

Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States

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[1] We investigated how the source and chemical character of aquatic dissolved organic carbon (DOC) change over the course of the runoff season (May–November, 1999) in Green Lakes Valley, a high-elevation ecosystem in the Front Range of the Colorado Rocky Mountains. Samples were collected on North Boulder Creek from four sites across an alpine/subalpine ecotone in order to understand how the transition from the lightly vegetated alpine to the forested reaches of the catchment influences aquatic DOC. Concentrations of DOC at the four sites peaked between 2.6 and 8.9 mg C L⁻¹ on the ascending limb of the snowmelt hydrograph, with the higher concentrations at the two subalpine sites. Seasonally, the chemical fractionation of DOC showed that there was a large range (29–72%) in the fulvic acid content of DOC at the four sites, with the highest fulvic acid percentages on the ascending limb of the hydrograph. Yields of DOC at the two gauged sites ranged from 10 to 11 kg ha⁻¹ over the season with between 45 and 50% of the yield occurring as fulvic acid DOC and the remainder as nonhumic material. The fluorescence properties of DOC from all four sites indicated that during peak runoff, DOC was derived primarily from terrestrial precursor material. However, seasonal changes in the fluorescence properties of fulvic acids at the highest elevation sites suggest that DOC derived from algal and microbial biomass in the lakes is a more important source of DOC above tree line during late summer and fall. We hypothesize that much of the autochthonous DOC production is a result of algal growth in alpine lakes. Further, comparison to a forested control catchment suggests that processes in the alpine reach of the catchment may alter both the amount and chemistry of DOC incident to the downstream subalpine aquatic system. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1615 Global Change: Biogeochemical processes (4805); 1851 Hydrology: Plant ecology; 1854 Hydrology: Precipitation (3354); 1860 Hydrology: Runoff and streamflow; *KEYWORDS:* DOC, biogeochemistry, snowmelt, chemical fractionation, fluorescence spectroscopy

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1. Introduction

[2] Dissolved organic carbon (DOC) constitutes the largest pool of organic carbon in most aquatic environments and consequently plays an important role in both biological and physical processes in these systems. The transport and fate of DOC in aquatic systems are determined by local

patterns of precipitation, biological and physical interactions, runoff, and river discharge [Hope *et al.*, 1997]. Despite the existence of DOC export budgets for rivers from a diversity of environments [e.g., Aitkenhead and McDowell, 2000], the chemical character of aquatic DOC and how it may change seasonally, longitudinally, and in response to extreme events has been studied in relatively few watersheds.

[3] The DOC load in aquatic ecosystems is a mixture of organic material derived from the soils and plants of the surrounding catchment (allochthonous) and from within the aquatic system (autochthonous). Allochthonous DOC is typically enriched in fulvic acids and highly colored

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[Thurman, 1985], while autochthonous DOC, derived from algal and bacterial biomass in aquatic systems, is characterized by a lower fulvic acid content and C:N ratio [McKnight *et al.*, 1994]. Thus the relative balance of these sources of DOC in aquatic systems can affect aquatic biota by altering the amount of energy available for heterotrophic growth [Schindler *et al.*, 1992; Wetzel, 1992], the depth of the photic zone [Scully and Lean, 1994], and the mobility of trace metals such as Al and Fe [McKnight *et al.*, 1992].

[4] In the past, most watershed-scale studies on carbon cycling have relied on measurements of bulk DOC concentrations because of the difficulty in chemically fractionating and characterizing DOC. The primary constraint on measuring the character of DOC has been the lack of analytical procedures that are readily applicable to large sample sets. The fractionation of DOC into operationally defined chemical constituents has proven useful for understanding how the quality of DOC changes as it percolates through organic and mineral soil horizons [e.g., Qualls *et al.*, 1991; Raastad and Mulder, 1999] and enters the stream channel [Easthouse *et al.*, 1992]. Moreover, several studies have cited shifts in DOC fractions as evidence that the dominant source of DOC in surface waters may change seasonally [Baron *et al.*, 1991; McKnight *et al.*, 1997]. Fractionation has also been used to investigate how the quality of DOC in freshwater and saltwater lakes is influenced by residence time and salinity [Curtis and Adams, 1995; Curtis and Schindler, 1997]. Here we apply analytical-scale chromatographic fractionation to evaluate how the chemical character of stream water DOC changes in an alpine/subalpine catchment over an entire runoff season.

[5] In addition to evaluating the nature and importance of changes in DOC chemistry, advances in the use of fluorescence spectroscopy to study DOM have the potential to aid in interpreting spatial and temporal changes in DOM precursor material. The analysis of DOM sources using fluorescence spectroscopy is based on the fact that allochthonous fulvic acids derived from terrestrial organic material have different fluorescence properties than autochthonous fulvic acids derived from aquatic organic material. Further, these differences can be quantitatively characterized by a relatively simple fluorescence index (FI) [McKnight *et al.*, 2001]. The FI values of fulvic acids have previously been used to track historic changes in the source of humic material in lake sediments [Wolfe *et al.*, 2002; Waters, 2003,] and marine sediments [Klapper *et al.*, 2002] as well as to identify differences in the source of DOM in surface waters between different geographic regions [McKnight *et al.*, 2001]. However, to our knowledge, fluorescence properties have not previously been used to track intra-annual changes in the source of aquatic DOM at the catchment scale.

[6] This study focuses on the source and chemical character of aquatic DOC in the North Boulder Creek watershed, a high-elevation alpine/subalpine catchment in the Colorado Front Range. In montane watersheds, as much as 80% of DOC enters the aquatic system during spring snowmelt [Lewis and Grant, 1979; Hornberger *et al.*, 1994; Boyer *et al.*, 1997]. We investigated DOC in soil and surface waters along a longitudinal transect in the North Boulder Creek watershed during the 1999 snowmelt runoff season from May to November. The chemical character and

fluorescence properties of DOC were measured in order to evaluate (1) how the chemical character and source of DOC change over time at an individual site, (2) how the chemical character and source of DOC change moving downstream from the alpine to the forested reaches of the catchment, and (3) the relative importance of aquatic versus terrestrial sources of DOC production. Further, samples from a subalpine site on North Boulder Creek are compared with samples from a nearby forested control catchment, Como Creek, in order to evaluate the influence of alpine landscapes on the quantity and chemical of DOC in downstream aquatic systems. The use of chemical fractionation in concert with fluorescence spectroscopy allows us to develop a conceptual model of the terrestrial/aquatic linkages governing DOC cycling at the catchment scale.

2. Site Description

[7] The North Boulder Creek basin drains east off the Continental Divide in the Colorado Front Range, United States (Figure 1). The watershed is located in the Green Lakes Valley, which is owned by the city of Boulder, and public access is prohibited. As a result, the watershed is not subject to the direct anthropogenic impacts of other high-elevation sites in the Front Range.

[8] Climate is characterized by long, cool winters and a short growing season (1–3 months). Mean annual temperature is -3.8°C , and mean annual precipitation is 1000 mm [Williams *et al.*, 1996a]. Approximately 80% of the annual precipitation occurs as snow that typically accumulates from October to April [Caine, 1996]. Inorganic N deposition in wetfall is approximately $4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ [Williams and Tonnessen, 2000]. Snowmelt is the dominant hydrologic event of the year, with about 70% of annual runoff occurring between late April and mid-July. Summer rainfall has very little hydrologic influence in the catchment [Caine, 1996]. Surface waters have low concentrations of inorganic and organic solutes; specific conductance ranged from 5 to $35 \mu\text{S cm}^{-1}$ at all sample sites in 1999.

[9] The 5 km^2 of the catchment above Lake Albion is unforested and alpine in nature (Figure 1). Steep rock walls and talus slopes are the dominant landforms, and soils are limited in extent, depth, and development as a result of late Pleistocene glaciation [Madole, 1982]. Catchment soils are a mixture of Cryic Inceptisols and Entisols with Histosols in wetter areas on the valley floor [Burns, 1980]. Primary production by phytoplankton and benthic diatom communities in the lakes located in the upper valley is seasonally variable. Measurements at Green Lake 4 show that chlorophyll *a* concentrations increased by almost a factor of 20, from $0.03 \mu\text{g L}^{-1}$ during spring snowmelt to $0.56 \mu\text{g L}^{-1}$ in the late summer and fall [Waters, 2003].

[10] Below Lake Albion the catchment is dominated by a mixed conifer forest composed primarily of subalpine fir (*Abies lasiocarpa*) and Engelmann spruce (*Picea engelmannii*) with some limber pine (*Pinus flexilis*) at tree line and regrowth lodgepole pine (*Pinus contorta*) lower in the basin. This portion of the catchment is typified by developed soils on glacial till and moraine deposits overlying granitic and metamorphic parent material. Soils are Inceptisols and intermixed Alfisols with Histosols in wet meadow areas. Soil depths range from 30 to 100 cm with deeper soils

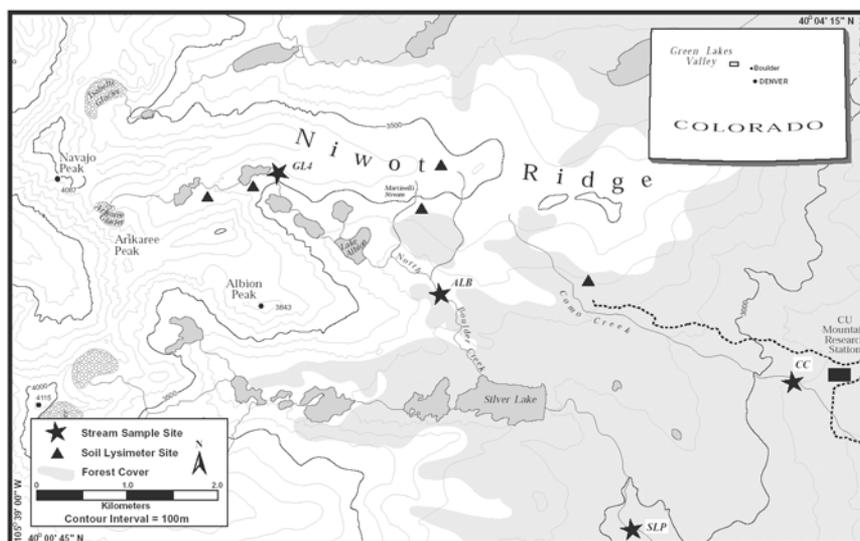


Figure 1. North Boulder Creek watershed in the Green Lakes Valley, Colorado Front Range, United States. In 1999, surface water samples were collected at an alpine site above tree line (GL4), a tree line site (ALB), and a forested site (SLP). Additional samples were collected in the forested Como Creek catchment (CC) at a site adjacent to the University of Colorado Mountain Research Station. Soil water samples were collected from zero-tension lysimeters at five sites marked with triangles.

on well-drained glacial moraines. Soil pH values range from 4.5 to 6.0.

[11] Water samples were collected at three sites along a transect on North Boulder Creek extending from Green Lake 4 at 3535 m to a site located 5 km below tree line (SLP) at 2963 m (Figure 1). The sites extend from the high alpine upper valley to the subalpine forested reaches of the catchment and range in basin area from 42 to 2700 ha (Table 1). Additional samples were collected on Como Creek, a tributary stream draining the SE flank of Niwot Ridge (Table 1). The headwaters of Como Creek extend slightly above tree line to 3560 m in elevation. Greater than 80% of the watershed is mixed conifer forest with some aspen (*Populus tremuloides*). Como Creek watershed has similar climatology, snowfall amount, and atmospheric deposition as the adjacent North Boulder Creek Catchment [Hood *et al.*, 2003]. However, Como Creek differs from North Boulder Creek in two important respects: (1) There are no lakes in the catchment, and (2) there is little alpine area and no talus or exposed bedrock. Thus Como Creek drainage acts as a control to evaluate the influence of alpine areas on the downstream concentrations, chemical character, and source areas of DOC. Stream samples from Como Creek were collected at the University of Colorado Mountain Research Station at an elevation of 2900 m (Figure 1). The watershed area above the sampling site is 664 ha.

3. Methods

3.1. Water Samples and Discharge Measurements

[12] During the 1999 snowmelt season (May–October), surface water samples were collected as 1 L or 500 mL grab samples at weekly to biweekly intervals at all four sites (GL4, ALB, SLP, and CC). In order to better evaluate seasonal changes in fluorescence characteristics, grab samples were collected again from GL4 in June and August

2000. Soil water samples were collected from five locations in 1999 after they became snow-free in June and July (Figure 1). Soil water was collected from zero-tension lysimeters at shallow depths (10–30 cm). The design and installation of the soil lysimeters are described by Litour [1993] and Williams *et al.* [1996b]. All water samples were collected in precombusted amber glass bottles with Teflon-lined caps and filtered through precombusted Gelman G/F glass fiber filters with a nominal pore size of 0.7 μm . The majority of samples were filtered in the field, and all samples were filtered within a day of collection. Samples were stored at 4°C until fractionation and analysis, which occurred within 2 weeks of sample collection. DOC was determined by high-temperature catalytic oxidation using a Dohrmann organic carbon analyzer at the Institute of Arctic and Alpine Research in Boulder, Colorado. Three replicate analyses were conducted for each sample. Standard deviation was typically 0.08 mg C L⁻¹ with a range of 0.01–0.2 mg C L⁻¹.

[13] At two sites (GL4 and ALB), water level was measured with a pressure transducer and converted to volumetric discharge by empirical ratings that are validated by gauging at different flow levels for each season [Caine,

Table 1. Stream Sampling Sites on North Boulder Creek and Como Creek for 1999^a

Site	Abbreviation	Elevation, m	Catchment Area, ha	Landscape Type
Green Lake 4	GL4	3550	221	alpine
Albion Townsite	ALB	3250	710	tree line
Silverlake Road	SLP	2963	2720	subalpine forest
Como Creek	CC	2910	664	subalpine forest

^aThe GL4, ALB, and SLP sites extend from the alpine to the subalpine along an 8 km elevational transect on North Boulder Creek. The CC site on Como Creek is located in a forested subsidiary catchment of North Boulder Creek.

1996]. These ratings remained consistent through the period of study. During 1999, water levels were recorded on a 10-min interval at GL4 and an hourly interval at ALB. At the SLP and CC sites, stage height measurements were taken weekly in Parshall flumes.

3.2. DOC Characterization

3.2.1. Fractionation

[14] A 200 mL subsample of every 1 L surface water sample was fractionated into hydrophobic (humic) and hydrophilic (nonhumic) fractions using analytical-scale column chromatography with XAD-8 Amberlite resin according to the methods of *Thurman and Malcolm* [1981]. The hydrophobic fraction, which sorbs to the XAD-8 resin, is composed of fulvic and humic acids. However, in the surface waters we are measuring, the hydrophobic fraction is typically composed primarily (>90%) of fulvic acids [*Thurman*, 1985]; therefore we refer to the hydrophobic fraction as fulvic acids following the terminology of *Baron et al.* [1991]. The fulvic acid fraction was determined by back-eluting the XAD-8 resin with 0.1 N NaOH and measuring the DOC concentration of the eluate after acidification to pH 2 with concentrated phosphoric acid. What we refer to as the nonhumic fraction is a heterogeneous class of substances that passes through the XAD-8 resin and is composed predominantly of hydrophilic organic acids and low molecular weight compounds including carbohydrates, carboxylic acids, and amino acids [*Thurman*, 1985]. The nonhumic fraction was calculated by measuring the DOC concentration of the effluent from the XAD-8 resin. Mass balance analyses show that DOC recovery was almost complete, with the sum of the DOC measured in the fulvic and nonhumic fractions typically between 95 and 105% of DOC in the original sample.

3.2.2. Fluorescence

[15] The fluorescence of fulvic acids is primarily related to the presence of quinone moieties and their oxidation state [*Klapper et al.*, 2002]. Fluorescence measurements were made on fulvic acids isolated from the weekly surface water samples. Fulvic acid solutions from the fractionation procedure were adjusted to pH 2 using concentrated phosphoric acid. Fluorescence was measured using a Fluoromax-2 multiwavelength fluorescence spectrophotometer with a xenon lamp. Emission intensities were measured at 450 nm and 500 nm using an excitation of 370 nm in order to calculate the fluorescence index (FI) following the procedure of *McKnight et al.* [2001]. The intensity values for both the 450 nm and 500 nm scans were adjusted by subtracting the intensity of the blank. The FI was calculated as the ratio of the emission intensity at 450 nm to that at 500 nm with the 370 nm excitation. The standard deviation of samples analyzed in triplicate was typically less than 0.01. *McKnight et al.* [2001] describe a difference in the FI of ~0.1 as being potentially indicative of a difference in fulvic acid precursor material. For a small number of samples, fluorescence measurements were made over a wide range of emission (400–550 nm) and excitation (250–400 nm) values in order to construct three-dimensional excitation-emission matrices (EEMs).

[16] Fluorescence properties of fulvic acids are related to the presence or absence of lignin in precursor materials and, as such, can serve as a simple tool to distinguish whether

fulvic acids are derived from aquatic microbial material or terrestrial material. Following the procedure of *McKnight et al.* [2001], the fluorescence properties of aquatic fulvic acids isolated from North Boulder Creek were compared to the fluorescence properties of two reference fulvic acids that are derived predominantly from either aquatic or terrestrial precursor material. The fulvic acids characteristic of aquatic precursor material were isolated from Lake Fryxell in the McMurdo Dry Valleys of Antarctica where algal and bacterial material in the water column and littoral zone are the primary source of dissolved organic material [*McKnight et al.*, 1994]. The fulvic acids characteristic of terrestrial precursor material were isolated from the Suwannee River in the Okefenokee swamp in Georgia. These fulvic acids are derived from vegetation and decaying peat and are a well-characterized standard reference of the International Humic Substances Society [*Averett et al.*, 1989].

3.2.3. DOC Yield Calculations

[17] The seasonal yields of DOC in surface water were estimated at the two gauged sites (GL4 and ALB) for the period May–October according to the following equation:

$$\text{DOC yield(kg)} = ([\text{DOC}] \times Q)/1000,$$

where [DOC] is the measured DOC concentration (mg L^{-1}) in a given sample period and Q is the discharge (m^3) in a sample period centered on the day of sampling. Yields of fulvic acid and nonhumic fractions of DOC were estimated by multiplying the DOC yield for each sample period by the percentage of the coincident DOC sample that was either fulvic acid or nonhumic, based on results from the chromatographic fractionation.

[18] Weekly yields of DOC, fulvic acid, and nonhumic material were also calculated for both GL4 and ALB. For periods when samples were collected at intervals larger than 1 week (August–October), multiweek yields were divided into individual weeks based on weekly discharge.

4. Results

4.1. Hydrology

[19] Snowfall in Green Lakes Valley in 1999 was within 5% of the long-term average. At the ALB site, seasonal (May–October) discharge of 4,088,818 m^3 was 97% of a 16 year average. The hydrographs at the two gauged sites on North Boulder Creek, GL4 and ALB, demonstrate the markedly seasonal flows characteristic of snowmelt dominated catchments. At both sites, daily discharge began to increase in the third week of May and with peak discharge occurring in late June (GL4) and early July (ALB) (Figure 2a). The large spike in discharge at GL4 in early June was the result of the failure of a natural ice dam upstream on Green Lake 5 and a subsequent flood wave. Weekly stage height measurements at SLP and CC indicated that streamflow peaked between 15 June and 22 June at those two sites.

4.2. DOC: Concentrations and Yields

[20] Dissolved organic carbon concentrations at all four sites showed a peak on the ascending limb of the snowmelt hydrograph (Figure 2b). For the season, DOC concentrations were consistently highest at CC, the for-

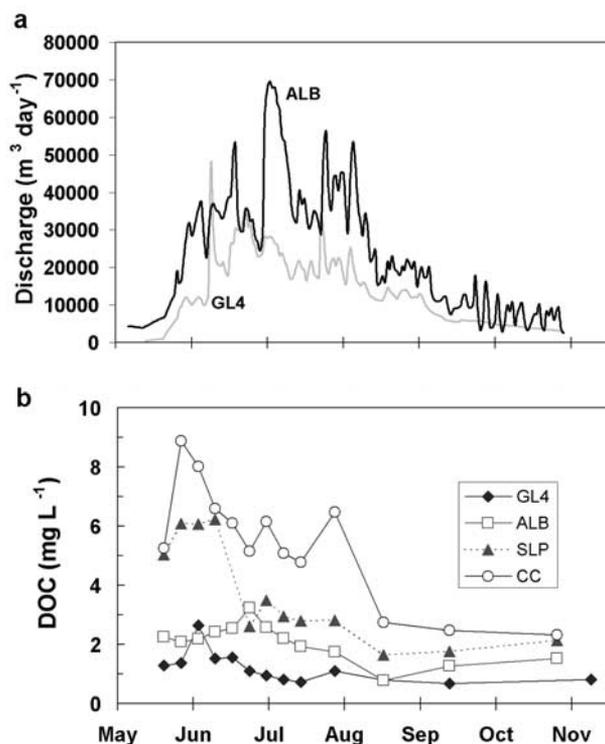


Figure 2. April to November 1999 stream discharge at the two gauged sample sites, GL4 and ALB (Figure 2a), and seasonal concentrations of dissolved organic carbon (DOC) at the four sample sites (Figure 2b). Peak DOC concentrations at all sites occurred early in the season in May and June.

ested control catchment, and lowest at the alpine GL4 site. However, after 19 August, concentrations were $<3 \text{ mg L}^{-1}$ at all four sites. The difference in concentrations among sites was most pronounced from mid-May to mid-June when DOC concentrations at the subalpine sites were 3–5 times higher compared to the alpine (GL4) and tree line (ALB) sites.

[21] Dissolved organic carbon concentrations in 10 hill-slope lysimeters varied substantially throughout the catchment (Table 2). Dissolved organic carbon concentrations ranged from 37.8 mg C L^{-1} at a site in the riparian zone near GL4 to 9.4 mg C L^{-1} at an alpine tundra site on the

south flank of Niwot Ridge. Concentrations were generally higher at the riparian sites, although this difference could be partially a result of the earlier sampling dates for the riparian sites (late June) compared to the forest, tundra, and snow-field sites which were sampled in late July. The range of soil water DOC concentrations was 10–20 times higher than surface water DOC concentrations measured at proximate sites on the same sample dates.

[22] Over the entire sampling season (May–October), the area weighted yields of DOC were relatively similar between the two gauged sites (Table 3). At GL4, the yield of DOC was 10.5 kg ha^{-1} and increased by only 4% to 10.9 kg ha^{-1} moving downstream to the ALB site at tree line. The yield of DOC for the area of the ALB catchment located below the GL4 catchment was 11.2 kg ha^{-1} , which was higher than either of the individual catchments.

4.3. Chemical Fractions of DOC: Seasonal Trends and Yields

[23] Seasonally, fulvic acids comprised between 29–72% of the DOC at the four sites (Figure 3a). Paralleling bulk DOC concentrations, the fulvic acid content of DOC at all four sites peaked on the ascending limb of the hydrograph and was highest at the two subalpine sites (CC and SLP) and lowest at the alpine site (GL4). The alpine GL4 site showed the widest range in the fulvic acid content of DOC, with a peak in fulvic acid content of 69% in late May followed by a reduction to 40% by mid-July (Figure 3a). The peak in fulvic acid content at ALB and SLP was similar to that at GL4, although the decline in fulvic acid on the descending limb of the hydrograph was less pronounced at these sites. Fulvic acid content at CC showed a diffuse peak 2–3 weeks later than the North Boulder Creek sites and remained elevated ($>50\%$) throughout the sampling period. At all four sites, seasonal variations in the fulvic acid content of DOC appeared to be related to discharge. The fulvic acid content of DOC from the GL4 site showed a clockwise hysteresis with consistently higher values on the ascending limb of the hydrograph compared to the descending limb (Figure 3b). This pattern was similar at the other sites, although the range for the fulvic acid content of DOC was smaller, particularly at the two forested sites.

[24] Partitioning of catchment DOC yields into fulvic acid and nonhumic constituents highlights downstream differences in the chemical composition of DOC being exported in North Boulder Creek. In the GL4 catchment,

Table 2. Dissolved Organic Carbon (DOC) Concentrations and Fulvic Acid Fluorescence Index (FI) Values for 10 Soil Lysimeters in the North Boulder Creek Catchment Sampled in 1999

Site	Date Sampled	Landscape Type	DOC, mg L^{-1}	FI
GL4 ZT2B	23 June	alpine riparian	20.7	1.22
GL4ZT2C	23 June	alpine riparian	27.6	1.26
GL4ZT13	23 June	alpine riparian	37.8	1.19
GL5ZTWL	19 July	alpine riparian	35.9	1.27
KIOZT10	19 July	alpine riparian	17.3	1.25
SODZT10A	23 June	subalpine forest	17.1	1.33
SUBZT10B	20 July	alpine tundra	14.4	1.20
SUBZT30A	20 July	alpine tundra	9.4	1.25
SUBZT30B	20 July	alpine tundra	16.1	1.25
MAZT4B	23 June	alpine snowfield	12.8	1.32
Average			20.9	1.25
Standard deviation			9.7	0.05

Table 3. Seasonal Area-Weighted Yields of Bulk DOC, Fulvic Acid DOC, and Nonhumic DOC at the Two Gauged Sites GL4 and ALB

Site	Bulk DOC, kg ha ⁻¹	Fulvic Acid DOC, kg ha ⁻¹	Nonhumic DOC, kg ha ⁻¹
GL4	10.5	4.7	5.8
ALB	10.9	5.5	5.4
ALB-GL4 ^a	11.2	5.9	5.2

^aRefers to the portion of the ALB catchment located below GL4.

the nonhumic DOC yield of 5.8 kg ha⁻¹ was 23% greater than the fulvic acid DOC yield of 4.7 kg ha⁻¹ (Table 3). Downstream at the tree line ALB site, there was a shift in the composition of the DOC yield with fulvic acid export of 5.5 kg ha⁻¹ only slightly greater than the yield of 5.4 kg ha⁻¹ for nonhumic DOC. The difference between the composition of the DOC yields from the GL4 and ALB catchments indicates that the DOC yield from the portion of the ALB catchment located below GL4 was composed of more fulvic acid material compared to the DOC yield from alpine reach of the catchment above GL4. Thus, as soils coverage and vegetation increased below GL4, the catchment yield of humic material increased by 25% to 5.9 kg ha⁻¹, while the yield of nonhumic material decreased by 9% to 5.3 kg ha⁻¹ (Table 3).

[25] Seasonally, the chemical character of the DOC yield at GL4 shifted from being predominantly fulvic acids during peak snowmelt to predominantly nonhumic material after mid-June (Figure 4a). At ALB, the character of the weekly yield of DOC was similarly dominated by fulvic acids during snowmelt; however, the shift toward a predominance of nonhumic material at ALB did not occur until August (Figure 4b). At both sites, this pattern illustrates that the decrease in the yield of fulvic acid material after peak flow is more rapid than the decrease in the leaching of nonhumic material. The peak in nonhumic material evident at both GL4 and ALB in late July was a result of a substantial increase in discharge associated with a large rain event (27 mm of precipitation) on July 24. It is likely that the proportion of DOC as fulvic acid was higher than we report during this event due to the flushing of humic material from catchment soils; however, this cannot be verified because the storm occurred between dates on which DOC was sampled and fractionated.

4.4. Fluorescence Characteristics of DOC

[26] For the 1999 snowmelt season, FI values for aquatic fulvic acids isolated in Green Lakes Valley had a range of 1.23–1.54, which was within the range of the terrestrial (Suwannee River) and aquatic (Lake Fryxell) reference fulvic acids (1.24–1.77). The FI values for fulvic acids from all four sites showed minima close to the terrestrial Suwannee River fulvic acid shortly preceding and coincident with peak snowmelt runoff in early to mid-June (Figure 5a). Fulvic acids from the subalpine Como Creek site had the lowest seasonal FI values, rarely exceeding 1.3. Fluorescence index values for fulvic acids from the alpine GL4 site were the highest measured on all but two dates and showed the largest seasonal range (0.28) of the four sites. The difference in the magnitude of the FI at GL4 relative to the other three sites was most pronounced after North Boulder

Creek returned to lower flows (<15,000 m³ d⁻¹ at GL4) in August. The temporal variations in the FI at GL4 were significantly correlated with the fulvic acid content of DOC ($R^2 = 0.54$, $p < 0.001$, $n = 12$). The relationship between the FI and the fulvic acid content of DOC was not significant at the other three sites ($p > 0.1$ for all comparisons). Similar to the fulvic acid content of DOC, the FI values of fulvic acids were related to discharge at all four sites. This relationship was most clearly defined at GL4 where the FI showed a counterclockwise hysteresis with lower values on the ascending limb of the hydrograph compared to the descending limb (Figure 5b). The pattern was similar at the other three sites although the range for the FI was smaller, particularly at the forested sites.

[27] To aid in the interpretation of FI values for fulvic acids collected in Green Lakes Valley, we evaluated the fluorescence properties of the two reference fulvic acids representing terrestrial material (Suwannee River) and aquatic microbial material (Lake Fryxell). For the Suwannee River fulvic acid, fluorescence measurements were made over a wide range of emission (400–550 nm) and excitation (250–400 nm) values. The resulting EEMs were very similar to results reported by McKnight *et al.* [2001] and had consistently similar FI values. In total, six Suwannee River fulvic acid samples ranging in concentration from 1 to 10 mg L⁻¹ had an average FI value of 1.24 with a standard deviation of 0.01. Thus it appears that FI values remain

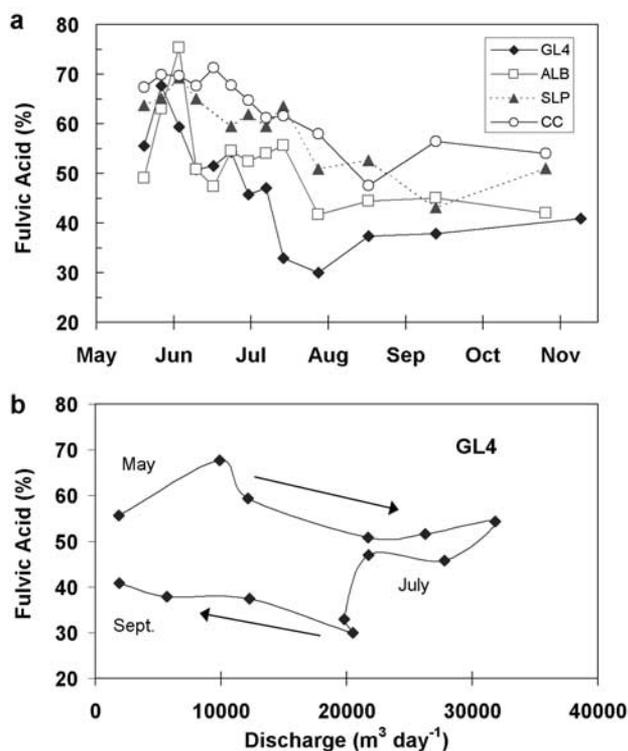


Figure 3. Fulvic acid content of DOC at the four sample sites over the snowmelt runoff season (Figure 3a) and the relationship between the fulvic acid content of DOC and discharge at a single site, GL4 (Figure 3b). Maxima in the fulvic acid content of DOC occurred close to the peak in snowmelt runoff in June.

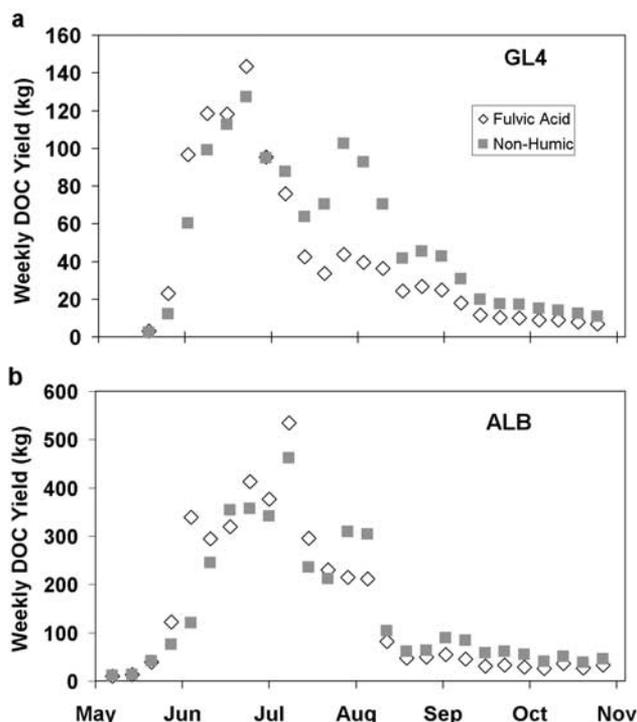


Figure 4. Weekly yields (kilograms) for fulvic acid and nonhumic DOC over the sampling season for (a) GL4 and (b) ALB. At both sites, yields of fulvic acid DOC were higher during the initiation and peak of snowmelt and yields of nonhumic material dominated catchment DOC yield on the descending limb of the hydrograph.

stable over the range of concentrations of the fulvic acid samples we collected in Green Lakes Valley. Moreover, the FI values of the Suwannee River fulvic acids were highly consistent with the FI values for fulvic acids collected from soil lysimeters throughout Green Lakes Valley, which had an average value of 1.24 and a range of 1.19–1.33 (Table 2). For the Lake Fryxell fulvic acids, EEMs from six samples ranging in concentration from 1 to 10 mg L⁻¹ were also similar to the results of *McKnight et al.* [2001] and had an average FI value of 1.72 with a standard deviation of 0.02. It is worth noting that the FI values of our reference fulvic acids (1.22 and 1.74) were very similar in range, but lower in magnitude, than those described by *McKnight et al.* [2001] (1.4–1.9), suggesting that FI values are somewhat dependent on fluorometer configuration and highlighting the need to calibrate an instrument with fulvic acids of known origin.

[28] The excitation-emission matrices for fulvic acids collected at GL4 during the snowmelt season in 2000 provide further evidence of the utility of the two reference fulvic acids by demonstrating that the seasonal change in the FI is a result of changes in the properties of the two dominant fulvic acid fluorophores. The fulvic acid sample collected near peak runoff (22 June) showed an emission peak of 444 nm for an excitation of 327 nm (Figure 6a) and a second emission peak of 445 nm for an excitation of 230 nm (not shown). The emission peaks in this sample are shifted toward slightly longer wavelengths, which is

similar to the EEM for the Suwannee River fulvic acid and is consistent with a larger proportion of terrestrial precursor material such as lignin [*McKnight et al.*, 2001; *Klapper et al.*, 2002; *Wolfe et al.*, 2002]. In contrast, the fulvic acids collected late in the runoff season (18 August) had emission maxima occurring at lower wavelengths for both fluorophores (Figure 6b), which is similar to the EEMs from fulvic acids isolated in Antarctica and indicates an increase in the amount of aquatic (algal and microbial) precursor material [*McKnight et al.*, 2001]. The corresponding FI values for the EEMs of the fulvic acids isolated at GL4 in 2000 were 1.28 in mid-June and 1.50 in August, which mirrors the seasonal pattern of FI values observed in 1999.

5. Discussion

5.1. Seasonal Concentrations and Yields of DOC

[29] The range of DOC concentrations in North Boulder Creek sites is consistent with the results of previous studies in alpine/subalpine catchments in the Colorado Rocky Mountains [*Baron et al.*, 1991; *Boyer et al.*, 1997; *Brooks et al.*, 1999]; however, DOC concentrations in Como Creek are on the high end for headwater catchments. The early

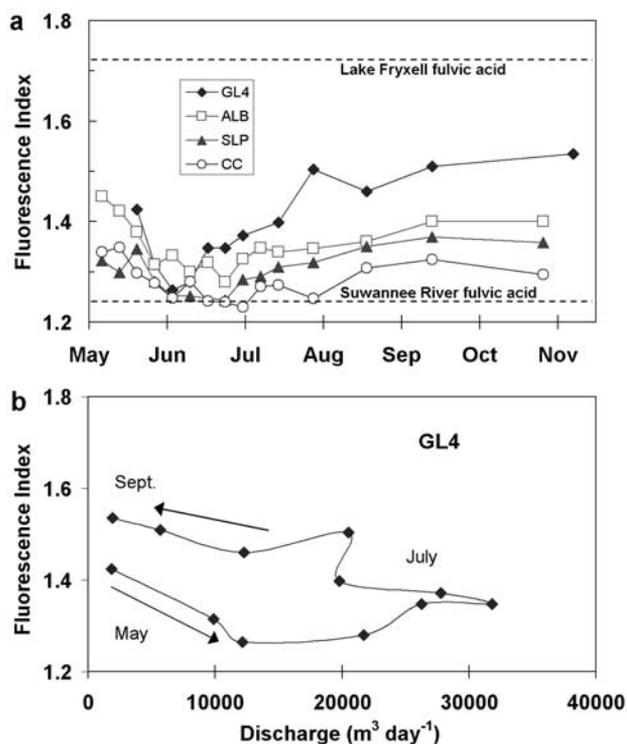


Figure 5. Fluorescence index (FI) of fulvic acid at the four sample sites over the snowmelt runoff season (Figure 5a) and the relationship between the FI and discharge at one site, GL4 (Figure 5b). Values of the terrestrial (Suwannee River = 1.24) and microbial (Lake Fryxell = 1.74) end-member fulvic acids are shown as dashed lines. The FI of fulvic acids at all four sites approached the value of the Suwannee River terrestrial reference fulvic acid during peak snowmelt runoff in June.

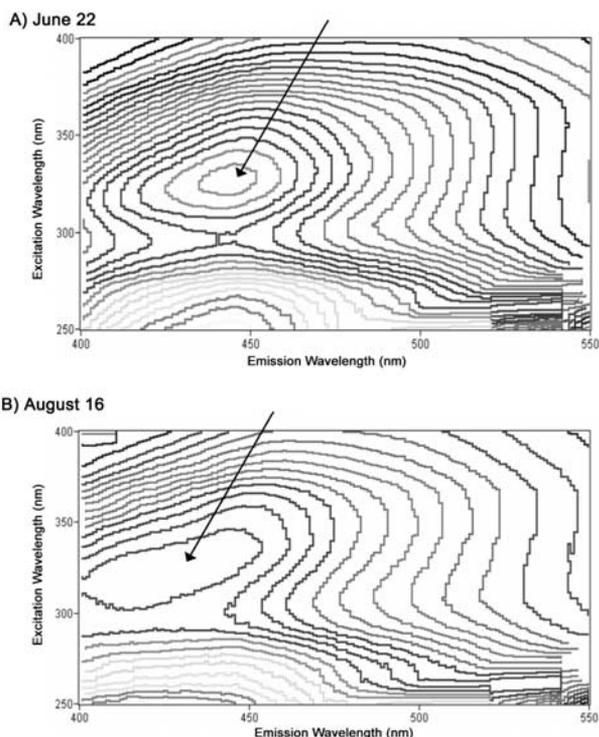


Figure 6. Excitation emission matrices (EEMs) for fulvic acids collected at GL4 near peak flow (Figure 6a) and during lower flows late in the season (Figure 6b). The primary emission peaks for both EEMs are denoted by arrows. The FI values for these samples were 1.28 (Figure 6a) and 1.50 (Figure 6b).

season peak in DOC concentrations evident at all four sites is consistent with the hypothesis that in seasonally snow covered catchments a finite reservoir of soluble organic carbon builds up in near-surface soils over the winter and is flushed during spring snowmelt [Hornberger *et al.*, 1994; Boyer *et al.*, 1997; Brooks *et al.*, 1999]. The dramatic difference between soil water DOC concentrations ($9\text{--}38\text{ mg C L}^{-1}$) and surface water DOC concentrations ($1\text{--}5\text{ mg C L}^{-1}$) in late June and July suggests that sorption processes in mineral soil horizons play an important role in catchment DOC retention [e.g., Kaiser *et al.*, 1996] during peak snowmelt runoff. Previous research in both arctic [Michaelson *et al.*, 1998] and alpine/subalpine [Boyer *et al.*, 1997] watersheds has shown similarly large decreases in DOC concentrations (as much as 95%) moving from soil solution into the stream channel. After peak snowmelt, concentrations of DOC declined to low levels ($1\text{--}3\text{ mg C L}^{-1}$), consistent with the concept that near-surface reservoirs of soluble organic carbon become depleted and streamflow is increasingly sustained by groundwater flow. This temporal trend is markedly different from catchments with deciduous forests where leaching from freshly produced deciduous litter in the fall explains much of the seasonality in DOC concentrations [Hongve, 1999].

[30] The increase in DOC concentrations (2–5 times) moving from the alpine to the subalpine is consistent with previous work showing that DOC concentrations in stream water are strongly related to soil organic C pools at small

spatial scales [Aitkenhead *et al.*, 1999]. The GL4 catchment has limited soils coverage ($\sim 25\%$), sparse vegetation, and soil microbial activity is generally C limited [Williams *et al.*, 1997]. DOC leaching from alpine tundra can be substantial [Williams *et al.*, 2001]; however, in Green Lakes Valley tundra vegetation is limited in areal extent, occurring only on ridge tops and in small outcrops and riparian zones in the valley bottom. As a result, stream water DOC concentrations are low throughout the season in the alpine. Below tree line at the SLP and CC sites, the stocks of organic carbon in catchment soils increase [Hood *et al.*, 2003], which is consistent with the higher DOC concentrations in stream water. The fact that concentrations of DOC were higher at CC compared to SLP may be due to differences in land cover. The Como Creek catchment is predominantly forested, whereas the SLP site receives streamflow from the lightly vegetated alpine reach of North Boulder Creek that is dilute with respect to DOC. In contrast to previous results demonstrating that alpine areas subsidize the inorganic nitrogen load in downstream aquatic systems [Hood *et al.*, 2003], this finding suggests that stream water from the alpine may be diluting the DOC load in downstream aquatic systems.

[31] Reports of DOC yields for high-elevation catchments are rare. The $10\text{--}11\text{ kg C ha}^{-1}$ we report for our gauged catchments is on the low end of yields reported from 21 forested watersheds in the United States ($7\text{--}34\text{ kg C ha}^{-1}$ [Tate and Meyer, 1983]) and 30 forested catchments from the cool conifer biome ($15\text{--}74\text{ kg C ha}^{-1}$ [Aitkenhead and McDowell, 2000]). The DOC yield for the ALB catchment was very similar to that for the GL4 catchment despite the substantial increase in soil coverage and vegetation below GL4. This finding suggests that the area of the catchment that is actively contributing to the yield of DOC may be similar in both catchments.

5.2. Chemical Characteristics of DOC

[32] The seasonal range for the fulvic acid content of DOC that we report encompasses published figures for other seasonally snow-covered catchments in Colorado [Baron *et al.*, 1991; McKnight *et al.*, 1992] but is substantially higher than ranges reported for a variety of forested lake ecosystems in Canada where the fulvic acid content of DOC varied by less than 10% annually [Schiff *et al.*, 1990; Curtis and Adams, 1995]. On North Boulder Creek, the early season peak in fulvic acid content of DOC at all four sample sites indicates that there is a pronounced shift in the chemical character of stream water DOC during snowmelt. In a tundra-dominated catchment on the North Slope of Alaska, Michaelson *et al.* [1998] reported a similar fulvic acid component of DOC during snowmelt and noted a strong similarity in the chemical composition of DOC in soil and stream water. The clockwise hysteresis in the fulvic acid content of DOC at our sites similarly suggests that the higher stream water DOC concentrations during peak runoff in North Boulder Creek reflect an increase in the transport of humic DOC from catchment soils. The relative increase in the fulvic acid content of DOC during snowmelt should be accompanied by a shift in the elemental content of DOM toward higher C:N ratios because fulvic acids have a low N content (1.5–3.5%) relative to nonhumic material [McKnight *et al.*, 1985; McKnight *et al.*, 1997]. Thus our chemical data are consistent with previous research in

snowmelt dominated catchments showing an increase in the C:N ratio of bulk DOM during snowmelt [Stepanauskas *et al.*, 2000; Williams *et al.*, 2001].

[33] The decrease in the fulvic acid content of DOC evident at all four sites on the descending limb of the hydrograph is consistent with potential changes in both hydrologic flow paths and DOM yield at the catchment scale. In terms of hydrology, high-elevation catchments are characterized by a shift toward deeper flow paths after peak snowmelt, with as much as 69–95% of streamflow originating from subsurface flow via mineral soil horizons [Caine, 1989; Sueker *et al.*, 2000]. This has important implications for the chemical composition of stream water DOC because in mineral soil horizons fulvic acids are preferentially sorbed compared to nonhumic material [Qualls and Haines, 1991; Easthouse *et al.*, 1992]. As a result, periods when water is routed via deeper flow paths through mineral soils should be accompanied by a relative decrease in the fulvic acid fraction of DOC in surface waters. This hypothesis is consistent with the seasonal trend in DOC chemistry we observed in that during the late summer and fall the fulvic acid content of DOC decreased to 50% or less at all four sample sites. The seasonal decrease in the fulvic acid content of DOC is also consistent with a relative increase in the amount of DOC derived from within-lake aquatic production. McKnight *et al.* [1994] have previously shown that DOC in Antarctic lakes derived from algal/microbial sources has a low fulvic acid content (~15–25%) compared to DOM derived from terrestrial sources, which have a fulvic acid content of 50–90% [Thurman, 1985]. Thus the late summer decrease in the fulvic acid content of DOC to ~30–40% at GL4 and ALB suggests that stream water DOC in the alpine reaches of the catchment may be increasingly derived from algal precursor material on the descending limb of the hydrograph. In addition to the seasonal trend in DOC character, there was a consistent longitudinal trend toward a higher fulvic acid content of DOC with decreasing elevation. This pattern would suggest that autochthonous DOM may comprise a relatively smaller proportion of stream water DOC moving in the downstream direction.

[34] To our knowledge, there are no reports of watershed yields of the humic and nonhumic components of DOC in surface waters. Similar to the total DOC yield, the character of the DOC yield on North Boulder Creek did not shift dramatically moving from the alpine GL4 site to the tree line ALB site. However, comparing the GL4 catchment to the area of ALB below GL4 (ALB-GL4), the shift in the chemical quality of the DOC yield is more apparent and reflects the differences in land cover and soils between these two reaches of the ALB catchment. At the downstream forested sites (SLP and CC), the chemical composition of the DOC yields shifts toward a predominance of humic material, consistent with the higher humic material content of DOC at these sites.

5.3. Fluorescence Properties of DOC

[35] The similarities between the FI values and the EEMs for fulvic acids collected in Green Lakes Valley and those of the reference fulvic acids suggest that the Suwannee River and Lake Fryxell fulvic acids are reasonable end-members for evaluating shifts in DOM precursor

material between terrestrial and aquatic sources. As such, the fluorescence properties of stream water fulvic acids provide a semiquantitative method for evaluating seasonal changes in the sources of DOM in surface waters. During peak snowmelt, the FI values of fulvic acids at all four sites converged on the value for the terrestrial end-member. This finding provides an independent line of evidence to corroborate the inferences from changes in the concentration and chemical composition of DOC that terrestrial precursor material is the dominant source of stream water DOC on the ascending limb of the hydrograph.

[36] At the GL4 site, elevated FI values both before the onset of snowmelt and on the descending limb of the hydrograph similarly agree with changes in DOC chemistry in suggesting that aquatic production can be an important source of stream water DOC in the alpine reach of the catchment. The likely source of this aquatic DOC is autochthonous algal and microbial production in alpine lakes. The importance of these lakes as a DOC source has been inferred previously based on downstream changes in particulate/dissolved organic carbon ratios, stable carbon isotope ratios, and the elemental composition of fulvic acids [Baron *et al.*, 1991; McKnight *et al.*, 1997]. Moreover, the timing of shifts in the FI is consistent with phytoplankton studies in Front Range alpine lakes showing that algal growth is substantial during winter and spring ice cover [Spaulding *et al.*, 1993] and during late season base flow [McKnight *et al.*, 1990; Waters, 2003].

[37] Over the entire study period, FI values for fulvic acids showed a relatively consistent decrease moving from the alpine to the subalpine. This trend is again consistent with the downstream increase in the fulvic acid content of DOC in suggesting that there is an increase in the proportion of DOC derived from terrestrial material in the lower reaches of the catchment. However, because DOC from algal/microbial precursor material is predominantly non-humic material, it is a more efficient substrate for bacterial growth [Moran and Hodson, 1990]. Thus it is alternatively possible that the longitudinal trend in FI values is due in some part to the depletion of aquatic DOC as a result of metabolism in the water column and hyporheic zone. Interestingly, the FI values at SLP, the forested site on the North Boulder Creek transect, were consistently higher than FI values at CC, the forested control catchment at the same elevation. This finding suggests that stream water from the high-elevation lakes in the North Boulder Creek catchment may be altering the composition of DOC in downstream aquatic systems by acting as a source of aquatic DOC that is lacking in catchments without lakes.

5.4. Conceptual Model of DOC Production in High-Elevation Catchments

[38] The evidence from the FA and FI data allow us to develop a conceptual model of DOM dynamics in high-elevation catchments. The focus of this model is the alpine reach of the catchment above the ALB site where lakes appear to play a substantial role in influencing both the amount and chemistry of DOC being exported from the catchment. On the ascending limb of the hydrograph, our data suggest that DOC inputs to the aquatic system are dominated by flushing of soluble organic carbon from catchment soils via relatively shallow flow paths (Figure 7a). The effect of this is an increase in the fulvic acid content of DOC

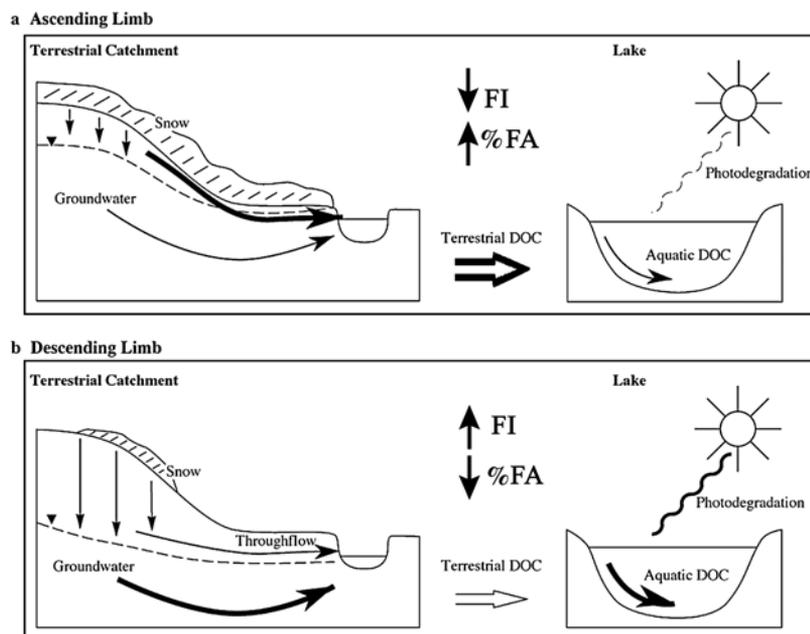


Figure 7. Conceptual model of DOC cycling in terrestrial system and the alpine lakes above tree line in Green Lakes Valley. On the ascending limb of the snowmelt hydrograph (Figure 7a), shallow hydrologic flow paths and high flushing rates lead to a predominance of terrestrial DOC and result in an increase in the fulvic acid content of DOC and a decrease in the FI value of fulvic acids. On the descending limb of the snowmelt hydrograph (Figure 7b), deeper hydrologic flow paths, smaller pools of terrestrial DOC, and increased residence time in the lakes lead to lower production of terrestrial DOC and higher net production of aquatic DOC; these changes result in a decrease in the fulvic acid content of DOC and an increase in the FI of fulvic acids.

and a concomitant decrease in the FI values of fulvic acids. At this time, the lakes in the alpine function almost as wide points in the stream with high flushing rates and very low water residence times. As a result, we hypothesize that there is a high import of allochthonous DOC but little net production of autochthonous DOC and small losses of DOC through photodegradation within the lakes. These processes are similarly consistent with a high fulvic acid content of DOC and low FI values.

[39] On the descending limb of the hydrograph, our data are consistent with several processes that could occur simultaneously and affect the concentrations and chemistry of stream water DOC (Figure 7b). In the terrestrial system, lower DOC concentrations are consistent with both the depletion of the reservoir of soluble organic carbon in near-surface soils and increased sorption of DOC in mineral soils as a result of deeper flow paths to the stream channel. Further, soil sorption would alter DOC chemistry by preferentially removing fulvic acids. The net effect of these processes would be to lower the fulvic acid content of DOC and to potentially increase the FI value of fulvic acids by decreasing terrestrial inputs to lakes and streams. In the alpine lakes, we hypothesize that longer water residence times result in increased net production of aquatic DOC as well as increased photodegradation of DOC. Photodegradation has previously been hypothesized not to be important in alpine lakes because of low residence times and suspended material loads [Baron *et al.*, 1991]. However, recent research has shown that colored fulvic acid DOC is lost more rapidly than uncolored DOC [Curtis and Schindler, 1997]

and further that substantial DOC losses via photodegradation can occur on the timescale of a day or less [Bertilsson and Tranvik, 2000]. The net result of these lake processes would be a seasonal decrease in the fulvic acid content of DOC and an increase in the FI of fulvic acids, both of which were observed at GL4 and ALB.

[40] Over the entire season, the fact that the FI values for fulvic acids were significantly correlated with the fulvic acid content of DOC at the GL4 site suggests that observed changes in DOC chemistry are linked with changes in DOC precursor material in the alpine reach of the catchment. Moreover, the lack of correlation between indices of DOC chemistry and precursor material at the other sites is likely a result of the smaller range in the indices at the forested sites. One potentially important implication of this conceptual model is that autochthonous production may exert substantial influence on the amount and chemical character of DOC in high-elevation catchments with appreciable lake area. To illustrate this point, a simple end-member mixing analysis using the fluorescence index to apportion the seasonal yield of DOC at GL4 to terrestrial and aquatic sources suggests that between 30 and 40% of the seasonal DOC yield is derived from net production in lakes. Care must be taken in interpreting these yields because they are based on the assumptions that the fluorescence index can be used in a quantitative manner and that the Lake Fryxell and Suwannee River fulvic acids are valid end-members for net production of autochthonous and allochthonous DOC in our study catchment. However, even with these limitations, these calculations strongly

suggest that the alpine lakes in the upper Green Lakes Valley, which account for less than 5% of the total catchment area, act as centers of DOC production in a relatively unproductive landscape and therefore have disproportionately high area-weighted yields of DOC compared to the terrestrial portion of the catchment.

[41] In the Colorado Front Range, developing a better understanding of the role of lakes in the DOC yield of high-elevation catchments is important in light of recent studies showing that the provenance of sediment organic matter in the lakes has changed markedly since the mid-twentieth century. Stratigraphic records from sediment cores in Green Lake 4 as well as several high-elevation lakes in Rocky Mountain National Park in Colorado indicate that diatom assemblages have changed in concert with an increase in carbon storage in sediments and a decrease in sediment C:N ratios [Waters, 2003; Wolfe *et al.*, 2002]. At the same time, the FI values of organic material in sediments have increased, which is consistent with an increase in inputs of autochthonous organic material to sediments. These findings indicate that algal production in alpine lakes is increasing, likely as a result of nutrient enrichment from anthropogenic N emissions and a decrease in ice-cover thickness and duration during the last several decades [Sommaruga-Wogratz *et al.*, 1997; Waters, 2003; Wolfe *et al.*, 2001, 2002]. In relation to our study, these findings suggest that changes in chemical inputs and climate in the high-elevation reaches of the Green Lakes Valley are increasing the net production of autochthonous organic material in alpine lakes. This, in turn, has the potential to alter both the amount and chemical character of DOC exported to downstream aquatic systems. Moreover, recent reports of elevated concentrations of inorganic N in high-elevation lakes in both the western United States [Campbell *et al.*, 1995; Williams and Tonnessen, 2000] and Europe [Psenner, 1989; Kopacek *et al.*, 1995] suggest that a wide range of high-elevation ecosystems may be susceptible to shifts in DOC dynamics similar to those that appear to be occurring in Green Lakes Valley.

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