). Our estimated fractionation factors and the differences between organic and inorganic chemical species are consistent with those reported previously. Fractionation of carbon and solutes between ice and water during ice formation and the decoupling between organic and inorganic species during fractionation has important implications for organic carbon cycling, nutrient transport, coastal productivity and climate change (Belzile et al. 2002; Guéguen et al. 2007).

As a first approximation, the quantitative importance of river ice formation in the Yukon River can be estimated as follows. The Yukon River is about 3,000 km long and 1 km wide, with an annual discharge of ~200 km^3 (Brabets et al. 2000; Striegl et al. 2007). Using an ice thickness of 2 m, the implied river ice formation amounts to 6 km^3, which is about 20% of the winter discharge and 3% of the annual discharge. In other words, 20% of the winter discharge could be withdrawn during winter and released in spring, enhancing water interactions with soils during freshet and causing heterogeneous distribution of fluxes between seasons. Overall, the exclusion of solutes by river ice will enhance concentrations of carbon and nutrient species under the ice during winter, resulting in their continued export toward the ocean. Therefore, river fluxes of carbon and nutrient species are subject to bias without time series sampling during winter frozen season in Arctic river systems.

Export fluxes of carbon and nutrient species from the Yukon River basin

Riverine export fluxes of carbon and nutrient species can be estimated using the USGS LOADEST program (http://water.usgs.gov/software/loadest/), regression between instantaneous species flux and discharge (Warnken and Santschi 2004), and other methods as summarized in Worrall and Burt (2007). Table 4 presents annual export fluxes of carbon and nutrient species from the Yukon River during 2004–2005 and their uncertainties under different scenarios (without spring freshet data vs. without winter data) based on the above flux quantification methods. Using the USGS LOADEST program and daily stream flow rates and observed concentrations, the annual export fluxes of DOC, POC and DIC were 1.62 × 10^{12}, 0.89 × 10^{12}, and 4.40 × 10^{12} g-C/year, respectively. For nutrient species, the flux of DON, PN, and DIN were 5.09 × 10^{10}, 4.90 × 10^{10}, and 2.85 × 10^{10} g-N/year. Fluxes of P species are comparable to N species, with particulate P the highest (6.79 × 10^{10} g-P/year), followed by DIP (0.15 × 10^{10} g-P/year) and DOP (0.14 × 10^{10} g-P/year). Flux of dissolved silicate was 8.1 × 10^{11} g-Si/year, which is higher than those of N and P species (Table 4). Fluxes estimated using flow weighted mean concentration are similar to those estimated using LOADEST program. However, fluxes estimated using the interpolation method are significantly different from those estimated by the other two methods due to the non-linear relationship between daily flux and instantaneous discharge (Table 4). Export fluxes of total N and P are similar to or slightly higher than those reported for the Yukon River between 2001 and 2005 (Dornblaser and Striegl 2007) although there were strong seasonal and annual variability.

Regardless of methods used (grab samples or depth-integrated samples), our DOC and DIC fluxes (1.62 × 10^{12} and 4.40 × 10^{12} g-C/year) are within the range of values (1.34–2.18 × 10^{12} g-DOC/year, and 4.4–5.4 × 10^{12} g-DIC/year) reported by Striegl et al. (2007), Raymond et al. (2007), and Spencer et al. (2009) for the Yukon River at Pilot Station during 2004 and 2005 (Table 5). Interestingly, our POC fluxes (0.89 × 10^{12} g-POC/year) derived from surface sampling are also within the range of values (0.60–1.0 × 10^{12} g-POC/year) reported for depth-integrated samples by Striegl et al. (2007). Within the variability inherent in sampling, we find no significant difference in flux estimation for particulate species between our measurements and those made using depth-integrated samples (Table 5). Instead, sampling time and frequency likely play a more important role in providing an unbiased material flux estimation for Arctic rivers.

Within the annual export fluxes, 75% of the DOC, 70% of DIC and 87% of POC fluxes were contributed

Table 4 Export fluxes of carbon and nutrient species estimated using (1) USGS LOADEST program, (2) discharge weighted mean solute concentrations, and (3) the relationship between daily solute flux and instantaneous river discharge

	DOC	POC	DIC	DON	PON	DIN	DOP	POP	DIP	Si
Flux (g-C (N, P, or Si)/year) estimated using USGS LOADEST program										
All data point	1.62×10^{12}	0.89×10^{12}	4.40×10^{12}	5.09×10^{10}	4.90×10^{10}	2.85×10^{10}	0.14×10^{10}	6.79×10^{10}	0.15×10^{10}	8.10×10^{11}
Without spring freshet data	−16%	−8%	+1%	–	–	–	–	–	–	–
Without winter data	+3%	−1%	−1%	–	–	–	–	–	–	–
Flux (g-C (N, P, or Si)/year) estimated using flow weighted mean concentration										
Flux (g/year) with all data point	2.04×10^{12}	1.04×10^{12}	3.79×10^{12}	5.99×10^{10}	5.15×10^{10}	2.71×10^{10}	0.10×10^{10}	7.28×10^{10}	0.11×10^{10}	6.59×10^{11}
Without spring freshet data	−54%	−20%	+7%	−51%	−36%	−12%	−42%	−54%	−2%	+11%
Without winter data	+5%	+7%	−3%	+6%	+8%	−9%	+3%	+37%	+0.3%	−7%
Fluxes (g-C (N, P, or Si)/year) estimated using correlation between daily flux and instantaneous discharge[a]										
Flux using slope w/o spring data	1.30×10^{12}	0.80×10^{12}	3.18×10^{12}	3.75×10^{10}	3.47×10^{10}	1.40×10^{10}	9.19×10^{8}	3.91×10^{10}	1.15×10^{9}	5.31×10^{11}
Flux using slope w/i spring data	4.22×10^{12}	1.41×10^{12}	3.02×10^{12}	12.0×10^{10}	8.71×10^{10}	3.02×10^{10}	18.5×10^{8}	11.0×10^{10}	1.19×10^{9}	4.58×10^{11}

Two scenarios (fluxes without spring freshet data vs. without winter data) were also considered either in terms of flux or deviation, with underestimation (−) or overestimation (+). Total water discharge of 227 km^3 during 2005 was used for the Yukon River at Pilot Station, Alaska

(a) Adding spring data resulted in a nonlinear curve and using the slope value in the linear regression line causes overestimation and thus these flux values are upper limit fluxes. In contrast, using slope values without spring freshet data results in flux underestimation and these are lower limit flux numbers

Table 5 Comparison of reported carbon and nutrients fluxes (in gram of C, N, P or Si per year) from the Yukon River at Pilot Station, Alaska

Time period	Sampling points/year	DOC	POC	DIC	$NO_3 + NO_2$	PN	DIP	PP	$Si(OH)_4$	Reference
Before 1980	n.a.	0.48×10^{12}	2.49×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Leenheer (1982)
1978–1980	6–8	0.88×10^{12}	n.a.	1.80×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	Striegl et al. (2005)
2001–2003	6–8	0.53×10^{12}	n.a.	1.86×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	Striegl et al. (2005)
2002[a]	6	1.75×10^{12}	2.76×10^{12}	3.53×10^{12}	n.a.	2.17×10^{10}	n.a.	n.a.	n.a.	Guo and Macdonald (2006)
2001–2005	6–8	n.a.	n.a.	n.a.	1.96×10^{10}	4.5×10^{10}	0.2×10^{10}	5.5×10^{10}	n.a.	Dornblaser and Striegl (2007)
2001–2005	6–7	1.58×10^{12}	0.75×10^{12}	4.96×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	Striegl et al. (2007)
2004	6–7	1.34×10^{12}	0.60×10^{12}	4.41×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	Striegl et al. (2007)
2005	6–7	1.92×10^{12}	1.00×10^{12}	5.41×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	Striegl et al. (2007)
2004	6–7	1.21×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Raymond et al. (2007)
2005	6–7	2.18×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Raymond et al. (2007)
2004–2005	27	1.75×10^{12}	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Spencer et al. (2009)[b]
2004–2005	9–11	1.62×10^{12}	0.89×10^{12}	4.40×10^{12}	2.85×10^{10}	4.90×10^{10}	0.15×10^{10}	6.79×10^{10}	8.10×10^{11}	This study (loadest)
2004–2005	9–11	2.04×10^{12}	1.04×10^{12}	3.79×10^{12}	2.71×10^{10}	5.15×10^{10}	0.11×10^{10}	7.28×10^{10}	6.59×10^{11}	This study (FWM)[c]

[a] Estimated from the upper Yukon River

[b] Based on CDOM measurements

[c] Fluxes estimated from flow weight mean concentration method

during ice-open season. Although the DOC export flux from the Yukon River is lower than other major Arctic rivers, its POC flux is much higher than those from other Siberian Arctic rivers, and similar to that of another particle-rich river, the Mackenzie (McGuire et al. 2009). Winter POC flux is less important because particles transport by the river and concentration of TSS are low during that period even though POC/TSS is high.

Daily DOC export fluxes show a similar variation as daily discharge (not shown). The highest daily DOC flux was observed in May 2005, with up to 580×10^8 g-C, whereas the lowest daily DOC flux (2.4×10^8 g-C) was observed between February and April 2005. Daily DOC flux during the open water period was up to two orders of magnitude higher than fluxes when the river was frozen. Daily POC flux also varied widely, ranging from 0.91×10^8 to 193×10^8 g-C, in contrast to smaller variation in daily DIC fluxes, which ranged from 28.5×10^8 g-C in April to 408×10^8 g-C in May. Considerable variation in daily DOC fluxes presents challenge in planning sampling time and frequency and could result in large uncertainty in export flux estimations. As shown in Table 5, estimated DOC fluxes differ significantly between studies and years using the same river flow data for the Yukon River at Pilot Station. The large uncertainties in river fluxes of carbon and nutrient species have to be reduced before the export fluxes can be used confidently to assess climate and environmental changes in the river basin.

Uncertainties in export flux estimation

River export fluxes of solutes are traditionally (practically) estimated from their average concentrations measured during the ice-open season and annual fresh water discharge. This practice assumes similar solute abundances in river waters during different seasons and assumes a linear relationship between daily solute fluxes and river discharge. However, our measurements and other recent studies show that DOC and other solute concentrations in northern river waters vary considerably between sampling seasons (Table 2; Finlay et al. 2006; Guo and Macdonald 2006; Striegl et al. 2007; Spencer et al. 2009) and this difference can be up to one order of magnitude for organic carbon species (Table 2). In addition, river discharge in high latitude rivers peaks during spring freshet or snowmelt. Thus, high DOC concentrations concurrent with high river discharge during spring give rise to a disproportional share of annual DOC export flux (e.g. Spencer et al. 2009). Sampling that misses spring freshet will result in underestimation of organic carbon and nutrient fluxes (Table 4), as also observed for other high latitude rivers (Finlay et al. 2006). Similarly, sampling that misses winter under the ice could overestimate riverine organic carbon and nutrient fluxes (Table 4). For example, based on the USGS LOADEST program, underestimation of export fluxes was up to 16% for DOC and 8% for POC without the spring freshet data (Table 4). On the other hand, DOC flux can be overestimated by 3% without the winter data. For inorganic species, seasonal variations are opposite the organic C and nutrient species, with a dilution effect occurring during spring freshet, and higher concentrations accumulating under the ice (Fig. 4). Therefore, export fluxes for inorganic C and nutrient species could be overestimated without spring freshet sampling but underestimated without winter sampling under the ice regardless of the methods used for flux estimation (see also discussion below).

Additional examples showing flux uncertainties and ranges between lower and upper limits are depicted in Fig. 7 and Table 4. The interpolation method based on correlation between daily solute flux and instantaneous discharge has been widely used in other river systems (Hope et al. 1994; Warnken and Santschi 2004). However, large uncertainty may occur in flux estimation due to the non-linear relationship for solutes in high latitude rivers (Finlay et al. 2006), especially for organic species (Fig. 7). Unlike organic species, the linear relationship between daily solute flux and instantaneous river freshwater discharge does not seem to be significantly different with or without spring freshet sampling for DIC, DIP, and $Si(OH)_4$, except for DIN which is similar to those of organic species (Fig. 7). Nevertheless, due to the dilution effect for inorganic C and nutrient species during spring freshet, slope values from the linear relationship between daily solute flux and instantaneous river freshwater discharge are slightly higher without spring freshet sampling (Fig. 7), especially for DIC and $Si(OH)_4$, which are mostly weathering chemical components in contrast to DIN and DIP, which are more prone to biological control. Thus, overestimation of river export fluxes

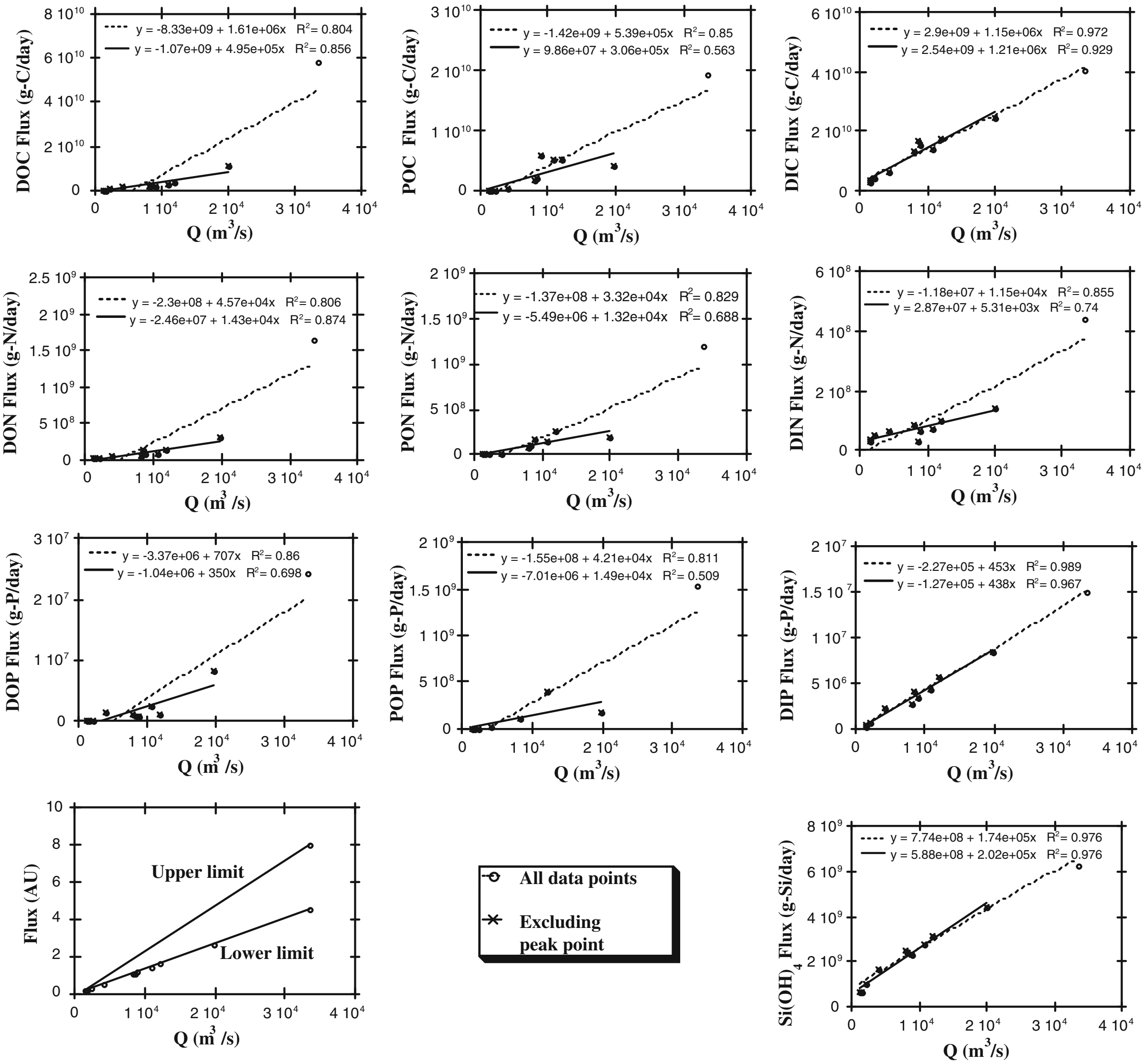

Fig. 7 Correlation between daily solute flux (g/day) and instantaneous river discharge (m^3/s) for selected C and nutrient species. Note that there is a difference in the correlation between organic and inorganic components. While inorganic solutes except DIN show little different in slope values between two correlation lines, the opposite is true for organic components with a non-linear correlation when spring sampling is included

through omission of spring sampling is indeed possible for inorganic species although this over- or under-estimation is smaller compared to estimations of organic C species (Table 4; Fig. 7).

Fluxes estimated using flow weighted mean concentrations also give large biases. On average, fluxes of DOC and other organic species may be underestimated by as much as 50% if spring freshet sampling is omitted. Flux overestimation for DOC and other organic species without winter sampling is not as serious (3–8%), except for particulate phosphorus (Table 4). In general, flux estimation without spring freshet sampling will underestimate organic species and overestimate inorganic species. In contrast, flux estimation without winter sampling overestimates organic species and underestimates inorganic species.

It is clear that snapshot and even seasonal sampling will not produce an appropriate estimate of C and nutrient fluxes for monitoring carbon dynamics and potential impacts of climate change.

As shown in Table 5, there are no clear trends in river export fluxes for C and nutrient species from the Yukon River based on available literature data. Although few nutrient data are available for comparison, fluxes of DOC and DIC have been reported since the early 1980s (Table 5). Considering uncertainties in export flux estimation, projections of increased or decreased export fluxes of carbon and nutrients in Arctic and subarctic rivers need to be better tested, not only through intensive sampling during a given year, but also through long-term observation designed to capture all stages of river flow. Likewise, projected changes in hydrology, and, in particular, ice formation and extreme events, need to be monitored in their potential to affect the transfer of carbon, nutrients and trace elements by polar rivers to coastal seas.

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