Biogeochemistry (2006) 77: 139–155
DOI 10.1007/s10533-005-0806-1

Chemical characteristics and origin of dissolved organic matter in the Yukon River

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Received 23 December 2003; accepted in revised form 18 January 2005

Key words: Carbohydrate, Colored dissolved organic matter, Dissolved organic carbon, Soil organic carbon, Yukon River

Abstract. Monthly (or bi-weekly) water samples were collected from the Yukon River, one of the largest rivers in North America, at a station near the US Geological Survey Stevens Village hydrological station, Alaska from May to September 2002, to examine the quantity and quality of dissolved organic matter (DOM) and its seasonal variations. DOM was further size fractionated into high molecular weight (HMW or colloidal, 1 kDa–0.45 μm) and low molecular weight (LMW, <1 kDa) fractions. Dissolved organic carbon (DOC), colored dissolved organic matter (C-DOM) and total dissolved carbohydrate (TCHO) species were measured in the size fractionated DOM samples. Concentrations of DOC were as high as 2830 μmol-C l^{-1} during the spring breakup in May and decreased significantly to 508–558 μmol-C l^{-1} during open-water season (June–September). Within the DOC pool, up to 85% was in the colloidal fraction (1 kDa–0.45 μm) in early May. As DOC concentration decreased, this colloidal portion remained high (70–85% of the bulk DOC) throughout the sampling season. Concentrations of TCHO, including monosaccharides (MCHO) and polysaccharides (PCHO), varied from 722 μmol-C l^{-1} in May to 129 μmol-C l^{-1} in September, which comprised a fairly constant portion of bulk DOC ($24 \pm 2\%$). Within the TCHO pool, the MCHO/TCHO ratio consistently increased from May to September. The C-DOM/DOM ratio and the size fractionated DOM increased from May to September, indicating that DOM draining into the Yukon River contained increased amounts of humified materials, likely related to a greater soil leaching efficiency in summer. The average composition of DOM was 76% pedogenic humic matter and 24% aquagenic CHO. Characteristics of soil-derived humic substances and low chlorophyll-*a* concentrations support a dominance of terrestrial DOM in Yukon River waters.

Introduction

Dissolved organic matter (DOM) is an important component and an intermediary in global carbon cycles (Hedges et al. 1997). It plays significant roles in aquatic food webs (Thingstad 2003 and references therein), regulates the bioavailability of dissolved nutrients and metals (Koukal et al. 2003; Guéguen et al. 2004), and affects the optical properties of natural waters (Schindler et al. 1997; Guéguen et al. 2003). The composition and transport of DOM depend primarily on whether the origin is from soil and plant material or from *in situ*

production. Pedogenic organic matter results from leaching of decomposition byproducts of microorganisms and higher plants. It is largely composed of refractory and aromatic humic substances (or colored dissolved organic matter, C-DOM) (Buffle 1988). The aquagenic DOM produced by the excretion and decomposition of aquatic macrophytes and plankton includes mainly carbohydrates (CHO; Bertilsson and Jones 2003 and references therein). The contribution of other organic molecules such as lipids, amino acids and proteins is relatively small in rivers because of their sorption onto particles and their rapid degradation (Wilkinson et al. 1997). The *in situ* production of DOM is often small compared to the soil-derived DOM in major rivers (Thurman et al. 1985; Buffle 1988).

The typical concentration of dissolved organic carbon (DOC) in river waters varies primarily by climate and watershed characteristics (Meybeck 1998). The highest DOC values are usually measured in taiga and tundra tropics (up to $\sim$600 μmol-C l^{-1} ; Meybeck 1998; McLean et al. 1999). Furthermore, a peak in DOM flux has been measured in high latitudes during spring breakup, when 40–80% of arctic river discharge occurs (Gordeev et al. 1996). Rember and Trefry (2004) showed that DOC decreased from 742 μmol-C l^{-1} during spring floods to 167 μmol-C l^{-1} at off peak flow in Alaskan streams. Similar results have been reported for the Mackenzie River where $\sim$35% of the annual DOC flux occurred during the spring breakup (Telang 1985). Nevertheless, the variation in chemical composition of DOM from the river breakup to the end of the Arctic summer remains poorly understood.

The Yukon River is one of the largest river systems in North America, and drains an area of 840×10^3 km^2 in a taiga-dominated system. With an annual discharge of more than 200 billion m^3 of freshwater, it contributes $\sim$8% of the total freshwater to the Arctic Ocean (Aagaard and Carmack 1989). The Yukon River is frozen from October to May/June. Due to its remoteness and the extreme weather conditions, the Yukon River Basin remains pristine and understudied. Biogeochemical processes as a result of climate change in the Yukon River watershed are poorly understood. Knowledge of how the environmental change influences the carbon cycle in Arctic rivers will provide insights into biogeochemical consequences of climate change. In the present study, we examined the seasonal variations in concentration, flux and partitioning of DOM, C-DOM, and CHO species in the upper Yukon River from spring breakup to open-water season.

Material and methods

Site description and sampling

Yukon Flats is a $\sim$ 40,000 km^2 complex of wetlands and contributes large amounts of organic carbon to the Yukon River. The sampling site (65 °52′ N,

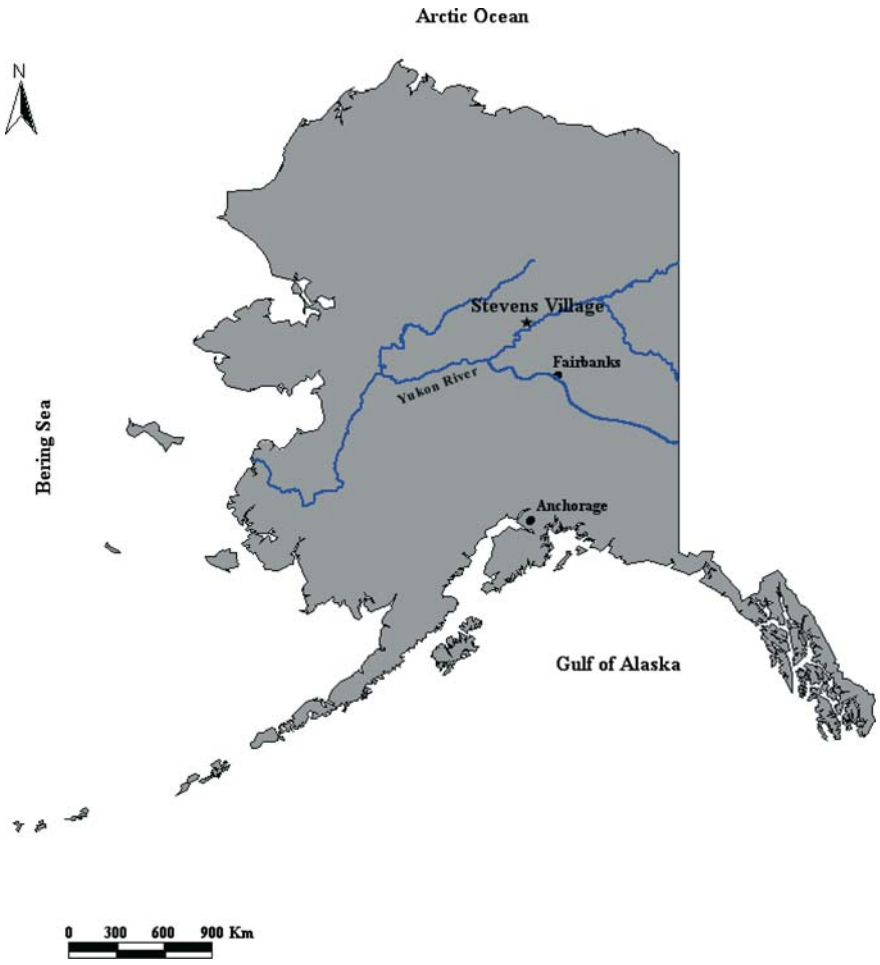

Figure 1. Map of the Yukon River Basin and the sampling location.

149 °43′ W) was located between the Dalton Highway Bridge and the USGS Stevens Village hydrological station, downstream of Yukon Flats (Figure 1).

The long-term (1977–2000) mean discharge of the Yukon River at the Stevens Village station shows a flow pattern typical of arctic rivers (Figure 2), with a low flow rate during the frozen season and high flow in the summer (Lammers et al. 2001). Due to the increase of air temperatures in May, spring breakup results in a peak in river discharge, sometimes amplified by rainfall. As shown in Figure 2, the discharge increased by a factor of ~10 in the period from early May to the end of May 2002.

Monthly (or biweekly) water samples were collected from May to September 2002 to cover the time period with significant flow rate variations (Figure 2; Table 1). During the spring breakup (May), two samples were collected

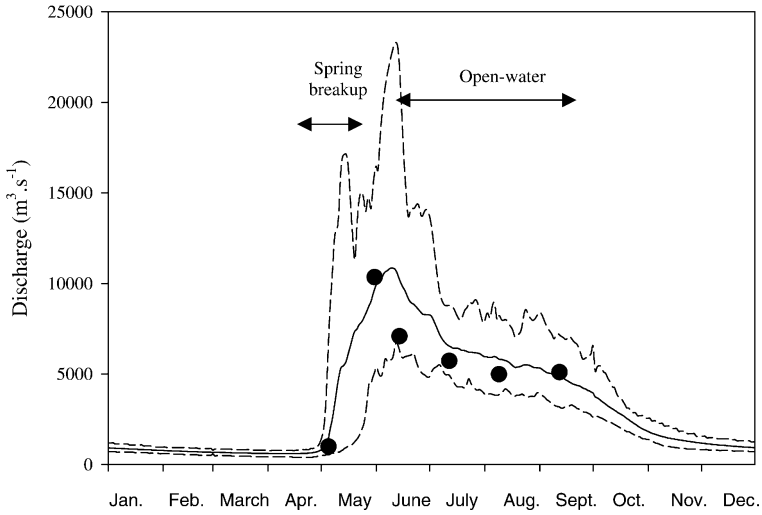

Figure 2. Long term daily mean flow rates of the Yukon River at the USGS Stevens Village Station (1977–2000), with the minimum and maximum of discharge in dashed lines (data from the USGS at www.usgs.gov). Open circles symbolize the sampling dates with their instantaneous discharge rate.

Table 1. Sampling dates, freshwater discharge, pH, conductivity, suspended particulate matter (SPM), chlorophyll a (Chl-*a*), concentrations of dissolved organic carbon (DOC) and optical properties in the Yukon River waters.

Sample ID	Date	Discharge (m^3 s^{-1})	pH	Cond. (μS cm^{-1})	SPM (mg l^{-1})	Chl*a* (μg l^{-1})	DOC (μmol-C l^{-1})	a_{280}/DOC (m^{-1}/(mmol-C l^{-1})
YR-01	05/15/02	991	7.5	163	92	< 0.20	2835	64.9
YR-02	05/31/02	10337	7.4	174	331	1.57	1158	70.4
YR-03	06/14/02	7080	7.7	209	153	0.97	725	61.4
YR-04	07/12/02	5721	7.9	227	175	5.07	558	57.3
YR-05	08/09/02	4984	7.9	224	101	0.73	508	73.0
YR-06	09/12/02	5098	7.9	226	53	0.56	533	72.3

(YR-01, YR-02). The other four samples (YR-03, YR-04, YR-05, YR-06) were taken from June to September when river discharge was relatively constant ($\sim$5000 m^3/s).

Surface water samples at $\sim$1 m depth were obtained using a peristaltic pump with acid cleaned polypropylene tubing. Water samples were pumped directly through a 0.45 μm polycarbonate filter cartridge (Osmonics) into acid cleaned 20 l polypropylene containers, or brought back to the laboratory for filtration within 4 h (Figure 3). Immediately after prefiltration, a ultrafiltration (UF) system equipped with a 1 kDa regenerated cellulose cartridge (Amicon, S10Y1) was used to size fractionate the $<$0.45 μm DOM into high molecular weight (HMW, 1 kDa–0.45 μm) and low molecular weight (LMW, $<$1 kDa) fractions

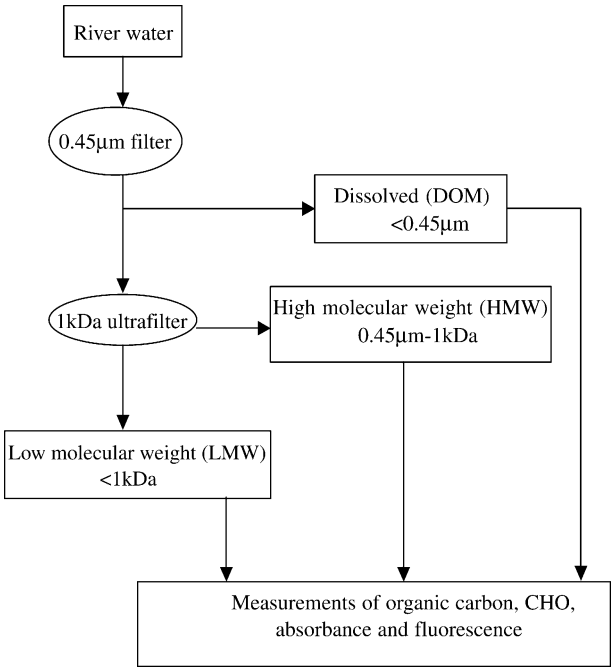

Figure 3. Schematic of organic matter size fractionation using filtration and ultrafiltration.

in the laboratory (Guo et al. 2000; Guéguen et al. 2002). The concentration factors (Cf) applied for ultrafiltration were between 7 and 13. Aliquots of all ultrafiltration samples, including the < 0.45 µm, the 1 kDa–0.45 µm, and the < 1 kDa fractions, were collected for measurements of DOC, C-DOM, and CHO concentrations. Mass balance for DOC ($88 \pm 6\%$, $n = 6$) was relatively low, likely due to the presence of high DOM concentrations and sorption lost in the cartridge.

River discharge data were obtained from the USGS website at http://www.usgs.gov. Conductivity was measured using an YSI Model 30 conductance meter. pH was measured using a DigiSense pH meter with an Orion electrode.

Analytical methods

DOC concentration was measured by the high temperature combustion method on a Shimadzu TOC-V analyzer (Guo et al. 1995). To remove inorganic carbon before the analysis, samples (~20 ml each) were acidified with two drops of concentrated HCl to a pH ≤ 2 and purged with ultra-pure air. Three to five replicate injections (150 µl each) were performed for each sample, resulting in a typical coefficient of variation $< 2\%$.

Carbohydrate species were determined on a spectrophotometer using a modified colorimetric method (Hung et al. 2001). Concentrations of monosaccharide (MCHO) were directly determined after oxidizing free reduced sugars with the 2,4,6-tripyridyl-*s*-triazine (TPTZ), while total dissolved carbohydrate (TCHO) concentrations were measured at 150 °C after hydrolysis with HCl (Hung et al. 2001). The concentration of polysaccharides (PCHO) was calculated from the difference between TCHO and MCHO concentrations (all in μmol-C l^{-1}). The reagent blank in Milli-Q water was subtracted before calculating the final concentration of the MCHO. The variation coefficient was $< 5\%$.

Absorbance of DOM was measured on an UV–visible spectrophotometer (Agilent 8453) with a 1 cm quartz cuvette using Milli-Q water as a reference. Values of average absorbance at 700 nm were set to zero to correct the spectra for refractive index effects (Green and Blough 1994). The absorbance acquired was converted to an absorption coefficient (m^{-1}) according to the equation: $a(\lambda) = 2.303\ A(\lambda)/L$, where $A(\lambda)$ is the absorbance and L the pathlength of the optical cell in meters. The pedogenic (soil derived) contribution to DOC was estimated by using the ratio of the absorbance (280 nm) to DOC and assuming that only pedogenic humic compounds contribute to the absorbance at 280 nm (Buffle 1988; Zumstein and Buffle 1989).

Both excitation and emission fluorescence measurements were made with a FluoroMax 3 Jobin Yvon fluorometer equipped with two monochromators. Samples were contained in a 1 cm path length quartz cell. The recorded spectra were corrected for instrumental response (Ewald et al. 1993; De Souza-Sierra et al. 1994). Milli-Q water was used as a blank and subtracted from sample spectra. All fluorescence intensities were converted to fluorescence units (Fl.U.), based on the measurement of corrected fluorescence intensity of 1 ppb quinine sulfate dihydrate (NIST 936a) in 0.105 M perchloric acid.

Chlorophyll-*a* (Chl-*a*), collected on a GF/F filter and extracted with 90% acetone, was measured by the method described in Strickland and Parsons (1972).

Total suspended particulate matter (SPM) concentrations were determined by filtering a known volume of river water sample through a pre-weighed polycarbonate membrane dried at 60 °C. The filters were dried and weighed 2–3 times until a constant weight was obtained.

Results and discussion

Hydrology

Values of conductivity and pH were lower during spring breakup in May as a result of dilution with melting snow and ice, and slightly increased from June to July–September (Table 1). From June to September, both conductivity and pH were relatively constant, with values of 224–227 μS cm^{-1} for conductivity and

7.9 for pH, respectively. In general, water conductivity decreased with increasing discharge except for data collected during the early spring breakup (YR-01). The steady increase in conductivity from spring breakup to open-water season to post peak discharge suggested more weathering between June and September. The SPM load had a maximum during the spring breakup (331 mg l^{-1}, YR-02) mainly due to the peak discharge associated with melting snow and rainfall. In the open-water season, SPM ranged from 53 to 173 mg l^{-1}, which is similar to other arctic rivers (8–207 mg l^{-1} ; Rachold et al. 2003). Chl-*a* concentrations were low (from <0.2 to 5 μg l^{-1}) (Table 1), indicating a small overall contribution of DOM derived from phytoplankton from spring breakup to open-water season.

Concentration and flux of dissolved organic carbon (DOC)

Concentrations of DOC in Yukon River waters decreased from 2835 μmol-C l^{-1} in mid-May to 725 μmol-C l^{-1} in June followed by a relatively constant value of 530 ± 30 μmol-C l^{-1} (ranging from 508 to 558 μmol-C l^{-1}) (Table 2). The typical DOC concentrations in the tundra and taiga climate zone were from 167 to 583 μmol-C l^{-1} (Meybeck 1988; McLean et al. 1999), which is consistent with DOC concentrations measured in the Yukon River during the open water season. Concentration of Yukon River DOC decreased with decreasing discharge during the open-water season ($n=4$, $R^2=0.97$). The positive correlation between DOC concentration and river discharge, which has also been observed in other stream systems (Heikkinen 1994; Schiff et al. 1997), is consistent with what has been measured in major world rivers (Spitzy and Leenheer 1991). A distinctive feature of dissolved organic matter variation in arctic river systems is a maximum concentration being measured during the breakup period.

Together with the discharge data, these DOC concentrations correspond to an instantaneous DOC flux from the upper Yukon River ranging from 30 to 144 kg-C s^{-1} (or 2.6 10^6 kg-C d^{-1}). The maximum flux occurred during the

Table 2. Concentrations of total DOC (μmol-C l^{-1}) and carbohydrate species (μmol-C l^{-1}) in dissolved (<0.45 μm) and LMW (<1 kDa) fractions in the Yukon River samples with values of SD inside parenthesis.

Sample ID	DOC	<0.45 μm				<1 kDa			
		TCHO	MCHO	PCHO	DOC/TCHO	TCHO	MCHO	PCHO	LMW DOC/TCHO
YR-01	2835	722	493 (0.68)	229 (0.32)	3.91	71	60 (0.84)	11 (0.16)	5.39
YR-02	1158	312	230 (0.74)	82 (0.26)	3.71	35	32 (0.91)	2.7 (0.08)	7.06
YR-03	725	160	122 (0.76)	38 (0.24)	4.53	25	23 (0.92)	1.2 (0.05)	6.51
YR-04	558	120	92 (0.77)	28 (0.23)	4.65	21	20 (0.95)	0.9 (0.04)	7.82
YR-05	508	138	107 (0.78)	30 (0.22)	3.68	24	21 (0.88)	2.8 (0.12)	5.00
YR-06	533	129	102 (0.79)	26 (0.21)	4.13	26	21 (0.81)	4.8 (0.19)	5.76

TCHO, total dissolved carbohydrates; MCHO, monosaccharides; PCHO, polysaccharides.

breakup season; ~50% of the annual total DOC flux measured in this study occurred during breakup. The open season instantaneous DOC fluxes were relatively constant, ranging from 30 to 34 kg-C s^{-1}. This seasonal cycle in the discharge of organic matter in the Yukon is consistent with that found in the Siberian Arctic Rivers where the spring breakup period accounts for 58–78% of the annual OC discharge (Maltseva et al. 1987).

DOC size distribution data showed that a considerable portion of the riverine DOC pool was present in a colloidal or HMW fraction (1 kDa–0.45 μm) (Figure 4). On average, colloidal organic carbon (COC) made up 73 ± 6% of DOC in all samples. Up to 84% of COC was observed in mid-May when the DOC concentration was the highest. Even though the DOC concentration dropped to an average of 533 ± 25 μmol-C l^{-1}, the percentage of DOC occurring as COC was still as high as 71 ± 3%, varying from 67 to 74%. This high percentage of COC indicated that colloids are the predominant phase in bulk DOC transported by the Yukon River, which is in agreement with observations for other river systems (e.g., Benner and Hedges 1993; Guo and Santschi 1997; Guéguen and Dominik 2003).

Partitioning and transformation of carbohydrate species

The distributions of MCHO, PCHO and TCHO in the < 0.45 μm fraction are summarized in Table 2 and Figure 4. Concentrations of TCHO decreased from 722 μmol-C l^{-1} during spring breakup in May to ~120 μmol-C l^{-1} during the open season from June to September. Within the < 0.45 μm TCHO pool, MCHO constituted, on average, 75 ± 4% of the TCHO. Even though concentrations of MCHO, PCHO and TCHO all consistently decreased from May to September, the percentage of MCHO in the TCHO increased from 68% in May to 79% in September. In contrast, the percentage of PCHO in the TCHO decreased from 32% in May to 21% in September (Table 2).

Measurements of carbohydrate species in size fractionated DOM phases showed that concentrations of TCHO in the < 1 kDa LMW fraction ranged from 21 to 71 μmol-C l^{-1}, with the highest value observed during breakup in May and an average of 24 ± 2μM-C measured from June to September. Within the LMW TCHO pool, on average, 89 ± 6% was measured as MCHO and only 11 ± 6% was in the PCHO fraction. Compared to the partitioning of CHO species in the < 0.45 μm pool, MCHO was more important in the LMW TCHO pool (89 ± 6% vs. 75 ± 4%).

Using TCHO concentrations measured in both the < 0.45 μm and the < 1 kDa fractions, the size distribution of TCHO between colloidal and < 1 kDa LMW fractions can be calculated. On average, 85 ± 4% of the TCHO was in the colloidal phase, ranging from 80% in September to 90% during breakup in May, and 15 ± 4% of the TCHO was in the < 1 kDa phase, varying from 10% in May to 20% in September. Interestingly, even though TCHO concentrations decreased from 722 μmol-C l^{-1} in May to

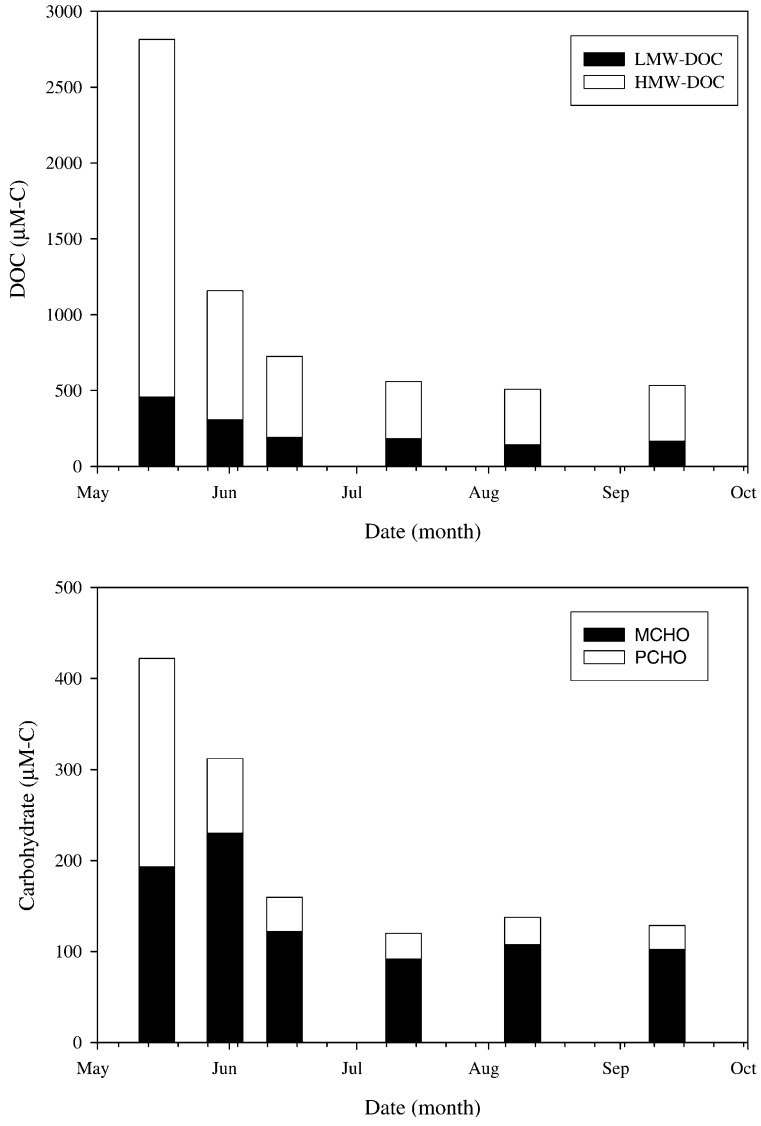

Figure 4. Variations of (a) dissolved organic carbon in the HMW (1 kDa–0.45 μm) and the LMW (< 1 kDa) fractions and (b) concentrations of carbohydrate species, including monosaccharides (MCHO) and polysaccharides (PCHO), in the < 0.45 μm DOM fraction.

137 ± 17 μmol-C l^{-1} between June and September, the percentage of colloidal CHO species remained fairly constant. For example, colloidal MCHO was, on average, $82 \pm 4\%$ of the total MCHO, whereas colloidal PCHO was $93 \pm 6\%$ of the total PCHO, similar to the colloidal TCHO (on average, $85 \pm 4\%$ of the total TCHO). High percentages of colloidal CHO species indicate that the

carbohydrates in Yukon River waters were mostly partitioned and transported in the colloidal phase. As shown in Figures 4 and 5, the MCHO fraction was consistently the dominant component of the TCHO pool, but the ratio of both MCHO and PCHO to TCHO changed as the season progressed; the PCHO/TCHO ratio was higher in May and lower in September, while the MCHO/TCHO ratio was lower in May and higher in September. This relationship between MCHO/TCHO and PCHO/TCHO indicated a transformation between carbohydrate and other organic carbon species during the sampling season; increases in water temperature, microbial activity and photochemical reactions could be responsible for the observed transformation. More studies are needed to better understand the pathways and mechanisms controlling the transformation of organic carbon species in the arctic river system.

The distribution of TCHO in the Yukon River showed a pattern analogous to that of DOC, with a significant correlation between concentrations of all carbohydrate fractions and DOC concentration (Figure 5). Since the intercept was close to zero, values of the linear regression slopes indicated that MCHO, PCHO and TCHO made up about 18, 8 and 25% of the < 0.45 μm DOC and 15, 2 and 17% of the LMW DOC, respectively. Interestingly, the percentage of TCHO in the bulk DOC reported here is similar not only to that found in freshwater systems (e.g. Wilkinson et al. 1997) but also to that measured in marine systems (e.g. Pakulski and Benner 1994; Skoog and Benner 1998). Comparable DOM composition (or TCHO/DOC ratio) between freshwater and seawater suggests common production and cycling processes for natural organic matter. These linear relationships also implied a constant carbohydrate fraction in the DOC pool from initial snowmelt to ice open season. Furthermore, a constant carbohydrate composition also indicated a consistent DOM source in the Yukon River Basin.

Characteristics of colored dissolved organic matter (C-DOM)

C-DOM in size fractionated DOM fractions was characterized by its optical properties, including absorption and fluorescence. The proportion of C-DOM in the DOM pool increased from May to September in both fractions (Figure 6), indicating that DOM draining into the Yukon River contained increased amounts of humified materials.

To study the compositional changes of C-DOM from spring breakup to open season, the variations in the spectral slope parameter and shifts in the wavelength of the emission maximum at an excitation wavelength of 313 nm were examined. In a previous study of the absorption spectra, Guéguen et al. (2003) showed that, while the *S*-values (spectral slope) in the < 0.45 μm C-DOM were relatively constant, the size fractionated HMW and LMW fractions were markedly different from each other. During the breakup season, *S*-values were lower than during the ice open season for both size fractions:

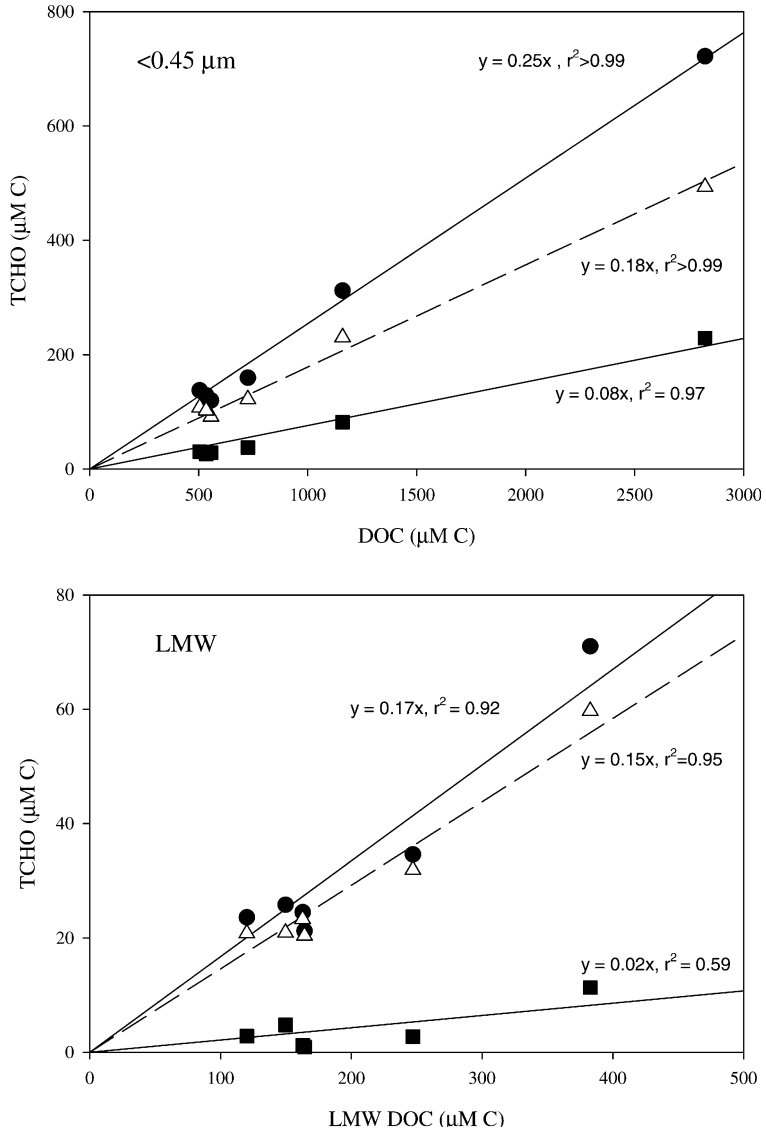

Figure 5. Linear correlations of TCHO (●), MCHO (△) and PCHO (■) with DOC concentrations in the <0.45 μm and the <1 kDa LMW fractions in Yukon River waters.

0.011–0.014 vs. 0.016–0.017 nm^{-1} for the HMW DOM and 0.013–0.017 vs. 0.021–0.023 nm^{-1} for the LMW DOM fractions, respectively, between breakup and open season (Guéguen et al. 2003). Within the <0.45 μm C-DOM pool, the wavelength of the emission maximum, related to the C-DOM origin (De Souza Sierra et al. 1994; Coble 1996), decreased from 444 nm during

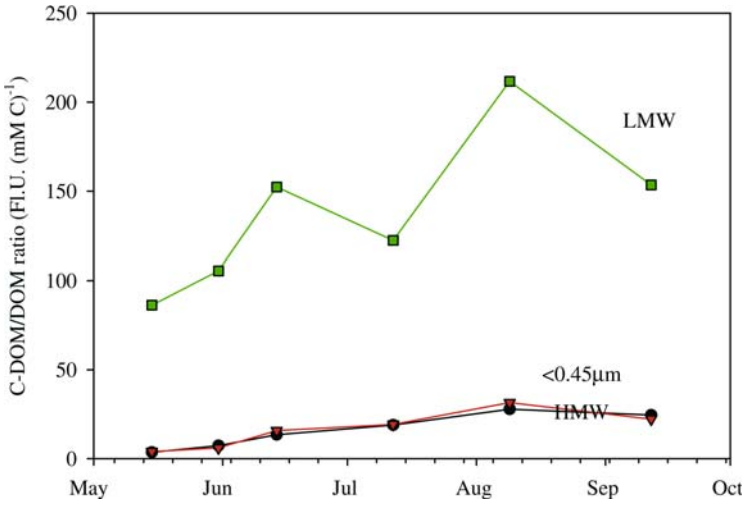

Figure 6. Variations in C-DOM /DOM* ratio in the < 0.45 µm, HMW (1 kDa–0.45 µM) and LMW (< 1 kDa) fractions. *assuming DOM $= 2 \times$ DOC.

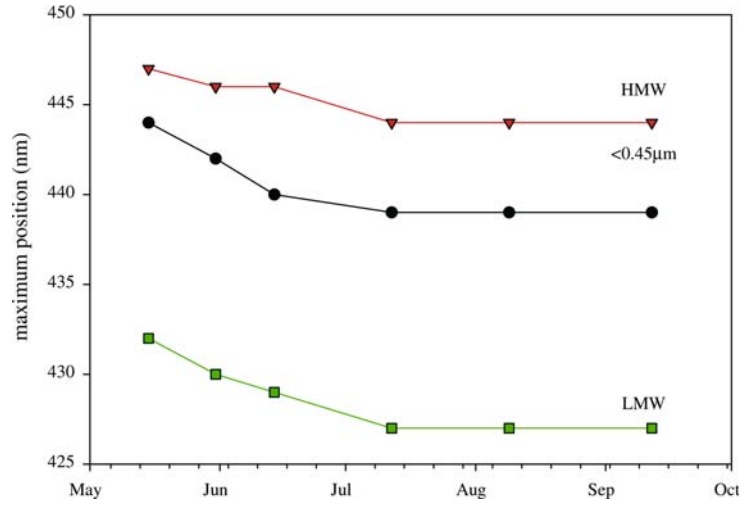

Figure 7. Changes in the emission maximum ($\lambda = 313$ nm) of colored DOM in the < 0.45 µm, HMW and LMW fractions.

breakup in May to 439 nm during the open season from June to September (Figure 7). Differences as large as 5 nm in emission maximum wavelength were observed between samples from breakup and those from open season for both size fractionated DOM fractions. It has been shown that HMW compounds are characterized by a longer emission wavelength maximum as compared to LMW molecules in fresh waters (Belin et al. 1993, 1996; Guéguen et al. 2002).

Indeed, the separation of C-DOM with ultrafiltration methods usually results in a longer wavelength for emission maximum in the HMW than in the LMW DOM fraction (Figure 7). This shift in emission maximum suggests a change in C-DOM molecular weight (MW) composition during the sampling season (Belin et al. 1996), from higher MW C-DOM in May to lower MW C-DOM in September in both fractions. This decrease in C-DOM MW composition is in agreement with *S*-value evolution and the phase partitioning of DOC and carbohydrate species (see previous sections). However, McKnight et al. (2001) found no consistent shift in fluorescence spectra of fulvic acid isolated from streams receiving predominantly terrestrial sources of organic materials. Chemical extraction using XAD or similar methods could have resulted in a significant alteration in C-DOM optical properties (Thurman et al. 1985; Green and Blough 1994; Mobed et al. 1996). In contrast, isolation of DOM by ultrafiltration, a physical separation method, does not significantly affect fluorescence properties of size fractionated DOM (Mopper et al. 1996; Mounier et al. 1999).

As shown in Figure 7, the size fractionated HMW and LMW DOM fractions have distinctly different characteristic emission maximum wavelengths compared to the bulk DOM pool. *S*-values are also markedly different between HMW and LMW DOM fractions (Guéguen et al. 2003). These results indicate that C-DOM is not uniformly partitioned between the HMW and LMW DOM fractions within the bulk DOM pool in river waters, consistent with the heterogeneous nature of DOM in aquatic systems (McKnight et al. 1997; Guo et al. 2003).

Variations of DOM composition

An increase in DOC concentration with increasing river discharge from the end of May, as reported for many other rivers (Grieve 1984; Meyer 1986; Heikkinen 1994), confirmed a terrestrial origin for the DOM in the Yukon River. The terrestrial origin of DOM can also be determined by fluorescence characteristics. For example, the emission maximum wavelength (λ_{em}), in the range of 425–450 nm (Figure 7) clearly shows a terrestrially derived fluorescence pattern for soil C-DOM (Seritti et al. 1994).

The proportion of C-DOM was lower during the breakup season (i.e. May, Figure 6). The overlying ice had a lower concentration of C-DOM (Belzile et al. 2002) owing to the fractionation of DOM during ice formation, and thus the concentration of C-DOM in riverine waters was diluted when ice and snow started to melt. Except for the May samples (YR-01), the ratio of C-DOM to DOM was negatively correlated to discharge for the < 0.45 μm and HMW fraction ($r^2 = 0.87$ and 0.83, respectively, $n = 5$). The proportion of C-DOM in the bulk DOM is therefore higher in late summer (Figure 6). Moreover, the soil temperatures, which are maximal at the end of summer in the Tanana/Yukon uplands, could cause flushing out of DOM from the upper organic horizons

(McLean et al. 1999), consistent with the maximal soil-derived fraction of DOM being found in August–September.

The pedogenic contribution to DOC can be estimated by using the ratio of absorbance at 280 nm to DOC (a_{280}/DOC ratio; Wilkinson et al. 1997). In natural environments, a much higher a_{280}/DOC ratio is found for pedogenic than for aquagenic organic matter (~1.7; Buffle 1988). The Yukon River DOM, with a_{280}/DOC ratio of 57.3–73.0 $m^{-1}/(mmol\text{-}C\ l^{-1})^{-1}$ (Table 1), showed a pedogenic origin throughout the sampling season. The relative DOM composition, pedogenic organic matter vs. carbohydrate, can be estimated from both the a_{280}/DOC ratio and CHO concentrations, assuming a constant a_{280}/DOC ratio for the pedogenic contribution (Zumstein and Buffle 1989). We also assume that carbohydrates and pedogenic humic matter are the dominant autochthonous and pedogenic sources, respectively, as carbohydrates leached from soil make only a small contribution (Wetzel 1983). Accordingly, the DOM sample collected in May (YR-01) contained 26% of CHO and 74% of pedogenic humic matter (i.e. a_{280} /DOC = 64.9 $m^{-1}/(mmol\text{-}C\ l^{-1})^{-1}$, Table 1). The high percentage of pedogenic organic matter indicated that soil derived organic matter dominated the bulk DOM in the Yukon River. On average, the proportion of pedogenic DOM was estimated to be 76 ± 7% of the total DOM. The highest proportion of soil-derived DOM was measured at the end of the summer (82 and 83% for YR-05 and YR-06 samples, respectively). The overall lower contribution of aquagenic DOM (~24%) is further supported by the low Chl-*a* concentrations, and consistent with previous studies. In a study of White Clay Creek, 20% of the DOC was found to be derived from *in situ* production (Kaplan and Bott 1982). Similarly, Wilkinson et al. (1997) suggested that 11–29% of the DOC in Lake Bret was derived from biological processes. Concordance between these independent determinations indicates that terrestrially-derived C-DOM dominates the DOM pool in the Yukon River from breakup to the open-water season.

Conclusions

Concentrations of DOC in the Yukon River had a significant temporal variation. The highest DOC (up to 2825 μmol-C l^{-1}) was measured before the river ice broke up, followed by a rapid decrease from the peak in May to a stable, lower level between June and September. DOC transported by the Yukon River was predominately in the colloidal form with a size range from 0.001 to 0.45 μm. Within the bulk DOC pool, on average, colloidal organic carbon comprised up to 73 ± 6% of the bulk DOC, ranging from 84% in May to 68% in September. Similar to the variation trend of DOC concentrations, concentrations of all carbohydrate species, including MCHO and PCHO, decreased consistently from 722 μmol-C l^{-1} in May to 129 μmol-C l^{-1} in September. Within the TCHO pool, the percentage of

MCHO consistently increased from May to September despite the overall decrease in TCHO concentration. The hypothesis that transformation between organic carbon species is occurring was further supported by the optical properties observed for C-DOM in the HMW and LMW organic matter fractions. The characteristics of C-DOM indicates a typical DOM source from land weathering associated with snow and ice melting. About 50% of DOC flux occurred during the breakup period. The optical properties of C-DOM, overall low Chl-*a* concentrations and CHO abundance all point to a consistent pedogenic-dominated DOM source throughout the sampling seasons. The contribution of pedogenic DOC is estimated to be $76 \pm 7\%$ of the bulk DOC.

Acknowledgements

We gratefully acknowledge Travis Hines for his assistance during the field sampling. We thank two anonymous reviewers for valuable comments on earlier version of the manuscript. This work was supported, in part, by the Frontier Observational Research System for Global Change/IARC and a Swiss NSF fellowship.

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