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Source and Transport of Terrigenous Organic Matter In the Upper Yukon River: Evidence From Isotope (?C-13, ΔC-14, and ?N-15) Composition of Dissolved, Colloidal, and Particulate Phases

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Source and transport of terrigenous organic matter in the upper Yukon River: Evidence from isotope ($\delta^{13}C$, $\Delta^{14}C$, and $\delta^{15}N$) composition of dissolved, colloidal, and particulate phases

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[1] Natural organic matter was collected from the upper Yukon River and size fractionated into the <1 kDa low-molecular-weight dissolved (LMW-DOC), colloidal (COC, 1 kDa to 0.45 μm) and particulate organic carbon (POC, >0.45 μm) phases for characterization of elemental (C and N) and isotopic (^{13}C, ^{14}C and ^{15}N) composition to examine their sources and transport. Concentrations of total organic carbon (TOC) decreased from 3010 μM in mid-May to 608 μM in September, accompanying an increase in river water $\delta^{18}O$ from the snowmelt to summer and early fall. COC was the predominant OC species, comprising, on average, 63 ± 8% of the TOC, with 23 ± 5% partitioned in the LMW-DOC and 14 ± 5% in the POC fraction. Annual riverine export flux to the ocean was 2.02×10^{12} g-C for TOC, 7.66×10^{10} g-N for total organic nitrogen (TON), and 3.53×10^{12} g-C for dissolved inorganic carbon (DIC), respectively. The C/N molar ratios were distinctly different between colloidal organic matter (COM, 46 ± 3) and particulate organic matter (POM, 15 ± 1.4). Similar $\delta^{13}C$ values were found for LMW-DOM (−27.9 ± 0.5‰), COM (−27.4 ± 0.2‰), and POM (−26.2 ± 0.7‰), although there was a general increase with increasing size, suggesting a common terrigenous organic source. In contrast, distinct $\Delta^{14}C$ values were found for LMW-DOC (−155 to +91‰), COC (40 to 140‰), and POC (−467 to −253‰) with a decreasing trend from snowmelt to ice-open season, suggesting that turnover pathways and transport mechanisms vary with organic matter size fractions. The high abundance of COC and its contemporary ^{14}C ages points to a predominant source from modern terrestrial primary production, likely from the leaching/decomposition of fresh plant litter in the upper soil horizon. The predominately old POC (average 3698 ± 902 years B.P.), in contrast, was largely derived from riverbank erosion and melting of permafrost. These results imply that ice-opening Yukon River flows are dominated by snowmelt (low $\delta^{18}O$) with high DOC (high $\Delta^{14}C$) but low DIC and $Si(OH)_4$ concentrations, whereas late summer flows contain more products of permafrost or ice melt and rain (high $\delta^{18}O$), with low DOC (low $\Delta^{14}C$) but high DIC and $Si(OH)_4$ concentrations. A warming climate with a deeper permafrost active layer in the Yukon River watershed would enhance the mobilization and export of old terrestrial OC, but largely in the particulate form into the Bering Sea and Arctic Ocean.

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1. Introduction

[2] World rivers deliver approximately 500 Tg of organic carbon (OC) (see Table 1 for a list of other abbreviations) annually to the ocean [*Meybeck*, 1982; *Hope et al.*, 1994]. Therefore the riverine export of OC from drainage basins to the ocean represents a major component of the global carbon cycle [*Spitzy and Leenheer*, 1991; *Hedges et al.*, 1997]. The Arctic drainage basin (∼24×10^6 km^2) processes ∼11% of the global runoff [*Lammers et al.*, 2001]. Heavily influenced by snow, ice and permafrost, arctic river basins are poised on the leading edge of climate change. However, the impact and biogeochemical consequences of climate and environmental change in the Arctic region remain largely unknown. With 23–48% of the world's soil organic carbon (SOC) stored in the high-latitude region, the arctic/subarctic river basins have an

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Table 1. A List of Abbreviations and Glossary[a]

Abbreviation	Term	Description or Definition
COC	colloidal organic carbon	1 kDa-0.45 μm
COM	colloidal organic matter	1 kDa-0.45 μm
CON	colloidal organic nitrogen	1 kDa-0.45 μm
DIC	dissolved inorganic carbon	<0.45 μm
DIN	dissolved inorganic nitrogen	NO_3, NO_2 and NH_4
DOC	dissolved organic carbon	<0.45 μm
DOM	dissolved organic matter	<0.45 μm
DON	dissolved organic nitrogen	<0.45 μm
LMW-DOC	low molecular weight dissolved organic carbon	<1 kDa
LMW-DOM	low molecular weight dissolved organic matter	<1 kDa
LMW-DON	low molecular weight dissolved organic nitrogen	<1 kDa
NOM	natural organic matter	...
OC	organic carbon	...
PN	particulate nitrogen	>0.45 μm
POC	particulate organic carbon	>0.45 μm
SOC	soil organic carbon	...
TDC	total dissolved carbon	DIC plus DOC
TOC	total organic carbon	DOC plus POC
TON	total organic nitrogen	DON plus PN

[a]Here kDa denotes kiloDalton.

enormous potential to mobilize and transport old terrestrial OC [*Guo et al.*, 2004a; *Goni et al.*, 2005]. If projected warming of northern regions by >5°C prove correct [*ACIA–Arctic Climate Impact Assessment*, 2005], OC currently sequestered in peatlands and permafrost will be mobilized and transported to the ocean [*Davidson et al.*, 2000; *Frey and Smith*, 2005]. OC budgets and biogeochemical cycles in the Arctic Ocean will be affected for terrestrial OC and other bioactive elements through increased river runoff, permafrost thawing, and coastal erosion [e.g., *Jorgenson et al.*, 2001; *Peterson et al.*, 2002; *Guo et al.*, 2004b; *Rember and Trefry*, 2004]. However, the quantities, transport mechanisms, and biogeochemical cycles of old terrigenous OC in northern ecosystems under a changing environment remain poorly understood.

[3] Knowledge of OC dynamics in river basins is required to quantify the role of rivers in global biogeochemical cycles and land/ocean interactions [*Hope et al.*, 1994; *McKee*, 2003], and to provide better parameterizations of biogeochemical processes in carbon cycle and climate models. Natural organic matter (NOM) delivered to the ocean by rivers is a significant component of ocean OC globally [*Meybeck*, 1982] and, especially, in the Mediterranean Arctic Ocean [*Stein and Macdonald*, 2004]. Understanding the composition, reactivity, and phase partitioning of OC and transformation processes of different OC species in river systems is therefore essential to predicting the manner in which terrestrial OC cycles within oceans or becomes buried [*Hedges et al.*, 1994; *Benner and Opsahl*, 2001; *Bianchi et al.*, 2004]. Organic carbon in river waters may be partitioned into dissolved (DOC), colloidal (COC), and particulate (POC) components. These size classes of OC species may exhibit different elemental and molecular compositions, and have different reactivity and biogeochemical cycling pathways in aquatic systems [*Guo and Santschi*, 1997; *Mcknight et al.*, 1997; *Mannino and Harvey*, 2000; *Wang et al.*, 2002]. However, measurements on all three OC phases remain scarce.

[4] The Yukon River, which discharges into the Bering Sea, drains an area of over 855,000 km^2 in northwestern Canada and central Alaska in the United States. It is one of the largest drainage basins in North America. Globally, the Yukon River ranks 23rd in water discharge (2×10^{11} m^3 yr^{-1}) and 19th in sediment discharge ($\sim 60 \times 10^6$ tons yr^{-1}) [*Brabets et al.*, 2000; *Milliman and Meade*, 1983]. Distinctive features of the Yukon River basin include its diverse ecosystems [*Brabets et al.*, 2000], large quantity of old SOC stored in permafrost [*Ping et al.*, 1997; *Waelbroeck et al.*, 1997], the influence of seasonal and perennial ice and snow cover, and unique seasonal flow pattern [*Guo et al.*, 2004b]. Containing vast alpine and arctic regions, the Yukon River Basin is especially sensitive to environmental and climate change. However, owing to remoteness and extreme weather conditions (in winter, temperature can fall below −60°C), the Yukon River drainage basin remains pristine and understudied [*Bailey*, 2005]. While there are a few studies on DOC dynamics in the Yukon River basin [*Michaelson et al.*, 1998; *MacLean et al.*, 1999; *Carey*, 2003; *Schuster*, 2003; *Guéguen et al.*, 2006], there are very few studies on the composition, reactivity and fluxes of OC species, including DOC, COC and POC phases. Such studies will provide particularly valuable insights into OC dynamics in arctic river basins, where a warming climate is likely to promote export of old terrestrial OC from peatlands and permafrost [*Freeman et al.*, 2001; *Worrall et al.*, 2003; *Frey and Smith*, 2005], but also alter the production and cycling of young OC through shifts in vegetation [*Freeman et al.*, 2004; *Hinzman et al.*, 2005].

[5] In this paper, we present baseline data on the composition, reactivity and fluxes of OC species from the upper Yukon River using size fractionation techniques and multiple isotope tracers, including stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$) and radiocarbon, for a better understanding of phase speciation, flux, composition, source, and transport of

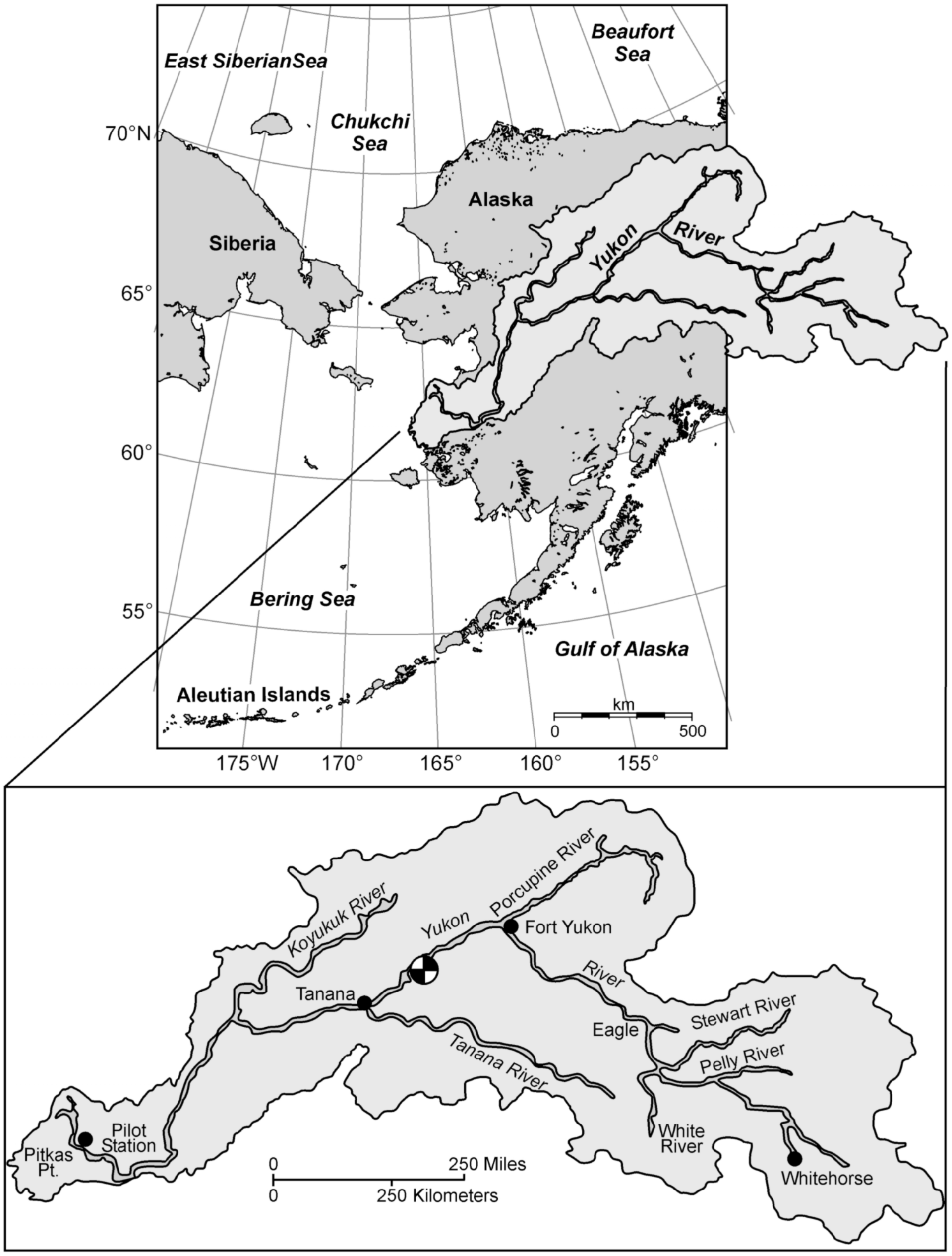

Figure 1. Map of the Yukon River Basin and sampling location.

terrestrial OC under current climate and hydrological conditions and for future trend analysis.

2. Methods

2.1. Sampling

[6] From May to September of 2002, six sample sets were collected from the Yukon River near the U.S. Geological Survey (USGS) hydrological station at Stevens Village, Alaska (Figure 1, Table 2). The first sample set (YR-01; May 15) was taken at the start of snowmelt. The river cleared of ice (ice-open season) in late May at freshet, and the flow rate decreased gradually afterward. Large volumes of river water were pumped from the Yukon River using a peristaltic pump fitted with polyethylene tubing, and filtered through a 0.45-μm polycarbonate filter cartridge (Osmonics) to separate the particulate organic matter (POM, >0.45 μm) from dissolved organic matter (DOM, <0.45 μm) phase. The 0.45-μm filtrate was collected in acid-cleaned 20-L polyethylene carboys. A total of 60–80 L of filtered water was collected for ultrafiltration to size-fractionate the <0.45-μm DOM into low molecular weight DOM (LMW-DOM) and colloidal organic matter (COM) fractions (see next section). Aliquots of filtrate samples were taken for the determinations of DOC, dissolved organic nitrogen (DON), river water stable oxygen isotopes ($\delta^{18}O$), and nutrient (N, P, Si) concentrations.

Table 2. Sampling Date, Stable Oxygen Isotope Composition ($\delta^{18}O$), Concentrations of Inorganic Nutrients (N, P, and Si), and Other Hydrographic Data[a]

Sample ID	Sampling Date (2002)	Discharge, m^3/s	Conductivity, $\mu S/cm$	$\delta^{18}O$, ‰	DIC, μM	NO_3, μM	PO_4, μM	$Si(OH)_4$, μM	Chl-a, $\mu g/L$
YR-01	15-May	991	163	−21.265	1176	2.98	0.127	64	<0.20
YR-02	31-May	10337	174	−21.203	1153	1.37	0.069	53	1.57
YR-03	14-Jun	7080	208	−21.172	1342	2.71	0.039	81	0.97
YR-04	12-Jul	5721	227	−20.374	1550	2.21	0.025	82	5.07
YR-05	9-Aug	4984	224	−20.441	1465	2.26	0.036	105	0.73
YR-06	12-Sept	5098	226	−20.297	1546	3.05	0.021	107	0.56

[a]Nutrient (N, P, and Si) data are from *Guo et al.* [2004b].

[7] Separate river water samples were collected for determinations of total suspended particulate matter (SPM) and POC concentrations. Samples of SPM were filtered on Nuclepore filters, while samples of POC and particulate nitrogen (PN) were filtered on GF/F glass fiber filters. Detailed sampling procedures are described by *Guo et al.* [2003a, 2004b].

2.2. Ultrafiltration

[8] The prefiltered river water (<0.45 μm) was ultrafiltered to isolate COM from the LMW-DOM fraction. Ultrafiltration was carried out using a home-made ultrafiltration system equipped with a S10Y1 Amicon 1 kilo-Dalton (1 kDa) ultrafiltration cartridge [*Guo et al.*, 2000]. Therefore COM here is operationally defined as the fraction with size or molecular weight ranges between 1 kDa and 0.45 μm, while the LMW-DOM is the <1 kDa fraction. The ultrafiltration cartridge was checked for integrity before sampling using standard macromolecules with known MW (such as vitamin B_{12} etc.) and thoroughly cleaned with Micro detergent, NaOH, HCl, and Milli-Q water using procedures described by *Guo et al.* [2000]. Before ultrafiltration, the cartridge was conditioned using 2–5 L of prefiltered water. Mass balance of DOC was checked for recovery for the first 20 L of sample. The final retentate from 60–80 L of prefiltered water was further reduced to $\leq$2 L for lyophilization. The ultrafiltration cartridge was cleaned between samples with NaOH solution and Milli-Q water.

[9] The isolated COM was freeze-dried to yield a powdered COM sample for isotopic ($\delta^{13}C$, $\Delta^{14}C$ and $\delta^{15}N$) and chemical characterization. A fraction of the LMW-DOM was also freeze-dried to result in powdered LMW-DOM samples for characterization along with freeze-dried COM and POM samples.

2.3. Determinations of DOC, DON, POC, PN, and Nutrients

[10] Concentrations of DOC were determined on a TOC analyzer (Shimadzu TOC-V) using the high temperature combustion method [*Guo et al.*, 1994]. DOC samples were acidified to a pH of $\leq$2 and sparged using ultra-pure zero air to remove dissolved inorganic carbon (DIC) before analysis. Concentrations of total dissolved carbon (TDC, including DOC and DIC) were determined on the same TOC analyzer but without acidification and sparging. Concentrations of DIC were calculated as the difference between TDC and DOC. Concentrations of POC and PN were determined by continuous flow isotope ratio mass spectrometry (see next section).

[11] Concentrations of total dissolved nitrogen (TDN) were measured using a high temperature combustion method on the Shimadzu TOC analyzer interfaced with an N detector. Concentrations of DON were then calculated from the difference between TDN and dissolved inorganic nitrogen (DIN) concentrations. Concentrations of DIN (NO_3, NO_2 and NH_4) and other nutrient species (PO_4 and $Si(OH)_4$) were determined colorimetrically [*Grasshoff et al.*, 1999], and have been reported elsewhere [*Guo et al.*, 2004b].

2.4. Measurements of Stable Isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$) and Radiocarbon ($\Delta^{14}C$)

[12] Freeze-dried LMW-DOM, COM, and POM samples were measured for $\delta^{13}C$, $\delta^{15}N$ and $\Delta^{14}C$ [*Guo et al.*, 2003a]. All samples were treated with HCl before OC determination. Stable C and N isotopes along with C and N contents were determined by a continuous flow isotopic ratio mass spectrometer [*Guo et al.*, 2003b]. Stable carbon and nitrogen isotope ratios were calculated in terms of $\delta^{13}C$ and $\delta^{15}N$, $(R_{sample}/R_{standard} - 1) \times 1000$, where R is the ratio of $^{13}C/^{12}C$, or $^{15}N/^{14}N$, in NOM samples or standard (PDB for carbon and atmospheric N_2 for nitrogen). The precision and accuracy of $\delta^{13}C$ and $\delta^{15}N$ analyses were ±0.1‰, and ±0.2‰, respectively, as determined by replicate analysis of standards and samples.

[13] Oxygen isotopic composition of river waters was determined using the Finnegan Mat 252 Mass Spectrometer with the Thermoquest CO_2 gas-water isotopic equilibrium device. The oxygen isotope ratio ($\delta^{18}O$), relative to the VSMOW standard water, was reported with the conventional delta notation (‰) [*Macdonald et al.*, 1999].

[14] Radiocarbon ($\Delta^{14}C$) in LMW-DOM, COM, and POM samples was determined using accelerator mass spectrometry (AMS) at the National Ocean Science AMS Facility at Woods Hole Oceanographic Institution [*Guo et al.*, 2003a, 2004a]. One-sigma errors are given in fraction of modern, $\Delta^{14}C$ and ^{14}C ages.

3. Results and Discussion

3.1. Abundance and Variations of Organic C and N Species

[15] Concentrations of organic C and N species, including dissolved, colloidal, and particulate phases, all showed tendencies to decrease with time during the sampling inter-

Table 3. Concentrations of Organic Carbon (DOC, CON, POC) and Nitrogen (DON, CON, PN) Species in Yukon River Waters

Sample ID	DOC, μM	LMW-DOC, μM	COC,[a] μM	POC, μM	TOC, μM	DON, μM	CON, μM	PN, μM	TON, μM	DOC/DON
YR-01	2825	452	2373	185	3010	64.5	52.0	10.8	75.3	43.8
YR-02	1158	312	846	309	1467	31.6	19.7	22.7	54.3	36.7
YR-03	725	188	537	156	881	20.8	12.7	10.6	31.4	34.9
YR-04	558	184	374	73	631	15.7	8.3	5.5	21.2	35.7
YR-05	508	142	366	112	620	13.2	7.6	7.5	20.7	38.6
YR-06	533	170	363	74	608	15.1	7.6	4.6	19.7	35.3
Average	1051 ± 902	241 ± 119	810 ± 788	152 ± 89	1203 ± 944	26.8 ± 19.6	18.0 ± 17.3	10.3 ± 6.6	37.1 ± 22.9	37.5 ± 3.4

[a]COC (1 kDa to 0.45 μm) is a portion of DOC (<0.45 μm).

val (Table 3). The TOC concentration, calculated as TOC = POC+DOC, decreased monotonically from 3010 μM in mid-May, during snowmelt, to 608 μM in September, with an average of 1023 ± 94 μM (Table 3), which is similar to TOC concentrations reported downstream at Pilot Station [*Leenheer*, 1982; *Brabets et al.*, 2000].

[16] Within the TOC pool, POC concentrations varied from 73 to 309 μM (average of 151 ± 89 μM), with the highest POC concentration observed in late May during the ice opening and the lowest between July and September (Table 3). DOC (<0.45 μm) concentrations varied from 508 to 2825 μM (average of 1051 ± 902 μM; data from *Guéguen et al.* [2006]). The peak POC concentration was observed two weeks after the peak DOC concentration. Concentrations of DON ranged from 13.2 to 64.5 μM (average 26.8 ± 19.6 μM), and concentrations of PN ranged from 4.6 to 22.7 μM, with an average of 10.3 ± 6.6 μM (Table 3). DON and PN showed decreasing trends with time similar to DOC and POC, with the PN peak likewise delayed by 2 weeks.

[17] Temporal trends of the inorganic components (DIC, NO_3, $Si(OH)_4$, and conductivity) differed from the organics

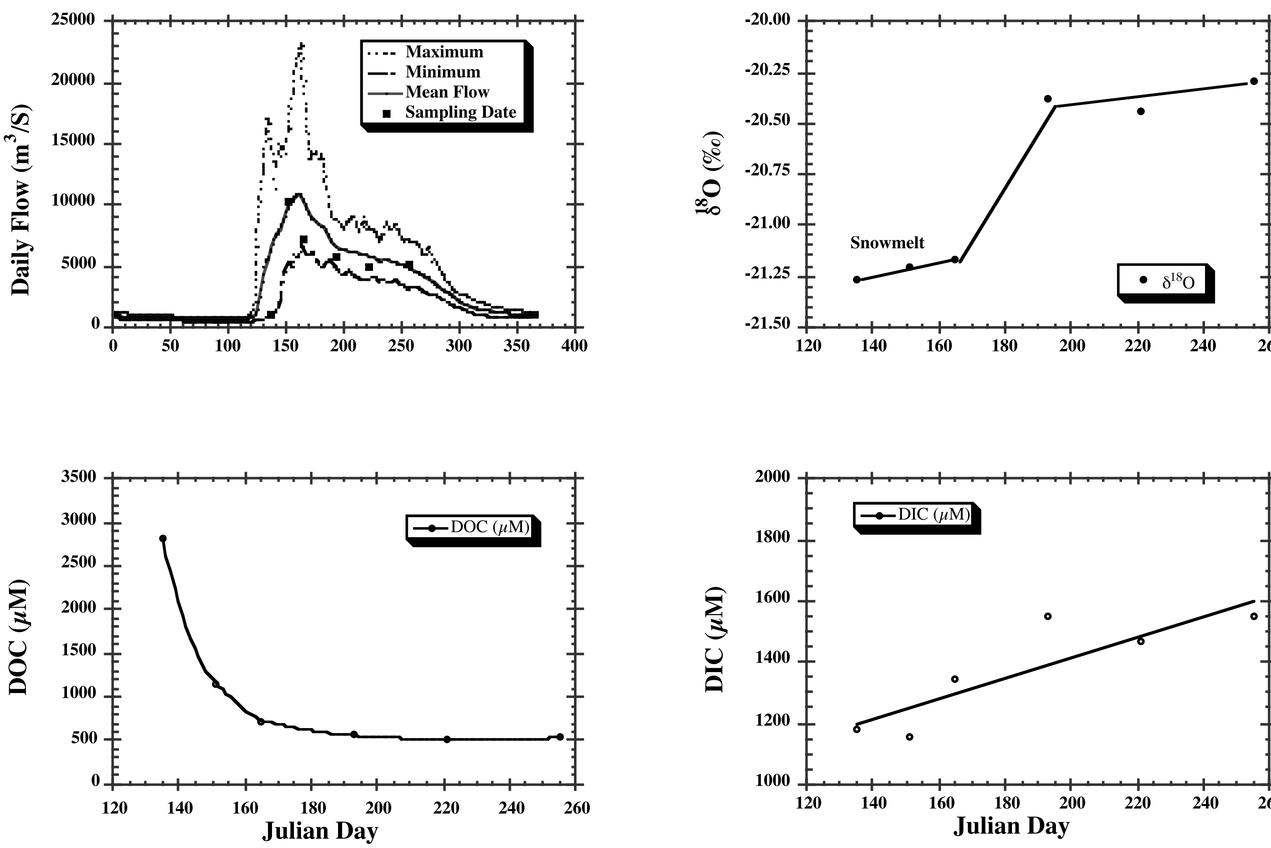

Figure 2. Temporal variations of daily freshwater discharge (m^3/s), dissolved organic carbon (DOC, <0.45 μm) and dissolved inorganic carbon (DIC) concentrations (all in μM), and stable oxygen isotope (δ^{18}O) composition in Yukon River waters. Discharge data are from 1976 to 2000 with maximal, minimal, and mean values (from U.S. Geological Survey at http://www.uags.gov). Also shown on this plot are the sampling dates (solid points) with their corresponding instantaneous freshwater discharge in 2002.

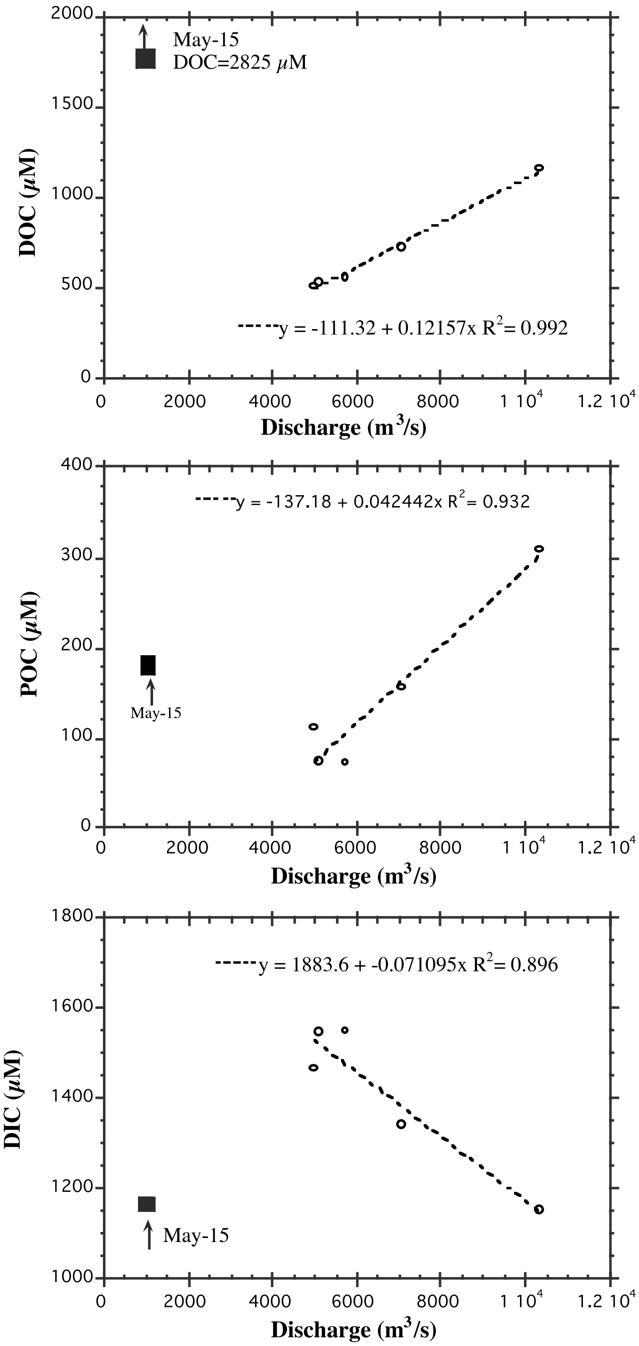

Figure 3. Relationship between river discharge (m^3/s) and dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC) concentrations.

(Figure 2 and Table 2). On average, the concentration of DIC (1372 ± 178 μM) was slightly higher than TOC, but DIC and $Si(OH)_4$ concentrations increased from snowmelt to ice-open season. Accompanying these increases in DIC and $Si(OH)_4$ concentration was an increase in conductivity, although conductivity did not change significantly after July (Table 2). These observations indicate that sources of organic (DOC, POC, and DON) and inorganic (e.g., DIC and $Si(OH)_4$) loadings to the Yukon River differ between snowmelt and ice-open seasons, likely owing to differing responses to hydrological conditions and the permafrost active layer dynamics in the basin. Both DOC and POC concentrations show a significant positive correlation with river discharge (Figure 3), indicating they are controlled by hydrology and that DOC is efficiently leached during snowmelt. Similar correlation has been observed in other river basins [e.g., *Hope et al.*, 1994; *Hornberger et al.*, 1994; *Warnken and Santschi*, 2004]. In contrast to organic species, DIC concentration was negatively correlated with river discharge (Figure 3), suggesting dilution during high flow season and a source of DIC primarily from the leaching of deeper active layer and soils.

[18] Values of $\delta^{18}O$ in river waters showed a slight increase of 0.09‰ during the snowmelt season followed by an abrupt increase of 0.8‰ between June and July (Figure 2). After the abrupt increase, the $\delta^{18}O$ value remained practically constant from July to September, with an average value of −20.37 ± 0.07‰ (Table 2). These $\delta^{18}O$ data clearly show lighter $\delta^{18}O$ values, reflecting the influence of snowmelt during late spring/early summer, and then heavier $\delta^{18}O$ values reflecting the influence of a combination of rainwater and thawed waters from the active layer in late summer/early fall. Higher concentrations of OC species (e.g., TOC and DOC) are accompanied by light $\delta^{18}O$ river waters characteristic of snowmelt, implying intensive leaching of fresh plant litter/upper soil horizons during this period. Later in the sampling season, lower values of DOC in the river coincide with heavier $\delta^{18}O$ values, indicating that deepening of the active layer and leaching of deeper soil horizons were not accompanied by greater concentrations of DOC and POC leaching into the Yukon River even though DIC and $Si(OH)_4$ concentrations increased continuously during this same period. Clearly, the leaching of plant litter/upper soil horizons and the leaching of deeper soil horizons should produce different biogeochemical signals, which can then be sought in the concentration and chemical composition of organic C species in the river, and be used as a proxy for hydrological and permafrost dynamics in the basin.

3.2. Partitioning of Organic Matter Between Dissolved, Colloidal, and Particulate Phases

[19] Within the TOC pool, POC comprised 6–21% (average 14 ± 5%) of the TOC, with the highest POC percentage observed in late May during ice opening (Figure 4). The percentage of COC in the TOC ranged from 58 to 79% (average 63 ± 8%) with the highest COC during snowmelt. LMW-DOC comprised from 15% of the TOC during snowmelt to 29% of TOC after ice opening in July, with an average of 23 ± 5%. Although TOC concentration varied considerably from 608 to 3010 μM, the percentages for POC, COC, and LMW-DOC changed little (Figure 4). Within the traditionally defined "dissolved" organic pool, COC comprised on average 73 ± 6% of the bulk DOC [*Guéguen et al.*, 2006], with the LMW-DOC accounting for the remaining DOC pool (27 ± 6%). These results indicate that DOM transported by the Yukon River is mostly colloidal (1 kDa to 0.45 μm),

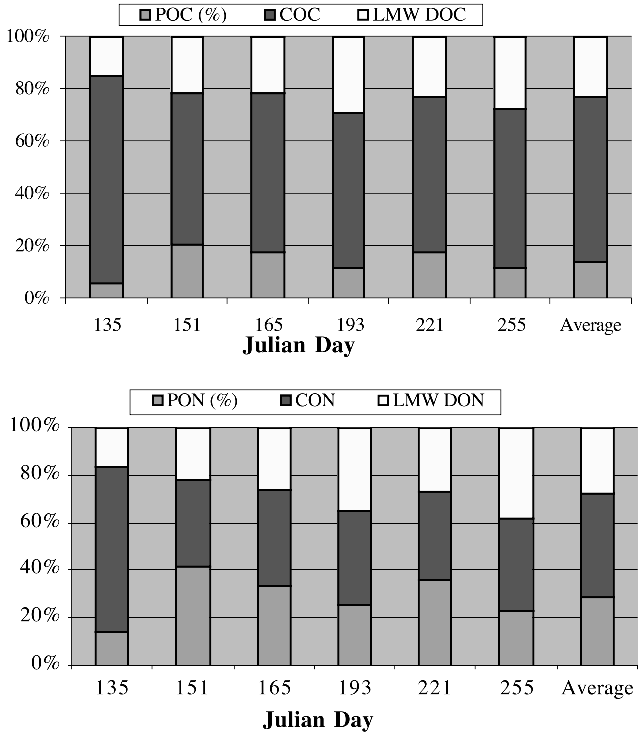

Figure 4. Partitioning of organic C and N among low-molecular-weight dissolved (LMW, <1 kDa), colloidal, and particulate phases in Yukon River waters and its temporal variation from May to September 2002.

which is consistent with what has been reported for other rivers in Alaska and tropical and temperate regions [e.g., *Benner and Hedges*, 1993; *Hedges et al.*, 1994; *Guo and Santschi*, 1997; *Guo et al.*, 2003a].

[20] Concentration of TON decreased from 75 μM in mid-May to ~20 μM in September, with an average concentration of 37 ± 22 μM (Table 3). Within the TON pool, 29 ± 10% was in particulate and 43 ± 13% was in colloidal form, leaving 27 ± 8% in the LMW-DON pool (Figure 4). While TON concentrations differed by threefold from May to September, TON partitioning among dissolved, colloidal and particulate phases is broadly similar except for the first sample taken during snowmelt in mid-May (Figure 4). Within the bulk DON pool, CON comprised 61 ± 11%, ranging from 51% in September to 81% in mid-May during snowmelt, and LMW-DON comprised 19–49% with an average of 39 ± 11% (Table 3). TON was more evenly distributed among dissolved, colloidal and particulate phases compared with the phase partitioning of TOC.

3.3. Fluxes of Carbon and Nitrogen Species

[21] The annual fluxes of OC (POC, COC, LMW-DOC, and TOC) and nitrogen (PN, CON, LMW-DON, and TON) species were calculated from the measured concentrations and the corresponding instantaneous freshwater discharges (Table 4). Since concentrations of OC and N species were not measured during the period of ice cover, these fluxes have been estimated from available freshwater discharge data and the concentrations of OC and N species measured before the river was frozen. This winter estimate therefore should be validated in the future by collecting samples below the ice. The annual TOC flux from the upper Yukon River at Stevens Village Station was 6.05×10^9 moles-OC/yr (7.26×10^4 tons-OC/yr) with 89% contributed during the ice-open season (Table 4), consistent with the long-term streamflow temporal variation shown in Figure 2. The annual TOC flux comprised 16% POC (9.63×10^8 moles-OC), 60% COC (3.64×10^9 moles-OC), and 24% LMW-DOC (1.44×10^9 moles-OC). In comparison, *Leenheer* [1982] reported that POC contributed 11–12% of the TOC flux for the Yukon River at Pilot Station.

[22] Annual DIC flux was about 1.05×10^{10} moles-C/yr (1.26×10^5 tons-C/yr; Table 4), or about 1.7 times higher than the annual TOC flux. This DIC/TOC discharge ratio is close to the world river average ratio, 1.76, estimated by *Garrels and Mackenzie* [1971]. However, the instantaneous TOC fluxes were higher than DIC fluxes during snowmelt and early ice-opening seasons, whereas instantaneous DIC fluxes were higher than TOC fluxes after ice opening, consistent with the contrasting sources between DIC and TOC (Table 3). About 84% of the DIC flux occurred during the ice-open season, comparing to 89% for the TOC flux.

[23] Annual TON flux from the upper Yukon River was 2.07×10^8 moles-N (2900 tons-N/yr), and distributed between PN (~28%), CON (~43%), and LMW-DON (29%). While most of the annual TOC flux (60%) was in the colloidal phase, the contribution by CON (43%) to the annual TON flux was considerably lower, with relatively higher contributions from PN and LMW-DON phases compared to those for OC. Similar to the annual TOC flux, up to 90% of the TON flux occurred during the ice-open season. Among the organic N species, 92% of the PN flux,

Table 4. Fluxes of Organic Carbon (POC, COC, LMW-DOC, TOC), Nitrogen (PN, CON, LMW-DON, TON), and DIC From the Upper Yukon River and Estimated Export Fluxes

Flux or Ratio	POC	COC	LMW-DOC	TOC	DIC	PN	CON	LMW-DON	TON
Moles/yr	9.63×10^8	3.64×10^9	1.44×10^9	6.05×10^9	10.5×10^9	6.68×10^7	8.1×10^7	5.88×10^7	2.07×10^8
Tons/yr	1.16×10^4	4.37×10^4	1.73×10^4	7.26×10^4	1.26×10^5	935	1140	823	2900
Fo/Ft[a]	0.92	0.89	0.87	0.89	0.84	0.92	0.90	0.86	0.90
Export flux, mole/yr	2.30×10^{10}	1.06×10^{11}	3.92×10^{10}	1.69×10^{11}	2.94×10^{11}	1.55×10^9	2.35×10^9	1.57×10^9	5.47×10^9
Export flux (Tons/yr)	2.76×10^5	1.28×10^6	4.7×10^5	2.02×10^6	3.53×10^6	2.17×10^4	3.29×10^4	2.20×10^4	7.66×10^4
Flux reported by *Leenheer* [1982]	2.49×10^6	...	...	2.97×10^6	...	...	...	...	...

[a]Fo/Ft denotes the ratio of ice-open season flux to annual flux. TOC = POC + DOC = POC + COC + LMW DOC; TON = PN + DON = PN + CON + LMW DON.

Table 5. C/N Molar Ratios, Stable Isotopic Composition, and Radiocarbon Signatures in Size Fractionated Organic Matter Fractions From Yukon River Waters[a]

Sample ID	C/N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	F-Modern	^{14}C Age	$\Delta^{14}C$ (‰)
YR-01-D	36.2	−27.73	−1.35	1.0981 ± 0.0038	>Mod.	91
YR-02-D	27.0	−28.09	−1.03	0.8924 ± 0.0029	915 ± 25	−113
YR-03-D	24.2	−27.68	−1.13	0.9102 ± 0.0034	755 ± 30	−96
YR-04-D	24.5	−28.84	−1.26	0.8994 ± 0.0030	850 ± 25	−106
YR-05-D	25.3	−27.72	−0.49	0.8765 ± 0.0054	1060 ± 50	−129
YR-06-D	23.2	−27.48	−1.44	0.8508 ± 0.0037	1300 ± 35	−155
YR-01-C	45.5	−27.43	−0.70	1.1500 ± 0.0043	>Mod	143
YR-02-C	42.9	−27.61	−0.43	1.1077 ± 0.0051	>Mod	101
YR-03-C	42.1	−27.43	−0.92	1.0738 ± 0.0046	>Mod	67
YR-04-C	45.0	−27.66	−0.95	1.0475 ± 0.0053	>Mod	41
YR-05-C	49.3	−27.13	−0.42	1.0551 ± 0.0057	>Mod	48
YR-06-C	49.8	−27.36	−0.53	1.0466 ± 0.0054	>Mod	40
YR-01-P	17.0	−26.65	0.54	0.7518 ± 0.0039	2290 ± 40	−253
YR-02-P	13.1	−26.26	0.59	0.6360 ± 0.0035	3630 ± 45	−368
YR-03-P	14.2	−26.18	0.31	0.6365 ± 0.0037	3630 ± 45	−368
YR-04-P	14.6	−24.87	1.6	0.5362 ± 0.0028	5010 ± 40	−467
YR-05-P	14.9	−26.65	0.75	0.5911 ± 0.0031	4220 ± 40	−413
YR-06-P	16.3	−26.72	0.85	0.6540 ± 0.0023	3410 ± 30	−350
LMW DOM-Avg	26.7 ± 4.8	−27.92 ± 0.49	−1.12 ± 0.34	0.9212 ± 0.0891	976 ± 212	−85 ± 88
COM-Avg	45.8 ± 3.2	−27.44 ± 0.19	−0.66 ± 0.24	1.080 ± 0.041	>Modern	73 ± 41
POM-Avg	15.0 ± 1.4	−26.22 ± 0.70	0.77 ± 0.45	0.6342 ± 0.0717	3698 ± 902	−369 ± 71

[a]D denotes low molecular weight dissolved (LMW-DOM, <1 kDa), C denotes colloidal (COM, 1 kDa to 0.45μm), and P denotes particulate organic matter (POM, > 0.45 μm). Note that DIN was not removed from the freeze-dried LMW-DOM fraction, and values of $\delta^{15}N$ and C/N ratio in the LMW-DOM are a mixture of DON and DIN.

90% of the CON flux, and 86% of the LMW-DON flux occurred during the ice-open season. Thus more organic C and N were contributed during the ice-open season than was the case for their inorganic counterparts (i.e., DIC and DIN). Nevertheless, future sampling during ice cover seasons is needed to confirm these findings.

[24] Our TOC and TON fluxes, which were estimated from measurements in the upper Yukon River near Stevens Village, may not be the same as the export fluxes to the ocean. Very few seasonal riverine DOC and POC data are available in the literature for Yukon River waters. Long-term average TOC concentration from the USGS hydrological station at Pilot Station was 875–916 μM [e.g., *Leenheer*, 1982; *Brabets et al.*, 2000], very close to our average TOC concentration in the ice-open season (Table 3). As a first approximation, we have estimated annual TOC and TON export fluxes from the Yukon River using the available long-term freshwater discharge data from the downstream hydrological station together with our average TOC and TON concentrations in 2002. Annual organic matter export fluxes to the Bering Sea were 1.7×10^{11} moles-C/yr (or 2.02×10^6 tons-C/yr) for TOC and 5.47×10^9 moles-N/yr (or 7.66×10^4 tons-N) for TON, respectively (Table 4). Our estimated TOC export flux is about 30% lower than that estimated (2.97×10^6 tons C/yr) by *Leenheer* [1982] (Table 4), likely owing to the relatively low discharge (Figure 2). However, this riverine export flux of TOC from the Yukon River alone is at least 1 order of magnitude higher than the TOC export to the Arctic Ocean from coastal erosion along the Alaskan and Canadian Beaufort Sea coasts [*Volker et al.*, 2004; *Jorgenson and Brown*, 2005]. The Yukon River annual TOC export flux is similar in size to those of other major arctic rivers [*Rachold et al.*, 2004]. Considering that Yukon River water is entrained into the Alaska Coastal Current, which enters the Chukchi Sea through the Bering Strait to influence surface water properties of the Canada Basin [*Macdonald et al.*, 2002], terrestrial OC inputs from the Yukon River Basin likely provide an important component of the terrigenous carbon budget in the western Arctic Ocean [e.g., *Mathis et al.*, 2005].

[25] The annual riverine DIC flux was 2.94×10^{11} moles-C/yr (3.53×10^6 tons-C/yr), which may be compared to the Mississippi River flux (13.5×10^6 tons-C/yr) [*Cai*, 2003].

3.4. Elemental and Isotope Composition of Size-Fractionated Organic Matter

[26] The percent of OC and TN in the freeze-dried LMW-DOM, COM and POM samples varied widely depending on the matrix in each phase. Therefore only the intensive property (i.e., C/N molar ratio) is listed in Table 5. Elemental composition as expressed by C/N ratio was significantly different between LMW-DOM, COM, and POM, but similar within each organic matter pool (Table 5). The average C/N ratio decreased going from COM (45.8 ± 3.2) to LMW-DOM (26.7 ± 4.8) to POM (15.0 ± 1.4), indicating different phase partitioning between organic C and N (Figure 4). The lower C/N ratio in the LMW-DOM compared to the COM pool likely resulted from the presence of DIN in the former, as indicated from the intercept (0.04%) of correlation line between OC and TN in the LMW-DOM (not shown). In the traditionally defined DOM pool (<0.45 μm), the DOC/DON ratio ranged from 35 to 44, with an average

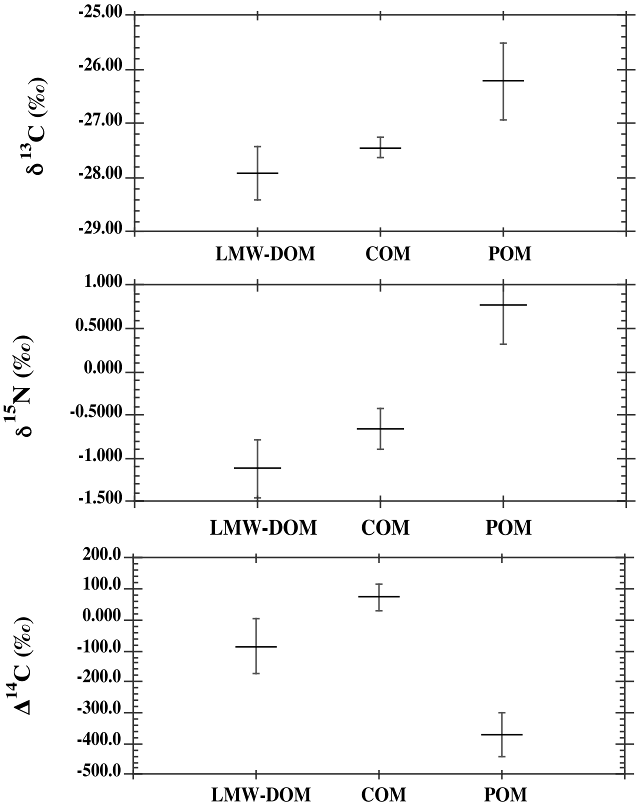

Figure 5. Distributions of stable isotope ($\delta^{13}C$ and $\delta^{15}N$) and $\Delta^{14}C$ values among dissolved, colloidal, and particulate organic matter showing the heterogeneity of riverine organic matter.

of 37.5 ± 3.4 (Table 3), which is significantly lower than those of COM pool (45.8 ± 3.2). These intermediate C/N ratios (DOC/DON), which reflect a combined mixture of LMW-DOM (lower C/N ratio) and COM (higher C/N ratio) components, thus hide the fact that traditionally defined DOM comprises organic material of mixed origin or diagenetic age. Differences in C/N ratios between different size classes could reflect the source or the degree of diagenesis as indicated by ^{14}C age (discussed below). For example, high C/N in the COM samples agrees well with its predominant humic source [*Guéguen et al.*, 2006], and low C/N in the POM could indicate highly degraded (or old) soil organic matter [*Ping et al.*, 1997] and potentially aquatic production.

[27] The $\delta^{13}C$ values increased consistently with size class from LMW-DOM (−27.92 ± 0.49‰) to COM (−27.44 ± 0.19‰) to POM (−26.22 ± 0.70‰) (Table 5 and Figure 5). The POM sample from July had the highest $\delta^{13}C$ value (−24.87‰), coincident with higher $\delta^{15}N$ and maximum Chl-a values (Table 2). However, aquatic plankton production generally results in lighter $\delta^{13}C$ values [*Mook and Tan*, 1991], implying that the heavier $\delta^{13}C$ value of POM in July results from variation in the terrigenous POM source although aquatic production could have a influence. Overall, these $\delta^{13}C$ values of LMW-DOM, COM, and POM from Yukon River waters lie within the range reported for other river basins [e.g., *Hedges et al.*, 1986; *Tan*, 1987; *Goni et al.*, 2005] and terrestrial ecosystems [e.g., *Schiff et al.*, 1997; *Wang et al.*, 2002]. They are also similar to $\delta^{13}C$ values in other rivers where C3 vegetation dominates in the drainage basin. Values of $\delta^{15}N$ also increased from LMW-DOM (−1.12 ± 0.34‰) to COM (−0.66 ± 0.24‰) to POM (+0.77 ± 0.45‰), although residual DIN may influence values of $\delta^{15}N$ in the LMW-DOM pool (Table 5).

[28] These $\delta^{13}C$ and $\delta^{15}N$ values point to a common terrestrial organic source for all size fractions of organic matter from the Yukon River Basin. The small differences in stable C (−27.19 ± 0.88‰) and N (−0.33 ± 0.89) isotope composition between size fractions and the consistent increase in both $\delta^{13}C$ and $\delta^{15}N$ values with increasing size classification (Figure 5) can be explained by fractionations as OC and ON re-partition during transformation or decomposition. Furthermore, the trends in $\delta^{13}C$ for the OC size fractions may also reflect the different ages of these pools (discussed below) because modern OC, formed after the addition of fossil-fuel derived CO_2, would exhibit a $\delta^{13}C$ value ∼1.5‰ lighter than OC formed in the preindustrial era.

[29] In contrast to stable C and N isotope composition, the radiocarbon ($\Delta^{14}C$) values do not show a simple monotonic relationship with size class (Figure 5). Instead, the COM exhibited a contemporary or modern ^{14}C age ($\Delta^{14}C$ values ranging from +40 to +140‰), POM exhibited the oldest ^{14}C ages of 2290−5010 years BP ($\Delta^{14}C$ values: −467 to −253‰), while the LMW-DOM fraction had intermediate ^{14}C ages from >modern to 1300 years BP ($\Delta^{14}C$ values: −155 to +91‰) (Table 5, Figure 6). Significantly different radiocarbon signatures for LMW-DOM, COM, and POM suggests that each of these size classes must have separate turnover pathways, transport mechanisms or sources in the

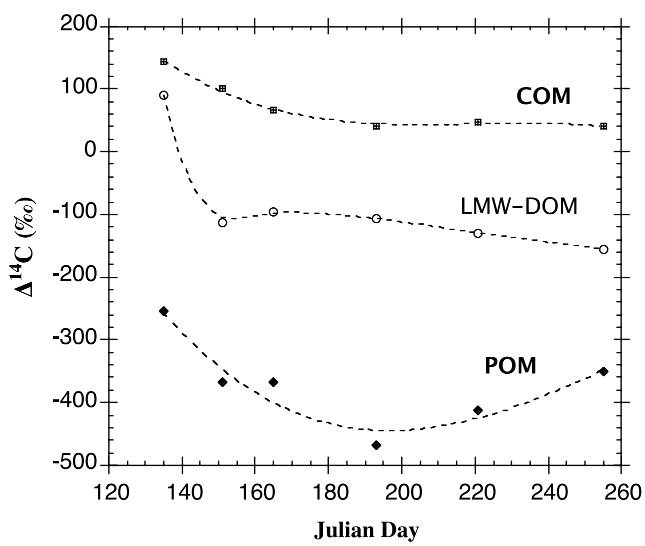

Figure 6. Variations of $\Delta^{14}C$ values (‰) of POM, COM and LMW-DOM with sampling date. Notice the general decrease in $\Delta^{14}C$ values (increase in ^{14}C age) from COM to LMW-DOM to POM, and the decreasing trend from snowmelt to river ice-open season.

Yukon River Basin. The high concentration of COM preceding breakup and its modern ^{14}C age identifies leaching and decomposition of fresh or recent plant litter and surface soil organic matter. The predominately old POM (average 3698 ± 902 years BP), on the other hand, must be derived largely from riverbank erosion, permafrost thawing, and the interaction of soils with aquatic systems. The LMW-DOM with intermediate ^{14}C ages (average 976 ± 212 years BP) may result from a mixture of sources including both COM and POM undergoing degradation, a notion that is supported by the intermediate C/N ratio in the LMW-DOM pool.

[30] These radiocarbon data indicate that riverine export of DOM (LMW-DOM and COM) from the Yukon River Basin to the ocean is mostly contemporary OC, consistent with the findings of *Benner et al.* [2004], whereas riverine export of POM to the ocean is mostly old OC that has been stored in permafrost and soils for several thousand years [*Schell*, 1983; *Ping et al.*, 1997; *Guo et al.*, 2004a; *Goni et al.*, 2005]. The age range observed for Yukon River POC (5010–2290 years BP; Table 5) can easily be supported by SOC inputs which have average ^{14}C ages in northern Alaska of 5440 years BP [*Ping et al.*, 1997] and in upper Yukon River bank of 5350 years BP (L. Guo et al., unpublished results, 2006). Assuming two-component mixing between high Δ^{14}C (modern OC with Δ^{14}C of 71 ± 0.5‰) and low Δ^{14}C (SOC with a Δ^{14}C of −489.8 ± 30‰) in the Yukon River, about 28% of the LMW-DOM was from low Δ^{14}C component with the rest (72%) coming from high Δ^{14}C component (or modern primary production on land), while 78% of the POM is derived from old soils with the remaining ~22% from modern sources.

[31] We infer from these results that young organic matter such as COM with high C/N ratio, is preferentially leached out, especially during snowmelt, whereas old POM with low C/N ratio is mostly from highly degraded soil organic matter mobilized under current climate and hydrological conditions. Contribution of old POM with low C/N ratio from aquatic production is also possible since DIC in Yukon river waters could be up to 3000 years BP (L. Guo et al., unpublished results).

[32] Similar to our findings, *Palmer et al.* [2001] observed a modern ^{14}C age for DOC in a stream draining a non-forested temperate watershed containing 2700 years BP SOC [*Palmer et al.*, 2001]. In contrast, *Wang et al.* [2002] found that both COM and LMW-DOM exhibited old ^{14}C ages in the Florida Everglades, with COM generally older than LMW-DOM.

[33] Our Δ^{14}C values showed not only a significant difference between LMW-DOM, COM and POM (Figure 5), but also a decreasing trend (i.e., increasing age) from snowmelt in May to ice-open season for all three size fractions of organic matter (Figure 6). While both LMW-DOM and COM exhibited a similar decrease in Δ^{14}C values from July to September, POM exhibited a slight increase from August to September (Figure 6), coinciding with the highest monthly precipitation in August (5.4 cm in August 2002; data from www.ncdc.noaa.gov). The seasonal trend in LMW-DOM and COM ^{14}C age can be explained by an increased proportion of older OC as the flushing within the active layer deepens and the rainy season commences in late summer/early fall. Overall, the composition and quantity of OC in the river basin are related to permafrost active layer dynamics and hydrological conditions as deduced from radiocarbon signatures, stable oxygen isotope composition, and variations of nutrient (N, P, Si) concentrations.

3.5. Permafrost Active Layer Dynamics and Organic Carbon Transport

[34] The Yukon River watershed contains extensive continuous and discontinuous permafrost deposits [*Brabets et al.*, 2000]. Recently, it has been strongly argued that permafrost in many arctic regions is showing signs of deterioration due to rising temperature [e.g., *Romanovsky and Osterkamp*, 1997; *Jorgenson et al.*, 2001; *ACIA–Arctic Climate Impact Assessment*, 2005]. While alteration of permafrost and northern hydrological cycles have clear implications for infrastructure such as buildings and roads, it is not nearly so clear what the impact might be on OC cycling. Clearly, the release of old terrestrial OC stored in peatlands and permafrost zones has potentially wide-ranging consequences for biogeochemical cycles in the Arctic's aquatic systems.

[35] During the initial spring snowmelt and subsequent runoff, northern rivers experience peak flow, which is accompanied by the highest DOC concentrations (Figure 2) mostly from the leaching of young/fresh plant litter (Table 5). After snowmelt the ground and the topsoil horizons begin to thaw, but the leaching of the upper soil horizon and DOM transport decreases as spring gives way to summer (Figure 2). On the basis of the radiocarbon data and variations of DOC concentrations, DOC release from plant litter and the topsoils and the flushing of DOM into the Yukon River occur mostly during the snowmelt, as indicated by low δ^{18}O values in river water (Figure 2). It seems that young plant litter and SOC contain readily leachable organic components mostly in dissolved and colloidal phases, resulting in contemporary COM and DOM in river waters, whereas old SOC is less leachable and mostly transported in the particulate (POM) phase (Figure 6).

[36] The flushing of DIC and $Si(OH)_4$ to the Yukon River increases gradually as the active layer extends downward and the frozen horizon deepens (Table 2 and Figure 2). With the active layer expanded downward from summer to fall, concentrations of DOC decrease with time, while the concentrations of DIC and $Si(OH)_4$ increase from May to September (Tables 2 and 3, Figure 2). It is evident that flushing of the active layer and deep soil horizons results in high concentrations of DIC and $Si(OH)_4$ but a low concentration of DOC.

[37] The transport of terrestrial OC is controlled by the seasonal cycle of the active layer over permafrost as shown by the δ^{18}O values of Yukon River waters, and the stable C and N isotopic composition and radiocarbon signatures of dissolved, colloidal and particulate organic samples. Given these findings, it seems clear that biogeochemical tracers in northern rivers provide excellent proxies to monitor change in permafrost active layer dynamics. For example, as

climate warms, permafrost deposits are degraded and the active layer deepens. The flushing of weathered products, such as DIC and $Si(OH)_4$, will increase [e.g., *Guo et al.*, 2004b], but the fluxes of old DOC from peat and soils might not necessarily increase depending on the composition of soil organic matter. By monitoring the age and isotopic structure of organic matter species in rivers, along with the seasonal cycle, the effects of warming in the Arctic drainage basins can be inferred directly.

4. Summary and Conclusions

[38] Concentrations of TOC decreased from 3010 μM in mid-May to 608 μM in September, with high TOC concentration and low river water $\delta^{18}O$ observed during the snowmelt, followed by low TOC concentration and high $\delta^{18}O$. Within the TOC pool, COC was the predominant OC species contributing 63 ± 8% followed by LMW-DOC (23 ± 5%) and POC (14 ± 5%).

[39] The C and N contents of dissolved, colloidal and particulate phases differed with low C/N ratio (15 ± 1.4) in POM and high C/N ratio (46 ± 3) in COM. Stable C and N isotopic composition was similar among three size fractions of organic matter, although there was an increasing trend in both $\delta^{13}C$ and $\delta^{15}N$ values from dissolved to colloidal to particulate phases. The similarity in stable isotope compositions suggests a common terrigenous source, with the small and consistent difference likely due to age (source) differences and fractionation during transformation/decomposition and re-partitioning between OC species. Higher $\delta^{13}C$ in the old POC phase could also be due to the higher $\delta^{13}C$ in the atmosphere prior to the addition of fossil fuel derived CO_2.

[40] Radiocarbon composition varied among the three size fractions, suggesting different turnover pathways and transport mechanisms. The COM contained modern OC, whereas POM contained predominantly old OC (average 3698 ± 902 years BP). The LMW-DOM fraction had intermediate $\Delta^{14}C$ values and ages. The ^{14}C age for all three size fractions increased generally from snowmelt to ice-open period. The high concentration of COC and its contemporary ^{14}C age implies a modern source such as leaching/decomposition of fresh plant litter and upper soil organic matter. The predominately old POM, on the other hand, implies an older source derived from riverbank erosion and permafrost thawing.

[41] DOM (LMW-DOM and COM) export to the ocean from the Yukon River Basin is mostly contemporary, whereas POM export is mostly old OC that has been stored in the arctic/subarctic terrestrial system for several thousand years. On the basis of the assumption that old OC is mostly from river bank soils ($\Delta^{14}C$ of −489.8 ± 30‰), 72% of the LMW-DOM was from modern OC with the other 28% from old SOC, whereas 22% of POM came from modern OC with the other 78% from old SOC.

[42] The mobilization of OC into the Yukon River follows the hydrological cycle and development of the active layer in permafrost. Our results support a model in which early summer Yukon River flows are dominated by snowmelt runoff with higher DOC but low DIC and $Si(OH)_4$ concentrations, and late summer flows contain more rains and thawed waters, with a lower DOC but higher DIC and $Si(OH)_4$ concentrations.

[43] Warming in the Yukon River and other arctic river basins would alter the mobilization and therefore the export flux of terrestrial OC into the ocean. Nevertheless, old OC stored in arctic peatlands and permafrost will mostly be transported through rivers in particulate phase under a warming scenario. The composition of the OC species would provide an interpretable record of the source of change in the OC flux.

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