

Temporal variations of organic carbon inputs into the upper Yukon River: Evidence from fatty acids and their stable carbon isotopic compositions in dissolved, colloidal and particulate phases

Li Zou ^{a,b}, Ming-Yi Sun ^{a,*}, Laodong Guo ^c

^a Department of Marine Sciences, University of Georgia, Athens, GA 30602-3636, USA

^b College of Environmental Science and Engineering, Ocean University of China, Qingdao 266003, China

^c Department of Marine Science, University of Southern Mississippi, Stennis Space Center, MS 39529, USA

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Abstract

To understand the variations of organic carbon inputs in high latitude rivers, we tracked the changes in fatty acid concentrations and their stable carbon isotopic compositions in dissolved (DOM, <1 kDa), colloidal (COM, 1 kDa to 0.45 μm) and particulate (POM, >0.45 μm) organic matter collected from the upper Yukon River (Alaska, USA) during ice-open season from May to September 2002. In spite of the high variability in discharge, total organic carbon in the river continuously declined from the beginning of snowmelt, while fatty acid contents (normalized to organic carbon in each pool) varied independently in the three organic pools with the largest fraction of total fatty acids in the POM. Fatty acid compositions in each pool were similarly dominated by short-chain saturated (14:0, 16:0, and 18:0) and monounsaturated [16:1 and 18:1($n-9$)] fatty acids (70–80%), while bacterial fatty acids [normal and branched 15:0 and 17:0 plus 18:1($n-7$)] comprised an important fraction (16–30% of the total) in all samples. The concentrations of individual fatty acids in the three pools varied greatly during the ice-open season, but the compound-specific stable carbon isotopic ratios of fatty acids in POM were less variable compared to those in DOM and COM. Mass balance calculation showed that land-derived fatty acids dominated in May (snowmelt) while aquatic produced fatty acids peaked in July, consistent with the maximum Chl-*a* concentration. In addition, bacteria-specific fatty acids (e.g., iso-15:0) had similar $\delta^{13}\text{C}$ ratios in all three pools, with little difference from those of bulk carbon. Our results suggest that relative inputs of organic matter from various sources into the upper Yukon River are significantly affected by snowmelt, rainfall, soil erosion, discharge, aquatic production, and biochemical degradation.

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1. Introduction

Terrigenous organic matter is one of the largest organic carbon pools on the earth. World rivers deliver approximately 0.25 Gt ($1 \text{ Gt} = 1 \times 10^{15} \text{ g}$)

* Corresponding author. Tel.: +1 706 542 5709; fax: +1 706 542 5888.

E-mail address: mysun@uga.edu (M.-Y. Sun).

of dissolved organic carbon (DOC) and 0.15 Gt particulate organic carbon (POC) to the ocean each year (Meybeck, 1982). Export of terrigenous organic matter through rivers plays an important role in the global carbon cycle, which has a great influence on climate changes (Hedges et al., 1997; Findlay and Sinsabaugh, 2003; Stein and MacDonal, 2003). Knowledge of the origin of organic matter and the transport mechanisms in river systems is urgently needed for understanding and modeling carbon cycling and climate changes. Of particular importance are the Arctic river basins where ongoing climate and environmental changes may significantly increase river runoff and export fluxes of organic carbon and other chemical species (Peterson et al., 2002; Guo et al., 2004a; Frey and Smith, 2005). However, source and composition, partition and transformation, and transport mechanisms of organic matter in Arctic rivers remain poorly understood.

The Yukon River drains an area over 855,000 km² in Canada and Alaska, USA, and annually delivers more than 2×10^{11} m³ of freshwater and about 60×10^6 tonnes of suspended sediment to the Bering Sea/Arctic Ocean (Brabets et al., 2000; Holmes et al., 2002). The discharge from the Yukon River contributes ~8% of the total freshwater which enters the Arctic Ocean (Aagaard and Carmack, 1989) and a large fraction (~50%) of sediment deposition in the Norton Sound is derived from the particle load of the Yukon River (Atlas et al., 1983). The annual export flux of TOC from the Yukon River to the ocean was estimated to be $\sim 2 \times 10^{12}$ g (Guo and Macdonald, 2006). The Yukon River is ice-covered for half the year and many of its tributaries are located in permafrost and glacier regions (Brabets et al., 2000). Being heavily influenced by snow, ice and permafrost, the Yukon River Basin is especially sensitive to environmental and climate changes (Jorgenson et al., 2001). Therefore, the input, transport and fate of organic matter in the Yukon River may be distinctly different from organic matter cycles in low and middle latitude river basins. However, due to its remoteness and extreme weather conditions, the Yukon River Basin has remained pristine and under-studied (Brabets et al., 2000).

In recent years, interest in biogeochemical cycles of organic matter in Arctic rivers and coastal environments has greatly increased (e.g., Benner et al., 2004; Guo et al., 2004a; Rember and Trefry, 2004; Goñi et al., 2005). Several studies of the Yukon

River have been conducted to determine the export fluxes of organic carbon and nutrients and to characterize carbon partitioning between DOM, colloidal organic matter (COM), and POM pools (Guo et al., 2004b; Guéguen et al., 2006; Guo and Macdonald, 2006). For example, Guo and Macdonald (2006) measured elemental (C and N) and isotope ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$) compositions to examine the age, source, and transport of bulk organic matter in the Yukon River. In the present study, we measured the fatty acid compositions and their molecular $\delta^{13}\text{C}$ ratios in DOM, COM, and POM samples collected from the upper Yukon River during an ice-open season and also examined the temporal variations of organic carbon inputs from various sources into the Yukon River.

2. Experimental

2.1. Study site and sampling

Samples were collected from the Yukon River at an upper stream station (65°52'N, 149°43'W) near the Dalton Highway Bridge and the USGS Stevens Village hydrological station (Fig. 1). From May to September 2002, we carried out six samplings at this site at 2-week or 1-month intervals. Average river discharge from 1977 to 2000 at the USGS Stevens Village station shows a general variation pattern characterized by very low flow rates during the frozen season and large, but variable, flow rates during the ice-open season. The maximum discharge in 2002 occurred in May due to a rapid snowmelt and the discharge gradually declined as ice cover increased (Fig. 2a). During July/August, large rainfall events (Fig. 2a, data from <http://www.noaa>.

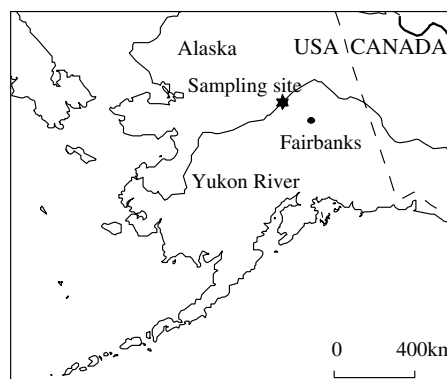


Fig. 1. Map of the Yukon River and the sampling location.

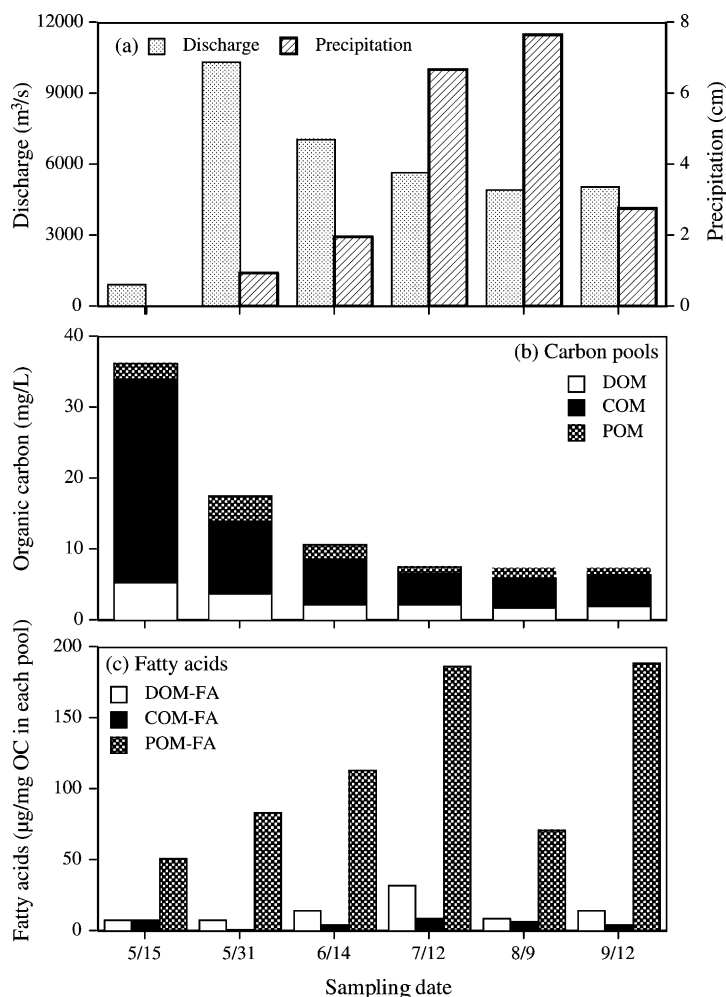


Fig. 2. Temporal variations of (a) discharge and precipitation; (b) organic carbon concentrations; and (c) fatty acid contents in DOM, COM, and POM pools.

gov) influenced the discharge, resulting in several small flow peaks.

Throughout the season, variations in water temperature, suspended particulate matter (SPM), Chlorophyll-*a* (Chl-*a*) concentration, bulk carbon content, and C/N ratio showed different patterns (Table 1, data from Guo and Macdonald, 2006). The SPM concentration seemed to follow the discharge variations while the highest temperature and Chl-*a* concentration occurred in July. Carbon contents in COM samples were the highest (from 17% to 32%) while carbon contents in low molecular weight DOM and POM samples were similar (1–4%). Total organic carbon concentrations in river waters were the highest in mid-May (the beginning of snowmelt) and gradually decreased to a relatively stable level (Fig. 2b). The proportion of colloidal

organic carbon (COC) to total OC ranged from 57% to 79% while DOC and POC proportions to total OC varied between 10% and 30% (Table 2). The C/N ratios of the three organic matter pools were distinctly different: 45.8 ± 3.2 for COM, 26.7 ± 4.8 for DOM, and 15 ± 1.4 for POM. However, the C/N ratios in each pool varied much less than the carbon contents from May to September.

Water sampling and organic matter size fractionation were reported elsewhere (Guo and Macdonald, 2006). Briefly, large volumes of surface water at ~1 m were pumped directly through a 0.45 µm polycarbonate filter cartridge (Osmonics) to separate the particulate organic matter (POM, >0.45 µm) from dissolved organic pools (<0.45 µm). The filtrate was collected in acid-cleaned 20 l polyethylene containers for later ultrafiltration. After transport

Table 1

Hydrological data, Chl-*a* concentrations, organic carbon contents and C/N ratios in three pools (DOM, COM, and POM) in the Yukon River

Sampling date (mm/dd/yy)	Discharge (m ³ s ⁻¹)	T (°C)	SPM (mg l ⁻¹)	Chl- <i>a</i> (μg l ⁻¹)	DOM-pool		COM-pool		POM-pool	
					C(%)	C/N	C(%)	C/N	C(%)	C/N
05/15/02	991	2	92	<0.20	4.18	36.2	32.4	45.5	2.41	17.0
05/31/02	10,337	6	331	1.57	2.08	27.0	3.0	42.9	1.12	13.1
06/14/02	7080	14	153	0.97	1.34	24.2	17.9	42.1	1.22	14.2
07/12/02	5721	15.5	175	5.07	1.26	24.5	18.3	45.0	0.5	14.6
08/09/02	4984	14	130	0.73	1.52	25.3	17.5	49.3	1.03	14.9
09/12/02	5098	8	53	0.56	1.48	23.2	17.7	49.8	1.67	16.3

Table 2

Concentrations and proportions (relative to TOC and total fatty acids) of DOC, COC, POC, DOC-FA, COC-FA, and POC-FA in the Yukon River

Sampling date (mm/dd/yy)	OC concentration (mg l ⁻¹)			OC proportion to TOC (%)		
	DOM	COM	POM	DOM	COM	POM
05/15/02	5.4	28.5	2.2	15.0	78.8	6.2
05/31/02	3.7	10.2	3.7	21.2	57.7	21.1
06/14/02	2.3	6.4	1.9	21.3	61.0	17.7
07/12/02	2.2	4.5	0.9	29.2	59.3	11.5
08/09/02	1.7	4.4	1.3	22.9	59.0	18.1
09/12/02	2.0	4.4	0.9	28.0	59.8	12.2
Mean	2.9	9.7	1.8	23.0	62.6	14.5
Range	±1.3	±8.6	±1.0	±4.7	±7.3	±5.0
Relative variation (%)	±44.8	±88.7	±53.9	±20.4	±11.7	±34.5

	FA concentration (μg l ⁻¹)			FA proportion to T-FA (%)			Normalized FA (μg/mg OC)		
	DOM	COM	POM	DOM	COM	POM	DOM	COM	POM
05/15/02	45.3	219.6	114.9	11.9	57.8	30.3	8.4	7.7	51.7
05/31/02	26.0	5.6	313.4	7.5	1.6	90.9	8.0	0.6	84.5
06/14/02	33.2	30.9	214.2	11.9	11.1	77.0	14.7	4.8	114.4
07/12/02	72.0	39.8	165.5	26.0	14.3	59.7	32.6	8.9	189.0
08/09/02	15.0	29.5	97.1	10.6	20.8	68.6	8.8	6.7	72.2
09/12/02	30.2	18.0	169.8	13.8	8.3	77.9	14.8	4.1	191.2
Mean	36.9	57.2	179.2	13.6	19.0	67.4	14.6	5.5	117.2
Range	±18.1	±73.4	±71.2	±5.8	±18.3	±19.1	±8.6	±2.7	±54.8
Relative variation (%)	±49.1	±128.3	±39.7	±42.6	±96.3	±28.3	±58.9	±49.1	±46.8

Fatty acids in each pool are normalized based on DOC, COC, and POC concentrations. Mean concentrations variation ranges, and relative variations (%) are listed.

to the laboratory in Fairbanks, about 60–80 l of filtered water was further fractionated into low molecular weight DOM (<1 kDa) and COM (1 kDa to 0.45 μm) using a home-made ultrafiltration system equipped with an 1 kDa regenerated cellulose cartridge (Amicon, S10Y1). POM samples were separately collected by filtering the river water through pre-combusted glass fiber filters (GF/F, Whatman 47 mm). All separated POM, DOM, and COM samples were freeze-dried for chemical and isotopic analyses.

2.2. Extraction and analysis of fatty acids

Aliquots of freeze-dried DOM, COM, and POM samples (~10–90 mg) were first extracted with 10 ml of methanol, followed by 3 × 10 ml of methylene chloride–methanol (2:1 v/v). The extracted lipids were further saponified at 100 °C with 0.5 M KOH in methanol/H₂O (95:5 v/v) for 2 h. Neutral lipids were first extracted from the solution at pH ~ 13 while fatty acids were extracted at pH < 2 after addition of HCl to the solution. Fatty acids were

methylated with BF_3 -methanol at 100 °C for 2 h to form fatty acid methyl esters (FAMES). The FAMES were quantified by capillary gas chromatography using a Hewlett-Packard 6890 GC with an on-column injector and a flame ionization detector. Prior to GC analysis, a known amount of internal standard (nonadecanoic acid methyl ester) was added to each extract to aid quantification. FAMES were analyzed on a 30 m × 0.25 mm i.d. HP-5 column coated with 5%-diphenyl-95%-dimethylsiloxane copolymer (0.25 μm film thickness). The following GC temperature program was implemented: 60–150 °C at 10 °C min⁻¹, then 150–310 °C at 4 °C/min and isothermally at 310 °C for 5 min. FAMES were identified from mass spectra obtained from a Shimadzu QP-5000 gas chromatograph-mass spectrometry system using a split injector and a 30 m × 0.25 mm i.d. XTI-5 column coated with 5% phenyl methyl silicone (0.25 μm film thickness). The operating conditions were: helium as carrier gas; mass range 50–610 kDa with a 0.4 s scan interval; 70 eV ionizing energy; GC temperature program 50–150 °C at 20 °C min⁻¹ followed by 150–310 °C at 4 °C min⁻¹ and a 5 min hold at 310 °C.

2.3. Compound-specific isotope analysis

Fatty acid molecular-carbon isotopic-ratios were measured using a Varian 3400 GC-combustion system interfaced with an isotope ratio mass spectrometer (IRMS, Finnigan MAT 252). Compounds were separated with a 30 m × 0.25 mm i.d. column (DB-1, J&W Scientific) and the GC temperature was programmed for 50–170 °C at 20 °C min⁻¹ followed by 170–300 °C at 4 °C min⁻¹ and a 15 min hold at 300 °C. Peaks eluting from the GC column (DB-1, J&W Scientific) were combusted to CO_2 over CuO/Pt wires at 850 °C and on-line transported to the IRMS. The isotopic composition of CO_2 peaks was measured by the IRMS operated at 10 kV acceleration potential and by magnetic sector mass separation. The $\delta^{13}\text{C}$ ratios were calibrated with a reference CO_2 gas and reported in parts per mil (‰) relative to the PDB standard. The standard deviation of IRMS analyses was about ±0.4‰ based on internal standard measurements ($n = 18$) over a few days operation. To obtain actual fatty acid isotope ratios, the $\delta^{13}\text{C}$ of FAMES was corrected for the carbon added during methylation.

3. Results and discussion

3.1. Variations of total organic carbon and total fatty acids

Total organic carbon and total fatty acids varied differently in the Yukon River during the ice-open season (Figs. 2b and c). Although total organic carbon concentration in the river water continuously decreased to a relatively constant level (~7.5 mg l⁻¹) from May to September, fatty acid contents (normalized to organic carbon) in the three pools increased from May to September (Fig. 2c). One exception occurred in August, coincident with the seasonal rainstorms. Moreover, most fatty acids were present in POM (with a mean fraction of 67% relative to the total fatty acids), while fatty acids in COM accounted for ~19% of total fatty acids (Table 2). The fatty acids in DOM represented ~14% of total fatty acids (Table 2). Temporal variations of fatty acid concentrations in the three pools differed in a large range (with 40–128% of relative variations). However, temporal variations of normalized fatty acid contents in the three pools were similar (with 47–59% of relative variations; Table 2).

During the ice-open season, the chemical compositions and inputs from potential sources varied considerably. The organic carbon sources in river waters include local aquatic production and allochthonous inputs from surrounding lands. A rapid snowmelt in May brought a large amount of land-derived organic carbon into the river (Guo and Macdonald, 2006), while aquatic production was limited at this time due to low water temperature and high turbidity. Therefore, allochthonous organic matter with a low fatty acid content from the land dominated in the river during May/June. In July, aquatic production reached its maximum level, as indicated by the Chl-*a* peak (Table 1) when environmental conditions were all favorable. Coincident with the maximum Chl-*a* concentration in the river, the maximum peak of total fatty acids also occurred in July. It is known that lipids can comprise a significant fraction (5–23%) of total organic carbon in fresh phytoplankton biomass (Parsons et al., 1961) and that fatty acids, which exist primarily as phospholipids, triacylglycerols, and wax esters in aquatic systems, are the dominant components in the lipid pool (Lee et al., 1971). An increase in total fatty acids under the stable hydrological conditions during this period indicates an elevated autotrophic

productivity and an increase in their relative contributions to particulate organic matter.

The different changes in fatty acid amounts in the three pools (DOM, COM, and POM) may be related to the original sources and delivery mechanisms of these different forms of organic materials. Recent studies (Benner et al., 2004; Guo and Macdonald, 2006) found that the terrigenous dissolved organic carbon from Arctic rivers, including DOC and COC, is predominately young and largely derived from newly fixed C in land plant litter and upper soil horizons. At the beginning of snowmelt, a vast amount of organic carbon exists as DOM and COM, likely being leached from plant litter and surface soils and delivered to the river (Guo and Macdonald, 2006). Due to the hydrophobic nature of lipid compounds, most esterified fatty acids do not enter the DOM and COM pools during this period. Instead, most lipids remain in the particulate phase and were delivered to the river as POM. On the other hand, organic carbon associated with POM in the Yukon River was found to be highly depleted in $\Delta^{14}\text{C}$, which suggests that the organic carbon is much older (Guo and Macdonald, 2006). The sources of old POM to Arctic rivers may be from sedimentary rocks in the drainage basin and from permafrost and peatlands (Guo et al., 2004a; Goñi et al., 2005; Guo and Macdonald, 2006). Although the highest SPM and POM concentrations occurred in late May, the total amount of fatty acids bound to POM was at a lower level in May relative to levels found in later months. This fact implies that the POM derived from terrestrial origins during the snowmelt carried relatively lower fatty acid content than the POM produced in the water during summer. With increases in aquatic production (as indicated by an increased Chl-*a* concentration), total fatty acids in POM and DOM increased by 2–3 times from May to July while the fatty acids in the COM pool showed small variations. In August, fatty acid contents in the POM and DOM pools suddenly decreased, possibly due to the increase of land-derived POM caused by high rainfall during this period (Fig. 2a).

3.2. Variations of fatty acid compositions in different organic pools

Like the variations of total fatty acids, their compositions also varied differently in the three pools from May to September (Fig. 3). Total fatty acid yields were approximately 6–12-fold greater in POM

than in DOM and 2–14-fold greater in DOM than in COM. A common feature of fatty acid composition in the three pools was the dominance by short-chain saturated (14:0, 16:0, and 18:0) and monounsaturated [16:1 and 18:1(*n*–9)] fatty acids, which accounted for ~70–80% of the total fatty acids, regardless of organic pools and sampling times. Bacterial fatty acids [all normal and branched 15:0 and 17:0 plus 18:1(*n*–7)] were an important fraction, ranging from 16% to 30% of the total fatty acids, in all samples. Only one polyunsaturated fatty acid (16:2) was found in these samples, but it was less than 2% of the total fatty acids in most samples. Long-chain saturated (20:0, 22:0, and 24:0) fatty acids mostly occurred in COM and POM pools after the discharge peak (late May). These fatty acids comprised 2–6% of the total fatty acids.

The concentrations of polyunsaturated and long-chain saturated fatty acids were very low in the three pools in May. Subsequently, total fatty acid contents in the three pools steadily increased to their highest levels in July at which time the long-chain saturated fatty acids occurred as a significant component (2–6% of the total) in POM and COM pools. In August, the fatty acids in POM and DOM pools dropped by 60–70% from levels measured in July, while in the COM pool the decrease was only 25%. At the end of ice-open season (September), fatty acids in POM returned to the highest level that was seen in July. Fatty acids in DOM increased significantly after August, but those in COM continued to decrease. Long-chain fatty acids were also significant fractions in POM and COM during these summer months and even occurred in the DOM pool in September. Throughout the season, bacterial fatty acids seemed to vary with the changes in total fatty acids while the amount of the polyunsaturated (16:2) fatty acid was little changed in the three pools. In addition, the ratio of monounsaturated to saturated fatty acids was usually less than 1 but that ratio exceeded 1 in DOM in July.

In general, the variations of fatty acid amount and composition during the ice-open season reflect the relative inputs of organic matter from various sources. Potential organic matter sources in the Yukon River include land vegetation, aquatic production, and soils (Guo and Macdonald, 2006). It appears that climatic, hydrological, and biogeochemical processes significantly affect the organic matter inputs into the river. In May, for example, gradual rising temperature resulted in a rapid snowmelt and the river discharge increased to a maximal

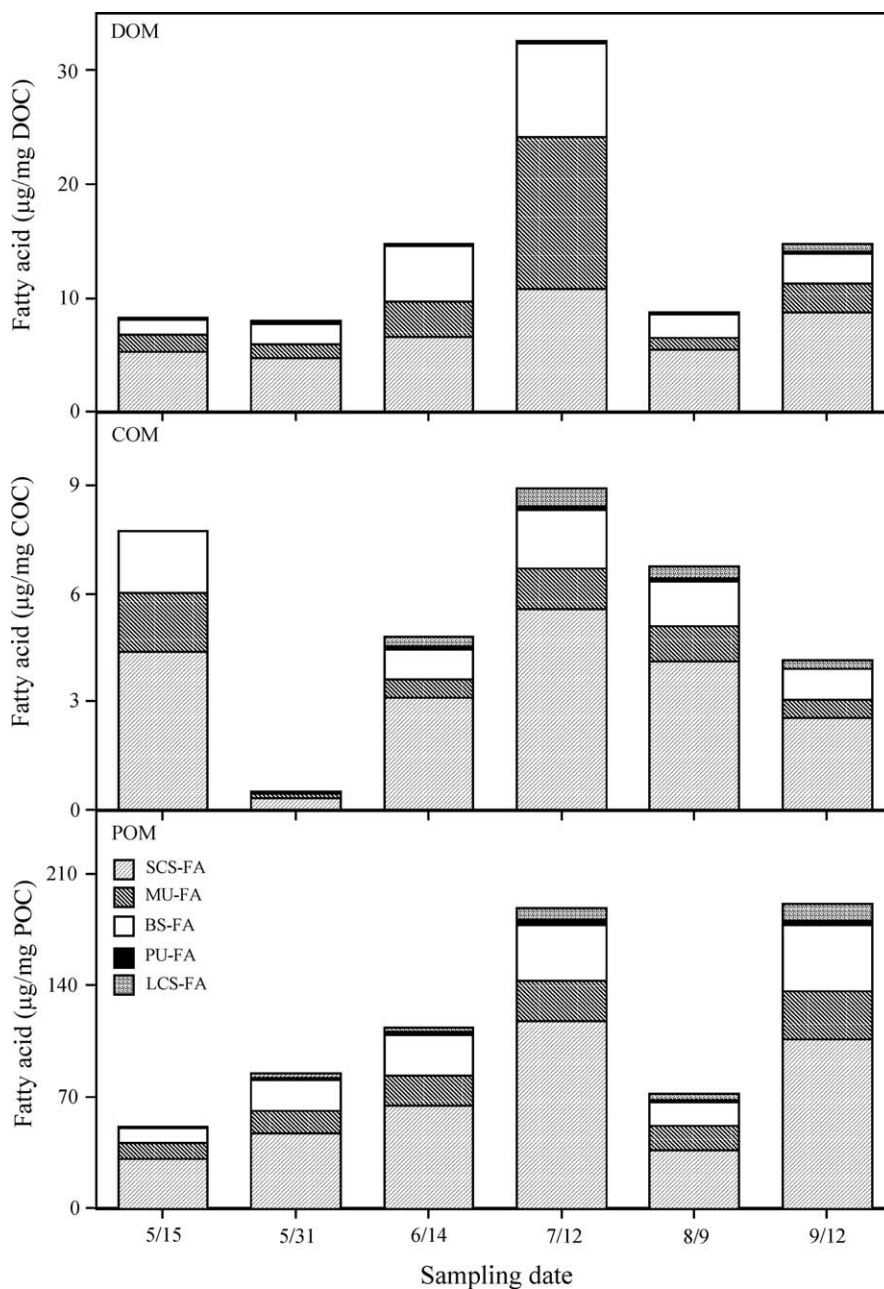


Fig. 3. Temporal variations of subgroup fatty acids in DOM, COM, and POM pools. SCS, short-chain saturated; MU, monounsaturated; BS, bacteria-specific; PU, polyunsaturated; and LCS, long-chain saturated.

level. Total organic carbon, especially from COM, was at its maximum, but the fatty acid contents (normalized to organic carbon in each pool) were the lowest and the Chl-*a* concentrations were very low during this period. Thus, most organic carbon in the river was predominately derived from land during snowmelt. However, fatty acids in the three pools varied differently in this period (dramatic

drop in COM and constant or slight increase in DOM and POM), implying that organic carbon in the three pools might come from different sources with different proportions. POM is probably derived mainly from soils and riverbank erosion because the SPM reached its maximum concentration but the fatty acids in POM varied slightly with the increase of SPM load. COM might be largely derived from

the surface organic matter as suggested by its young ^{14}C age and very low lipid content while DOM might consist of organic carbons from mixed sources. These speculations are supported by large differences in C/N ratios and $\Delta^{14}\text{C}$ values among the three organic matter pools (Guo and Macdonald, 2006).

In July, when temperature was the highest and hydrological conditions became stable, Chl-*a* and total fatty acids reached their highest levels in the river although total organic carbon was at lower level relative to that earlier in the season. Elevated Chl-*a* and fatty acid contents in the POM and DOM pools indicated an increase of contribution from aquatic production during this period. To quantify the relative contributions of organic carbon from aquatic production vs. land inputs, we adopted an end-member mixing model for POM fatty acid data measured in the peak aquatic production period:

$$(\text{FA})_{\text{sample}} (\mu\text{g}/\text{mg C}) = f_1 \times (\text{FA})_{\text{land}} + f_2 \times (\text{FA})_{\text{aquatic}} \quad (1)$$

$$f_1 + f_2 = 1 \quad (2)$$

where f_1 and f_2 are relative fractions of land-derived and aquatic produced organic carbon in the total carbon pool. We assume that $(\text{FA})_{\text{land}}$ is equivalent to the fatty acid content ($\sim 5\%$ of POM) measured at the beginning of snowmelt (mid-May) when the aquatic production was negligible. We also assume that the total fatty acid content, $(\text{FA})_{\text{aquatic}}$, in aquatic biomass is at least 25% because the aquatic organisms in high latitude areas contain $\sim 20\%$ of

their dry weight (50% of carbon) as total lipids, while fatty acids can account for 60–70% of total lipids (Falk-Petersen et al., 1998). Calculations (Fig. 4) showed that approximately 70% of POM (in terms of fatty acids) in July was produced by aquatic organisms in the river. For comparison, we used an average phytoplankton C/Chl-*a* ratio (60:1, w/w) (Whittaker, 1975; Sun et al., 1993) to estimate the phytoplankton-derived organic carbon in the water. The relative proportion of phytoplankton C in the total POM pool was $\sim 35\%$. Thus, the estimate from Chl-*a* data represents the minimum contribution from aquatic production, which only accounts for phytoplankton-produced organic carbon. The estimate from fatty acids may provide a maximum contribution from aquatic production, including bacterial and other organisms' contributions. Comparing the total fatty acid contents in DOM between May and July, it is clear that in July a large proportion of fatty acids in this pool can be attributed to in situ production. When aquatic production was high in July, the ratio of monounsaturated to saturated fatty acids in DOM was greater than one, an indication of high aquatic production (Jaffe et al., 1995).

In August, a sudden decline of fatty acids in POM and DOM pools was probably caused by heavy rainfall during this month (Fig. 2a). Two effects of a large rain storm may be responsible for this decline: (1) extra input of soil particles from land, resulting in a dilution of aquatic organic particles; (2) reduced light intensity on rainy days, decreasing aquatic production in the river. The much smaller decrease of total fatty acids in the

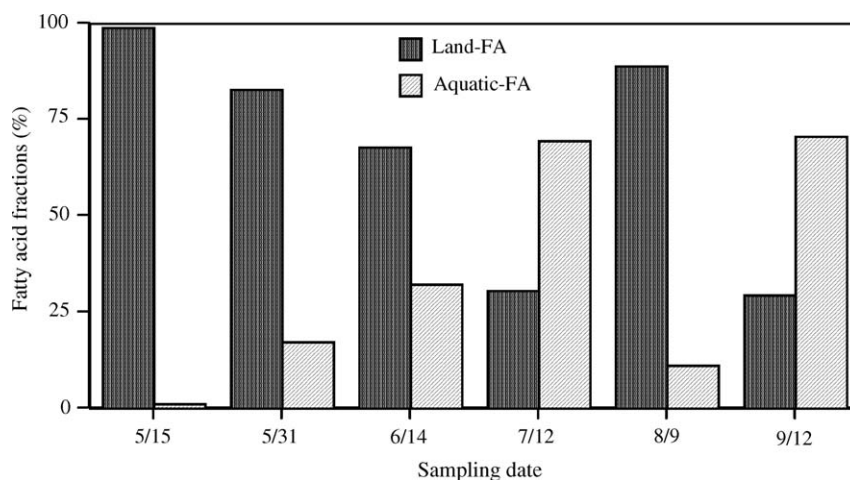


Fig. 4. Relative fractions of POM-fatty acids from land input and aquatic production.

COM pool than in the other two pools implies that organic carbon in COM might not be significantly affected by aquatic production. The ratio of mono-unsaturated to saturated fatty acids in the DOM was less than one in August, indicating a declined aquatic production, which was consistent with a large drop of Chl-*a*. In September, when rainfall decreased to a normal level, fatty acids in POM increased to a higher level (similar to that in July), but levels of fatty acids in the DOM and COM pools were still low. The reason for the increase of fatty acid in POM at this time is unclear because aquatic production was low, as indicated by the low Chl-*a* concentration (Table 1).

3.3. Variations of individual fatty acids and their isotopic compositions

Individual fatty acids in the three pools varied differently during the ice-open season (Fig. 5). Here, we focused on five major fatty acids [14:0, 16:0, 18:0, 16:1, and 18:1(*n*-9)] and one typical bacterial fatty acid (iso-15:0) because their relatively higher concentrations in the samples ensured reasonable measurements of molecular stable carbon isotopic compositions. Contents of individual fatty acids in the POM pool were mostly greater than those in the DOM and COM pools although their relative variations in each pool were similar (Table 2). In the DOM pool, 18:1(*n*-9) showed an unusually large variation in July compared to other major fatty acids in this pool. Most individual fatty acids in POM pool followed a pattern similar to that of total fatty acids: a gradual increase from May to July, a sudden drop in August, and then a return in September. One exception in the POM pool was 18:1(*n*-9), which was lower in July compared with June. However, when contributions from DOM are considered, the abundance of 18:1(*n*-9) also peaks in July.

Molecular stable carbon isotopic compositions of these fatty acids varied in different modes among the three pools (Fig. 5). For easy comparison of isotopic signatures between the total carbon pool and individual compounds, three straight lines (solid, dotted, and dashed) are drawn in Fig. 5, representing bulk $\delta^{13}\text{C}$ ratios (averaged for all samples) of total organic carbon in the DOM, COM, and POM pools (data from Guo and Macdonald, 2006). Three saturated fatty acids (14:0, 16:0, and 18:0) had similar or enriched $\delta^{13}\text{C}$ ratios compared to those in bulk carbon pools, increasing positively (from $\sim -25\%$ to

$\sim -20\%$) with increasing chain length. Two mono-unsaturated fatty acids showed either depleted (for 16:1) or enriched [18:1(*n*-9)] $\delta^{13}\text{C}$ ratios relative to those of bulk carbon. The $\delta^{13}\text{C}$ ratios of bacterial fatty acid (iso-15:0) were mostly similar to those of bulk carbon and only one exception was observed in POM from the first sample set. In all samples, $\delta^{13}\text{C}$ ratios of various fatty acids in the POM pool seemed to vary within a small range ($<4\%$) while those in the DOM and COM pools fluctuated over a relatively large range (up to 10%) throughout the season.

Saturated short-chain (C_{14} – C_{18}) fatty acids are generally ubiquitous and may come from many potential sources, including vascular plants, soil materials, aquatic algae, bacteria, and other organisms (Cranwell, 1982; Kattner et al., 1983; Zegouagh et al., 1996). They dominated the fatty acid composition in all samples but the greatest contribution came from the POM pool. These three saturated fatty acids varied in a similar way to the total fatty acids, but their $\delta^{13}\text{C}$ ratios in POM varied less than those in DOM and COM. Only a small positive shift in $\delta^{13}\text{C}$ ratios (~ 1 – 2%) of 16:0 and 18:0 in POM was observed in July (a time of high aquatic production) compared to May (a time of high land input). The reasons for small variations in $\delta^{13}\text{C}$ of fatty acids in POM are unclear since we do not know the fatty acid $\delta^{13}\text{C}$ ratios of the end member sources (e.g., soil material, land plants, and aquatic algae). However, bacterial inputs for these fatty acids and diagenetic alteration of original plant fatty acids may be potential factors controlling the ultimate $\delta^{13}\text{C}$ ratios of these compounds in the POM pool (Teece et al., 1999; Sun et al., 2004). Larger relative variations in $\delta^{13}\text{C}$ ratios of these fatty acids in COM and DOM pools may be related to fractionation during leaching and hydrolysis of esterified fatty acid components. There is accumulating evidence showing that hydrolysis of reactive compounds may cause ^{13}C alterations (e.g., Bada et al., 1989; Silfer et al., 1992; Fogel and Tuross, 1999).

It is unusual that most $\delta^{13}\text{C}$ ratios of these saturated fatty acids were relatively enriched compared to ratios found in bulk organic carbon and the enrichment seems to increase with increasing chain length. Many studies have shown that natural fatty acids carry $\delta^{13}\text{C}$ ratios that are depleted compared to their bulk carbon source (Ballentine et al., 1996; Canuel et al., 1997; Boschker et al., 1999). It was also observed that fatty acids isolated from some plants exhibited increased depletions in ^{13}C

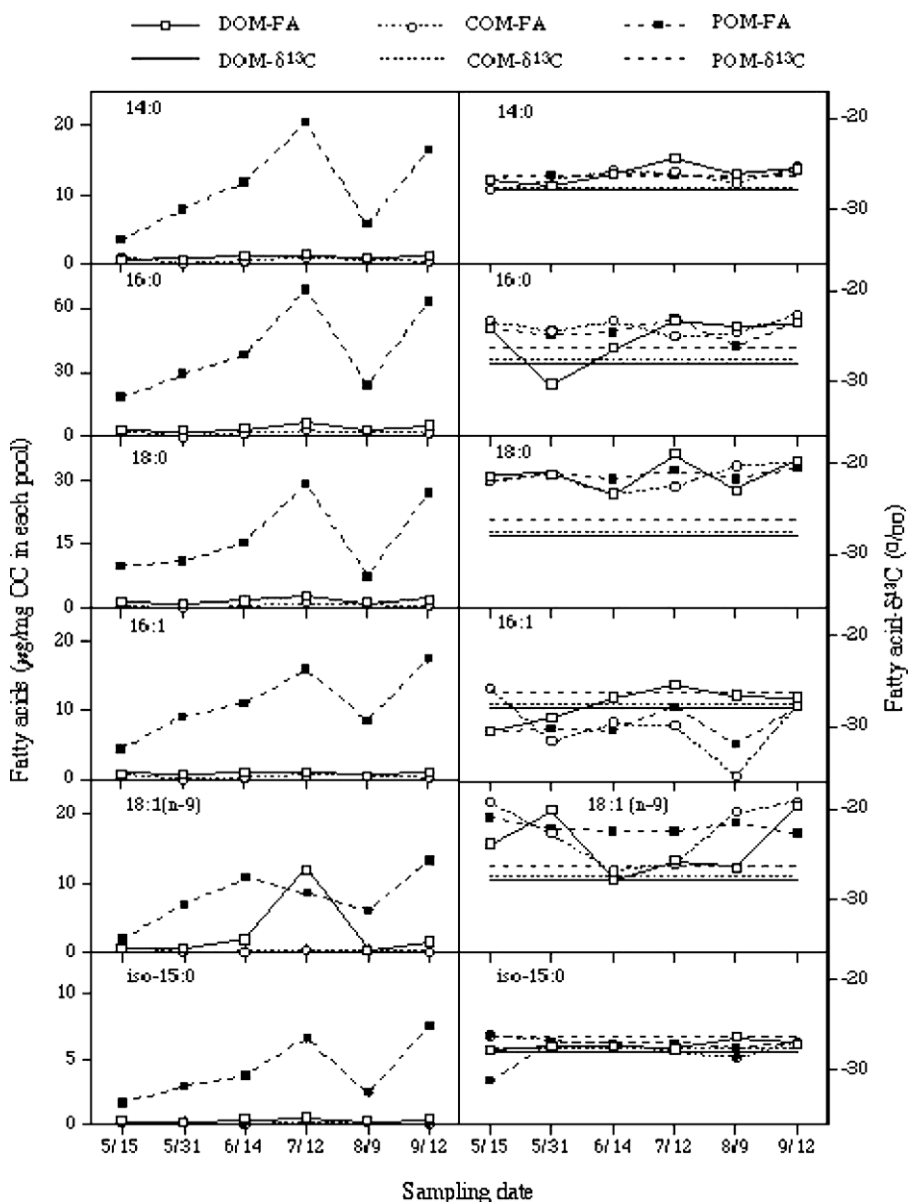


Fig. 5. Temporal variations of individual fatty acids and their stable carbon isotopic ratios in DOM, COM, and POM pools. The averaged bulk $\delta^{13}\text{C}$ values of DOM, COM, and POM are expressed as three straight lines (solid, dotted, and dashed). The error range of molecular isotope analysis is approximately $\pm 0.4\text{‰}$, based on internal standard measurements ($n = 18$).

as carbon chain-length increased (Canuel et al., 1997). Nevertheless, culture experiments demonstrated that the $\delta^{13}\text{C}$ ratios of most saturated short-chain fatty acids biosynthesized by algae were almost the same regardless of chain length (Schouten et al., 1998). In another Arctic river (the Mackenzie River), $\delta^{13}\text{C}$ ratios (-36 to -40‰) of C_{14} and C_{16} fatty acids in most suspended sediments were found to be highly depleted relative to those (-26 to -27‰) of bulk carbon (Goñi et al.,

2005). However, at one site in the Mackenzie River estuary, the $\delta^{13}\text{C}$ ratios of saturated fatty acids were similar to or slightly enriched above those of bulk carbon (Goñi et al., 2005). Similar $\delta^{13}\text{C}$ ratios between bulk carbon and fatty acids were observed in COM samples collected from several estuarine and coastal areas (Zou et al., 2004). At this point, we cannot explain the anomaly in $\delta^{13}\text{C}$ ratios of saturated short-chain fatty acids. However, several potential factors are likely involved: (1) uncertain

organic inputs from a myriad of shallow lakes and wetlands adjacent to the Yukon River; (2) bacterial contributions; and (3) different carbon sources and specific biosynthetic pathways of individual fatty acids.

Two monounsaturated fatty acids [16:1 and 18:1($n - 9$)] displayed different variation patterns during the ice-open season (Fig. 5). The 16:1 fatty acid varied in the same way as saturated short-chain components in all three pools while the 18:1($n - 9$) fatty acid did not, especially in the POM and DOM pools. The largest difference between 18:1($n - 9$) and other fatty acids occurred in July when aquatic production was high: a decrease of this compound in POM but an increase in DOM. Compared with saturated fatty acids, monounsaturated fatty acids are more likely produced by aquatic algae and bacteria rather than by vascular plants (Cranwell, 1982; Canuel et al., 1997; Volkman et al., 1998). The occurrence of higher concentration of these fatty acids in July indeed suggested that a major source of these compounds was from aquatic production. Interestingly, $\delta^{13}\text{C}$ ratios of these two monounsaturated fatty acids had different variation patterns (Fig. 5). For example, in the POM pool, the $\delta^{13}\text{C}$ of 16:1 had a $\sim 2.5\%$ enrichment in high aquatic production time while that of 18:1($n - 9$) had little variation at the same time. In the DOM pool, the $\delta^{13}\text{C}$ ratios of 16:1 and 18:1($n - 9$) showed opposite variations: enrichment for 16:1 and depletion for 18:1($n - 9$) in summer months. In the COM pool, the $\delta^{13}\text{C}$ ratios of 18:1($n - 9$) varied in a way similar to that in DOM, but those of 16:1 varied irregularly. Although even larger variations in the $\delta^{13}\text{C}$ of these monounsaturated fatty acids has been observed in other estuarine and coastal environments (Zou et al., 2004), understanding of the underlying causes remains elusive.

Iso-15:0 is a typical bacteria-specific fatty acid (Kaneda, 1991) and its variations in the three pools during the ice-open season followed the same pattern as most saturated and 16:1 fatty acids. Consistent variations of bacterial and other major fatty acids implied that there was a close coupling between aquatic production and bacterial growth. It has long been known that phytoplankton production stimulates heterotrophic processes (Bell and Wittchell, 1972; Gajewski and Chróst, 1995) and bacterial activities are also promoted by rising temperature (Mayer, 1989; Canuel and Martens, 1993). In July, the temperature and aquatic production in the river reached their maximum levels, so bacterial

fatty acids (and by inference the associated bacteria abundance) correspondingly increased to a higher level relative to that in May. More interestingly, the $\delta^{13}\text{C}$ ratios of iso-15:0 fatty acids in almost all samples (except one) varied over a smaller range ($1\text{--}2\%$) than those of other fatty acids during the ice-open season. Moreover, the $\delta^{13}\text{C}$ ratios of iso-15:0 fatty acid were very close to those of bulk carbon in the three pools. It was experimentally confirmed that fatty acids synthesized by aerobic bacteria had similar $\delta^{13}\text{C}$ as that of substrate, while fatty acids produced by anaerobic bacteria were considerably depleted in ^{13}C relative to that of substrate (Teece et al., 1999). Other studies (Boschker et al., 1998, 1999) also demonstrated that stable carbon isotopic signatures of bacterial fatty acids could be used to link microbial populations to specific biogeochemical processes. Therefore, no matter how organic carbon inputs varied with climatic, hydrological, and biogeochemical conditions, bacteria in the Yukon River might mostly utilize the bioavailable organic substrate from the same source.

4. Conclusions

This study demonstrated an application of combined fatty acid biomarker and molecular stable carbon isotope approaches to examine temporal variations of organic inputs from different sources into the Yukon River. Analytical results showed that, although bulk organic carbon in the three pools (DOM, COM, and POM) declined from the beginning of snowmelt to the end of ice-open season, the relative contributions of organic carbon from land and aquatic sources varied differently in the three pools. During snowmelt (mid-May), the organic carbon in the three pools was dominated by land inputs, while in summer (July) aquatic production may contribute a considerable fraction of organic carbon to the POM and DOM pools. Heavy rainfall in August might have enhanced land input but retarded aquatic production, and thus changed the relative inputs of organic matter from different sources. Consistent variations of bacterial fatty acids with other major fatty acids indicated a strong microbial activity related to plankton production in the river. Smaller variability in $\delta^{13}\text{C}$ of bacterial fatty acids compared with other fatty acids implies that bacteria utilize the bioavailable substrates from the same carbon source. Our results are consistent with the view that

further global warming will not only release more soil organic carbon from land but also promote aquatic production in high latitude regions, resulting in a significant increase in organic carbon export from the river basins to the ocean.

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