

# 1 Sources and chemical character of dissolved organic carbon across 2 an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front 3 Range, United States

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12 [1] We investigated how the source and chemical character of aquatic dissolved organic  
13 carbon (DOC) change over the course of the runoff season (May–November, 1999) in  
14 Green Lakes Valley, a high-elevation ecosystem in the Front Range of the Colorado Rocky  
15 Mountains. Samples were collected on North Boulder Creek from four sites across an  
16 alpine/subalpine ecotone in order to understand how the transition from the lightly  
17 vegetated alpine to the forested reaches of the catchment influences aquatic DOC.

18 Concentrations of DOC at the four sites peaked between 2.6 and 8.9 mg C L<sup>-1</sup> on the  
19 ascending limb of the snowmelt hydrograph, with the higher concentrations at the two  
20 subalpine sites. Seasonally, the chemical fractionation of DOC showed that there was a  
21 large range (29–72%) in the fulvic acid content of DOC at the four sites, with the highest  
22 fulvic acid percentages on the ascending limb of the hydrograph. Yields of DOC at the  
23 two gauged sites ranged from 10 to 11 kg ha<sup>-1</sup> over the season with between 45 and 50%  
24 of the yield occurring as fulvic acid DOC and the remainder as nonhumic material. The  
25 fluorescence properties of DOC from all four sites indicated that during peak runoff,  
26 DOC was derived primarily from terrestrial precursor material. However, seasonal  
27 changes in the fluorescence properties of fulvic acids at the highest elevation sites suggest  
28 that DOC derived from algal and microbial biomass in the lakes is a more important  
29 source of DOC above tree line during late summer and fall. We hypothesize that much of  
30 the autochthonous DOC production is a result of algal growth in alpine lakes. Further,  
31 comparison to a forested control catchment suggests that processes in the alpine reach of  
32 the catchment may alter both the amount and chemistry of DOC incident to the  
33 downstream subalpine aquatic system.

34 *INDEX TERMS:* 0322 Atmospheric Composition and  
35 Structure: Constituent sources and sinks; 1615 Global Change: Biogeochemical processes (4805); 1851  
36 Hydrology: Plant ecology; 1854 Hydrology: Precipitation (3354); 1860 Hydrology: Runoff and streamflow;

*KEYWORDS:* DOC, biogeochemistry, snowmelt, chemical fractionation, fluorescence spectroscopy

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## 42 1. Introduction

43 [2] Dissolved organic carbon (DOC) constitutes the larg-  
44 est pool of organic carbon in most aquatic environments and  
45 consequently plays an important role in both biological and  
46 physical processes in these systems. The transport and fate  
47 of DOC in aquatic systems are determined by local patterns

of precipitation, biological and physical interactions, runoff, 48  
and river discharge [*Hope et al.*, 1997]. Despite the exis- 49  
tence of DOC export budgets for rivers from a diversity of 50  
environments [e.g., *Aitkenhead and McDowell*, 2000], the 51  
chemical character of aquatic DOC and how it may change 52  
seasonally, longitudinally, and in response to extreme events 53  
has been studied in relatively few watersheds. 54

[3] The DOC load in aquatic ecosystems is a mixture of 55  
organic material derived from the soils and plants of the 56  
surrounding catchment (allochthonous) and from within the 57  
aquatic system (autochthonous). Allochthonous DOC is 58  
typically enriched in fulvic acids and highly colored [*Thur-* 59

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60 *man*, 1985], while autochthonous DOC, derived from algal  
61 and bacterial biomass in aquatic systems, is characterized by  
62 a lower fulvic acid content and C:N ratio [McKnight *et al.*,  
63 1994]. Thus the relative balance of these sources of DOC in  
64 aquatic systems can affect aquatic biota by altering the  
65 amount of energy available for heterotrophic growth [Schin-  
66 dler *et al.*, 1992; Wetzel, 1992], the depth of the photic zone  
67 [Scully and Lean, 1994], and the mobility of trace metals  
68 such as Al and Fe [McKnight *et al.*, 1992].

69 [4] In the past, most watershed-scale studies on carbon  
70 cycling have relied on measurements of bulk DOC concen-  
71 trations because of the difficulty in chemically fractionating  
72 and characterizing DOC. The primary constraint on mea-  
73 suring the character of DOC has been the lack of analytical  
74 procedures that are readily applicable to large sample sets.  
75 The fractionation of DOC into operationally defined chem-  
76 ical constituents has proven useful for understanding how  
77 the quality of DOC changes as it percolates through organic  
78 and mineral soil horizons [e.g., Qualls *et al.*, 1991; Raastad  
79 and Mulder, 1999] and enters the stream channel [East-  
80 house *et al.*, 1992]. Moreover, several studies have cited  
81 shifts in DOC fractions as evidence that the dominant  
82 source of DOC in surface waters may change seasonally  
83 [Baron *et al.*, 1991; McKnight *et al.*, 1997]. Fractionation  
84 has also been used to investigate how the quality of DOC in  
85 freshwater and saltwater lakes is influenced by residence  
86 time and salinity [Curtis and Adams, 1995; Curtis and  
87 Schindler, 1997]. Here we apply analytical-scale chromato-  
88 graphic fractionation to evaluate how the chemical character  
89 of stream water DOC changes in an alpine/subalpine catch-  
90 ment over an entire runoff season.

91 [5] In addition to evaluating the nature and importance of  
92 changes in DOC chemistry, advances in the use of fluo-  
93 rescence spectroscopy to study DOM have the potential to  
94 aid in interpreting spatial and temporal changes in DOM  
95 precursor material. The analysis of DOM sources using  
96 fluorescence spectroscopy is based on the fact that allochth-  
97 onous fulvic acids derived from terrestrial organic material  
98 have different fluorescence properties than autochthonous  
99 fulvic acids derived from aquatic organic material. Further,  
100 these differences can be quantitatively characterized by a  
101 relatively simple fluorescence index (FI) [McKnight *et al.*,  
102 2001]. The FI values of fulvic acids have previously been  
103 used to track historic changes in the source of humic  
104 material in lake sediments [Wolfe *et al.*, 2002; Waters,  
105 2003,] and marine sediments [Klapper *et al.*, 2002] as well  
106 as to identify differences in the source of DOM in surface  
107 waters between different geographic regions [McKight *et al.*,  
108 2001]. However, to our knowledge, fluorescence prop-  
109 erties have not previously been used to track intra-annual  
110 changes in the source of aquatic DOM at the catchment  
111 scale.

112 [6] This study focuses on the source and chemical char-  
113 acter of aquatic DOC in the North Boulder Creek water-  
114 shed, a high-elevation alpine/subalpine catchment in the  
115 Colorado Front Range. In montane watersheds, as much as  
116 80% of DOC enters the aquatic system during spring  
117 snowmelt [Lewis and Grant, 1979; Hornberger *et al.*,  
118 1994; Boyer *et al.*, 1997]. We investigated DOC in soil  
119 and surface waters along a longitudinal transect in the North  
120 Boulder Creek watershed during the 1999 snowmelt runoff  
121 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 sub-  
alpine 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 land-  
scapes 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 gov-  
erning DOC cycling at the catchment scale.

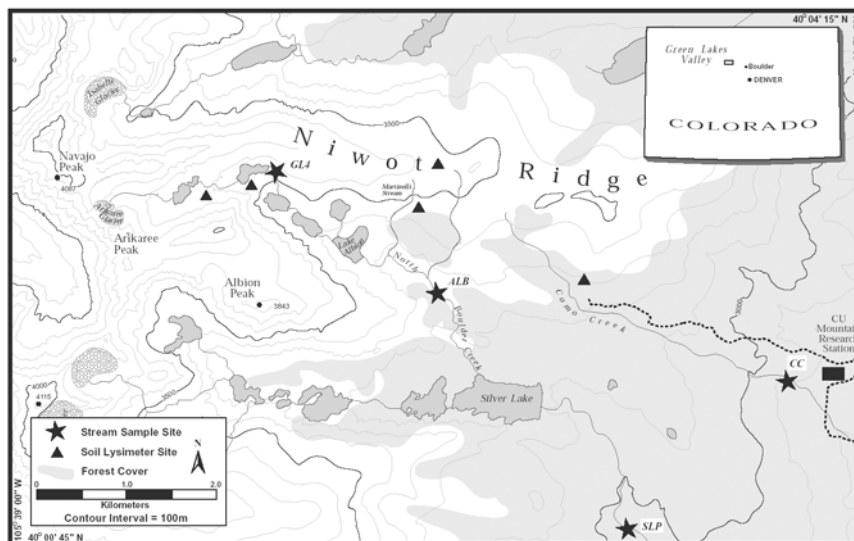
## 2. Site Description

[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 temper-  
ature is  $-3.8^{\circ}\text{C}$ , 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 occur-  
ring 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  
 $35\text{ }\mu\text{S cm}^{-1}$  at all sample sites in 1999.

[9] The  $5\text{ km}^2$  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 commu-  
nities in the lakes located in the upper valley is seasonally  
variable. Measurements at Green Lake 4 show that chloro-  
phyll *a* concentrations increased by almost a factor of 20,  
from  $0.03\text{ }\mu\text{g L}^{-1}$  during spring snowmelt to  $0.56\text{ }\mu\text{g L}^{-1}$  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 engelman-  
nii*) 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 devel-  
oped soils on glacial till and moraine deposits overlying  
granitic and metamorphic parent material. Soils are Incepti-  
sols 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.

182 on well-drained glacial moraines. Soil pH values range from  
183 4.5 to 6.0.

184 [11] Water samples were collected at three sites along a  
185 transect on North Boulder Creek extending from Green  
186 Lake 4 at 3535 m to a site located 5 km below tree line  
187 (SLP) at 2963 m (Figure 1). The sites extend from the  
188 high alpine upper valley to the subalpine forested reaches  
189 of the catchment and range in basin area from 42 to 2700  
190 ha (Table 1). Additional samples were collected on Como  
191 Creek, a tributary stream draining the SE flank of Niwot  
192 Ridge (Table 1). The headwaters of Como Creek extend  
193 slightly above tree line to 3560 m in elevation. Greater  
194 than 80% of the watershed is mixed conifer forest with  
195 some aspen (*Populus tremuloides*). Como Creek watershed  
196 has similar climatology, snowfall amount, and atmospheric  
197 deposition as the adjacent North Boulder Creek Catchment  
198 [Hood et al., 2003]. However, Como Creek differs from  
199 North Boulder Creek in two important respects: (1) There  
200 are no lakes in the catchment, and (2) there is little alpine  
201 area and no talus or exposed bedrock. Thus Como Creek  
202 drainage acts as a control to evaluate the influence of  
203 alpine areas on the downstream concentrations, chemical  
204 character, and source areas of DOC. Stream samples from  
205 Como Creek were collected at the University of Colorado  
206 Mountain Research Station at an elevation of 2900 m  
207 (Figure 1). The watershed area above the sampling site is  
208 664 ha.

209 **3. Methods**

210 **3.1. Water Samples and Discharge Measurements**

211 [12] During the 1999 snowmelt season (May–October),  
212 surface water samples were collected as 1 L or 500 mL grab  
213 samples at weekly to biweekly intervals at all four sites  
214 (GL4, ALB, SLP, and CC). In order to further evaluate  
215 seasonal changes in fluorescence characteristics, grab sam-  
216 ples were collected again from GL4 in June and August

217 2000. Soil water samples were collected from five locations  
218 in 1999 after they became snow-free in June and July  
219 (Figure 1). Soil water was collected from zero-tension  
220 lysimeters at shallow depths (10–30 cm). The design and  
221 installation of the soil lysimeters are described by Litour  
222 [1993] and Williams et al. [1996b]. All water samples were  
223 collected in precombusted amber glass bottles with Teflon-  
224 lined caps and filtered through precombusted Gelman G/F  
225 glass fiber filters with a nominal pore size of 0.7 μm. The  
226 majority of samples were filtered in the field, and all  
227 samples were filtered within a day of collection. Samples  
228 were stored at 4°C until fractionation and analysis, which  
229 occurred within 2 weeks of sample collection. DOC was  
230 determined by high-temperature catalytic oxidation using a  
231 Dohrmann organic carbon analyzer at the Institute of Arctic  
232 and Alpine Research in Boulder, Colorado. Three replicate  
233 analyses were conducted for each sample. Standard devia-  
234 tion was typically 0.08 mg C L<sup>-1</sup> with a range of 0.01–0.2  
235 mg C L<sup>-1</sup>.

[13] At two sites (GL4 and ALB), water level was  
236 measured with a pressure transducer and converted to  
237 volumetric discharge by empirical ratings that are validated  
238 by gauging at different flow levels for each season [Caine,  
239

**Table 1.** Stream Sampling Sites on North Boulder Creek and Como Creek for 1999<sup>a</sup>

Site	Abbreviation	Elevation, m	Catchment Area, ha	Landscape Type	
Green Lake 4	GL4	3550	221	alpine	t1.3
Albion Townsite	ALB	3250	710	tree line	t1.4
Silverlake Road	SLP	2963	2720	subalpine forest	t1.5
Como Creek	CC	2910	664	subalpine forest	t1.6

<sup>a</sup>The 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.

t1.7



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. The nonhumic hydrophilic fraction 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 ( $\text{mg L}^{-1}$ ) in a given sample period and  $Q$  is the discharge ( $\text{m}^3$ ) 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.

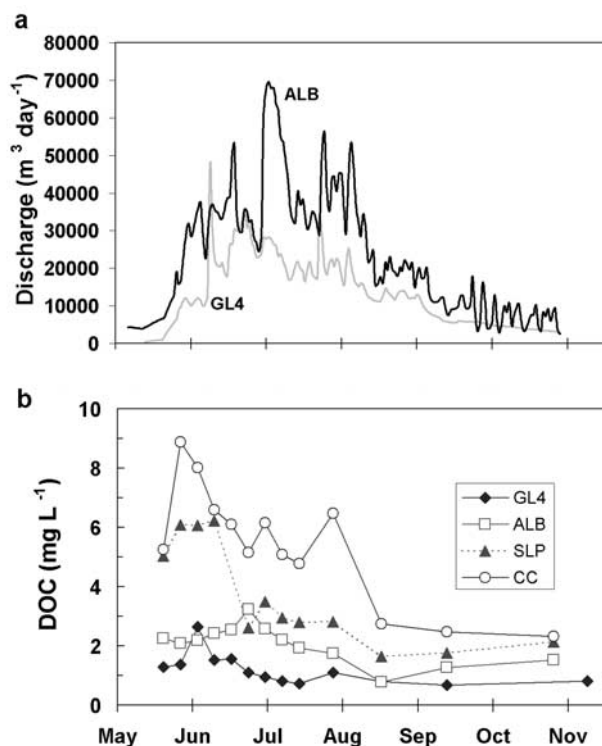
## 4. Results

### 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  $\text{m}^3$  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 at CC 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.

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

370 [21] Dissolved organic carbon concentrations in 10 hill-  
 371 slope lysimeters varied substantially throughout the catch-  
 372 ment (Table 2). Dissolved organic carbon concentrations  
 373 ranged from  $37.8 \text{ mg C L}^{-1}$  at a site in the riparian zone  
 374 near GL4 to  $9.4 \text{ mg C L}^{-1}$  at an alpine tundra site on the

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

[22] Over the entire sampling season (May–October), the  
 383 area weighted yields of DOC were relatively similar  
 384 between the two gauged sites (Table 3). At GL4, the yield  
 385 of DOC was  $10.5 \text{ kg ha}^{-1}$  and increased by only 4% to  $10.9$   
 386  $\text{kg ha}^{-1}$  moving downstream to the ALB site at tree line.  
 387 The yield of DOC for the area of the ALB catchment  
 388 located below the GL4 catchment was  $11.2 \text{ kg ha}^{-1}$ , which  
 389 was higher than either of the individual catchments.  
 390

#### 4.3. Chemical Fractions of DOC: Seasonal Trends and Yields

[23] Seasonally, fulvic acids comprised between 29–72%  
 394 of the DOC at the four sites (Figure 3a). Paralleling bulk  
 395 DOC concentrations, the fulvic acid content of DOC at all  
 396 four sites peaked on the ascending limb of the hydrograph  
 397 and was highest at the two subalpine sites (CC and SLP)  
 398 and lowest at the alpine site (GL4). The alpine GL4 site  
 399 showed the widest range in the fulvic acid content of DOC,  
 400 with a peak in fulvic acid content of 69% in late May  
 401 followed by a reduction in fulvic acid content to 40% by  
 402 mid-July (Figure 3a). The peak in fulvic acid content at  
 403 ALB and SLP was similar to that at GL4, although the  
 404 decline in fulvic acid on the descending limb of the hydro-  
 405 graph was less pronounced at these sites. Fulvic acid  
 406 content at CC showed a diffuse peak 2–3 weeks later than  
 407 the North Boulder Creek sites and remained elevated  
 408 ( $>50\%$ ) throughout the sampling period. At all four sites,  
 409 seasonal variations in the fulvic acid content of DOC  
 410 appeared to be related to discharge. The fulvic acid content  
 411 of DOC from the GL4 site showed a clockwise hysteresis  
 412 with consistently higher values on the ascending limb of the  
 413 hydrograph compared to the descending limb (Figure 3b).  
 414 This pattern was similar at the other sites, although the  
 415 range for the fulvic acid content of DOC was smaller,  
 416 particularly at the two forested sites.  
 417

[24] Partitioning of catchment DOC yields into fulvic  
 418 acid and nonhumic constituents highlights downstream  
 419 differences in the chemical composition of DOC being  
 420 exported in North Boulder Creek. In the GL4 catchment,  
 421

t2.1 **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

t2.2	Site	Date Sampled	Landscape Type	DOC, $\text{mg L}^{-1}$	FI
t2.3	GL4 ZT2B	23 June	alpine riparian	20.7	1.22
t2.4	GL4ZT2C	23 June	alpine riparian	27.6	1.26
t2.5	GL4ZT13	23 June	alpine riparian	37.8	1.19
t2.6	GL5ZTWL	19 July	alpine riparian	35.9	1.27
t2.7	KIOZT10	19 July	alpine riparian	17.3	1.25
t2.8	SODZT10A	23 June	subalpine forest	17.1	1.33
t2.9	SUBZT10B	20 July	alpine tundra	14.4	1.20
t2.10	SUBZT30A	20 July	alpine tundra	9.4	1.25
t2.11	SUBZT30B	20 July	alpine tundra	16.1	1.25
t2.12	MAZT4B	23 June	alpine snowfield	12.8	1.32
t2.13	Average			20.9	1.25
t2.14	Standard deviation			9.7	.05



t3.1 **Table 3.** Seasonal Area-Weighted Yields of Bulk DOC, Fulvic Acid DOC, and Nonhumic DOC at the Two Gauged Sites GL4 and ALB

t3.2 Site	Bulk DOC, kg ha <sup>-1</sup>	Fulvic Acid DOC, kg ha <sup>-1</sup>	Nonhumic DOC, kg ha <sup>-1</sup>
t3.3 GL4	10.5	4.7	5.8
t3.4 ALB	10.9	5.5	5.4
t3.5 ALB-GL4 <sup>a</sup>	11.2	5.9	5.2

t3.6 <sup>a</sup>Refers to the portion of the ALB catchment located below GL4.

422 the nonhumic DOC yield of 5.8 kg ha<sup>-1</sup> was 23% greater  
 423 than the fulvic acid DOC yield of 4.7 kg ha<sup>-1</sup> (Table 3).  
 424 Downstream at the tree line ALB site, there was a shift in  
 425 the composition of the DOC yield with fulvic acid export of  
 426 5.5 kg ha<sup>-1</sup> only slightly greater than the yield of 5.4 kg  
 427 ha<sup>-1</sup> for nonhumic DOC. The difference between the  
 428 composition of the DOC yields from the GL4 and ALB  
 429 catchments indicates that the DOC yield from the portion of  
 430 the ALB catchment located below GL4 was composed of  
 431 more fulvic acid material compared to the DOC yield from  
 432 alpine reach of the catchment above GL4. Thus, as soils  
 433 coverage and vegetation increased below GL4, the catch-  
 434 ment yield of humic material increased by 25% to 5.9 kg  
 435 ha<sup>-1</sup>, while the yield of nonhumic material decreased by 9%  
 436 to 5.3 kg ha<sup>-1</sup> (Table 3).

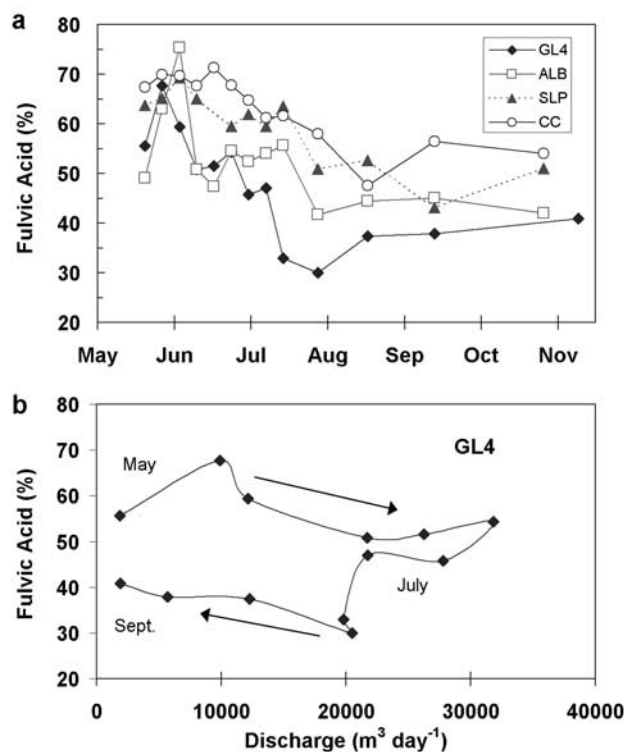
437 [25] Seasonally, the chemical character of the DOC yield  
 438 at GL4 shifted from being predominantly fulvic acids  
 439 during peak snowmelt to predominantly nonhumic material  
 440 after mid-June (Figure 4a). At ALB, the character of the  
 441 weekly yield of DOC was similarly dominated by fulvic  
 442 acids during snowmelt; however, the shift toward a pre-  
 443 dominance of nonhumic material at ALB did not occur until  
 444 August (Figure 4b). At both sites, this pattern illustrates that  
 445 the decrease in the yield of fulvic acid material after peak  
 446 flow is more rapid than the decrease in the leaching of  
 447 nonhumic material. The peak in nonhumic material evident  
 448 at both GL4 and ALB in late July was a result of a  
 449 substantial increase in discharge associated with a large rain  
 450 event (27 mm of precipitation) on July 24. It is likely that  
 451 the proportion of DOC as fulvic acid was higher than we  
 452 report during this event due to the flushing of humic  
 453 material from catchment soils; however, this cannot be  
 454 verified because the storm occurred between dates on which  
 455 DOC was sampled and fractionated.

457 **4.4. Fluorescence Characteristics of DOC**

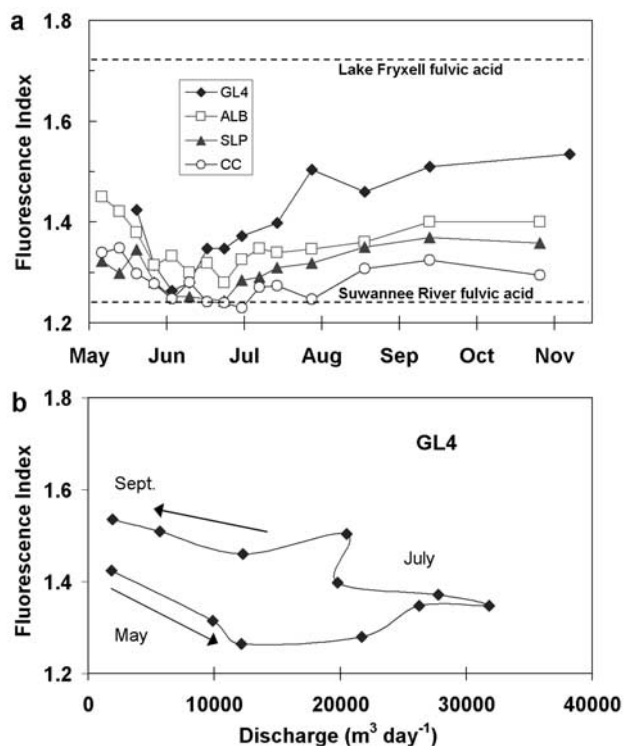
458 [26] For the 1999 snowmelt season, FI values for aquatic  
 459 fulvic acids isolated in Green Lakes Valley had a range of  
 460 1.23–1.54, which was within the range of the terrestrial  
 461 (Suwannee River) and aquatic (Lake Fryxell) reference  
 462 fulvic acids (1.24–1.77). The FI values for fulvic acids from  
 463 all four sites showed minima close to the terrestrial Suwan-  
 464 nee River fulvic acid shortly preceding and coincident with  
 465 peak snowmelt runoff in early to mid-June (Figure 5a).  
 466 Fulvic acids from the subalpine Como Creek site had the  
 467 lowest seasonal FI values, rarely exceeding 1.3. Fluores-  
 468 cence index values for fulvic acids from the alpine GL4 site  
 469 were the highest measured on all but two dates and showed  
 470 the largest seasonal range (0.28) of the four sites. The  
 471 difference in the magnitude of the FI at GL4 relative to the  
 472 other three sites was most pronounced after North Boulder

Creek returned to lower flows (<15,000 m<sup>3</sup> d<sup>-1</sup> at GL4) in 473  
 August. The temporal variations in the FI at GL4 were 474  
 significantly correlated with the fulvic acid content of 475  
 DOC ( $R^2 = 0.54$ ,  $p < 0.001$ ,  $n = 12$ ). The relationship 476  
 between the FI and the fulvic acid content of DOC was 477  
 not significant at the other three sites ( $p > 0.1$  for all 478  
 comparisons). Similar to the fulvic acid content of DOC, 479  
 the FI values of fulvic acids were related to discharge at all 480  
 four sites. This relationship was most clearly defined at GL4 481  
 where the FI showed a counterclockwise hysteresis with 482  
 lower values on the ascending limb of the hydrograph 483  
 compared to the descending limb (Figure 5b). The pattern 484  
 was similar at the other three sites although the range for the 485  
 FI was smaller, particularly at the forested sites. 486

[27] To aid in the interpretation of FI values for fulvic 487  
 acids collected in Green Lakes Valley, we evaluated the 488  
 fluorescence properties of the two reference fulvic acids 489  
 representing terrestrial material (Suwannee River) and 490  
 aquatic microbial material (Lake Fryxell). For the Suwannee 491  
 River fulvic acid, fluorescence measurements were made 492  
 over a wide range of emission (400–550 nm) and excitation 493  
 (250–400 nm) values. The resulting EEMs were very 494  
 similar to results reported by McKnight *et al.* [2001] and 495  
 had consistently similar FI values. In total, six Suwannee 496  
 River fulvic acid samples ranging in concentration from 1 to 497  
 10 mg L<sup>-1</sup> had an average FI value of 1.24 with a standard 498  
 deviation of 0.01. Thus it appears that FI values remain 499



**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.

500 stable over the range of concentrations of the fulvic acid  
 501 samples we collected in Green Lakes Valley. Moreover, the  
 502 FI values of the Suwannee River fulvic acids were highly  
 503 consistent with the FI values for fulvic acids collected from  
 504 soil lysimeters throughout Green Lakes Valley, which had an  
 505 average value of 1.24 and a range of 1.19–1.33 (Table 2).  
 506 For the Lake Fryxell fulvic acids, EEMs from six samples  
 507 ranging in concentration from 1 to 10 mg L<sup>-1</sup> were also  
 508 similar to the results of *McKnight et al.* [2001] and had an  
 509 average FI value of 1.72 with a standard deviation of 0.02.  
 510 It is worth noting that the FI values of our reference fulvic  
 511 acids (1.22 and 1.74) were very similar in range, but lower  
 512 in magnitude, than those described by *McKnight et al.*  
 513 [2001] (1.4–1.9), suggesting that FI values are somewhat  
 514 dependent on fluorometer configuration and highlighting  
 515 the need to calibrate an instrument with fulvic acids of  
 516 known origin.

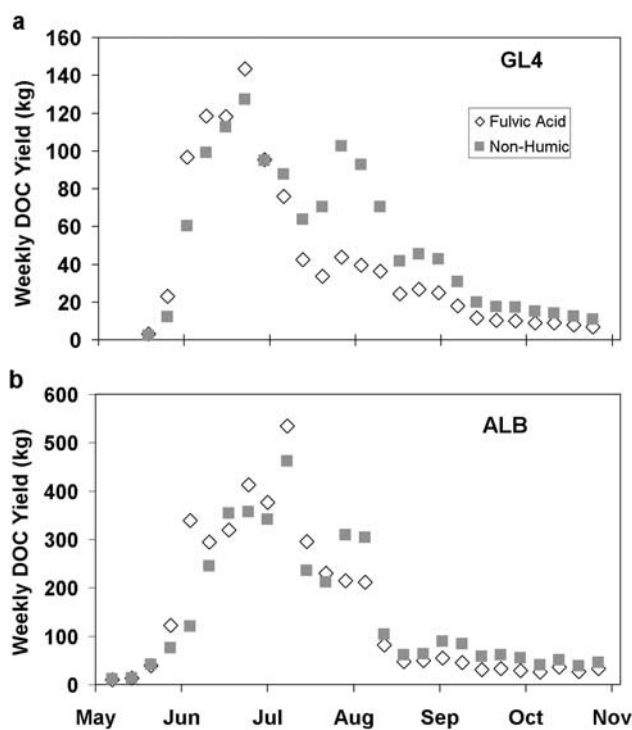
517 [28] The excitation-emission matrices for fulvic acids  
 518 collected at GL4 during the snowmelt season in 2000  
 519 provide further evidence of the utility of the two reference  
 520 fulvic acids by demonstrating that the seasonal change in  
 521 the FI is a result of changes in the properties of the two  
 522 dominant fulvic acid fluorophores. The fulvic acid sample  
 523 collected near peak runoff (22 June) showed an emission  
 524 peak of 444 nm for an excitation of 327 nm (Figure 6a)  
 525 and a second emission peak of 445 nm for an excitation of  
 526 230 nm (not shown). The emission peaks in this sample  
 527 are shifted toward slightly longer wavelengths, which is

similar to the EEM for the Suwannee River fulvic acid 528  
 and is consistent with a larger proportion of terrestrial precursor 529  
 material such as lignin [*McKnight et al.*, 2001; *Klapper* 530  
*et al.*, 2002; *Wolfe et al.*, 2002]. In contrast, the fulvic 531  
 acids collected late in the runoff season (18 August) had 532  
 emission maxima occurring at lower wavelengths for both 533  
 fluorophores (Figure 6b), which is similar to the EEMs 534  
 from fulvic acids isolated in Antarctica and indicates an 535  
 increase in the amount of aquatic (algal and microbial) 536  
 precursor material [*McKnight et al.*, 2001]. The corresponding 537  
 FI values for the EEMs of the fulvic acids 538  
 isolated at GL4 in 2000 were 1.28 in mid-June and 1.50 539  
 in August, which mirrors the seasonal pattern of FI values 540  
 observed in 1999. 541

## 5. Discussion 543

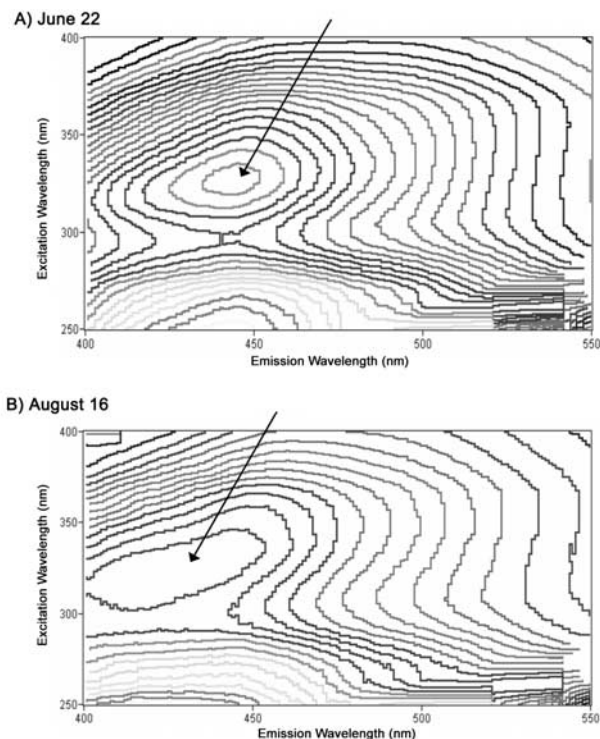
### 5.1. Seasonal Concentrations and Yields of DOC 544

[29] The range of DOC concentrations in North Boulder 545  
 Creek sites is consistent with the results of previous studies 546  
 in alpine/subalpine catchments in the Colorado Rocky 547  
 Mountains [*Baron et al.*, 1991; *Boyer et al.*, 1997; *Brooks* 548  
*et al.*, 1999]; however, DOC concentrations in Como Creek 549  
 are on the high end for headwater catchments in the Rocky 550  
 Mountains. The early season peak in DOC concentrations 551



**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).

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 (9–38 mg C L<sup>-1</sup>) and surface water DOC concentrations (1–5 mg C L<sup>-1</sup>) 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 (1–3 mg C L<sup>-1</sup>), 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 (~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 10–11 kg C ha<sup>-1</sup> we report for our gauged catchments is on the low end of yields reported from 21 forested watersheds in the United States (7–34 kg C ha<sup>-1</sup> [Tate and Meyer, 1983]) and 30 forested catchments from the cool conifer biome (15–74 kg C ha<sup>-1</sup> [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



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

646 [33] The decrease in the fulvic acid content of DOC  
647 evident at all four sites on the descending limb of the  
648 hydrograph is consistent with potential changes in both  
649 hydrologic flow paths and DOM yield at the catchment  
650 scale. In terms of hydrology, high-elevation catchments are  
651 characterized by a shift toward deeper flow paths after peak  
652 snowmelt, with as much as 69–95% of streamflow origin-  
653 ating from subsurface flow via mineral soil horizons  
654 [Caine, 1989; Sueker *et al.*, 2000]. This has important  
655 implications for the chemical composition of stream water  
656 DOC because in mineral soil horizons fulvic acids are  
657 preferentially sorbed compared to nonhumic material  
658 [Qualls and Haines, 1991; Easthouse *et al.*, 1992]. As a  
659 result, periods when water is routed via deeper flow paths  
660 through mineral soils should be accompanied by a relative  
661 decrease in the fulvic acid fraction of DOC in surface  
662 waters. This hypothesis is consistent with the seasonal trend  
663 in DOC chemistry we observed in that during the late  
664 summer and fall the fulvic acid content of DOC decreased  
665 to 50% or less at all four sample sites. The seasonal  
666 decrease in the fulvic acid content of DOC is also consistent  
667 with a relative increase in the amount of DOC derived from  
668 within-lake aquatic production. McKnight *et al.* [1994] have  
669 previously shown that DOC in Antarctic lakes derived from  
670 algal/microbial sources has a low fulvic acid content (~15–  
671 25%) compared to DOM derived from terrestrial sources,  
672 which have a fulvic acid content of 50–90% [Thurman,  
673 1985]. Thus the late summer decrease in the fulvic acid  
674 content of DOC to ~30–40% at GL4 and ALB suggests  
675 that stream water DOC in the alpine reaches of the catch-  
676 ment may be increasingly derived from algal precursor  
677 material on the descending limb of the hydrograph. In  
678 addition to the seasonal trend in DOC character, there was  
679 a consistent longitudinal trend toward a higher fulvic acid  
680 content of DOC with decreasing elevation. This pattern  
681 would suggest that autochthonous DOM may comprise a  
682 relatively smaller proportion of stream water DOC moving  
683 in the downstream direction.

684 [34] To our knowledge, there are no reports of watershed  
685 yields of the humic and nonhumic components of DOC in  
686 surface waters. Similar to the total DOC yield, the character  
687 of the DOC yield on North Boulder Creek did not shift  
688 dramatically moving from the alpine GL4 site to the tree  
689 line ALB site. However, comparing the GL4 catchment to  
690 the area of ALB below GL4 (ALB-GL4), the shift in the  
691 chemical quality of the DOC yield is more apparent and  
692 reflects the differences in land cover and soils between these  
693 two reaches of the ALB catchment. At the downstream  
694 forested sites (SLP and CC), the chemical composition of  
695 the DOC yields shifts toward a predominance of humic  
696 material, consistent with the higher humic material content  
697 of DOC at these sites.

### 699 5.3. Fluorescence Properties of DOC

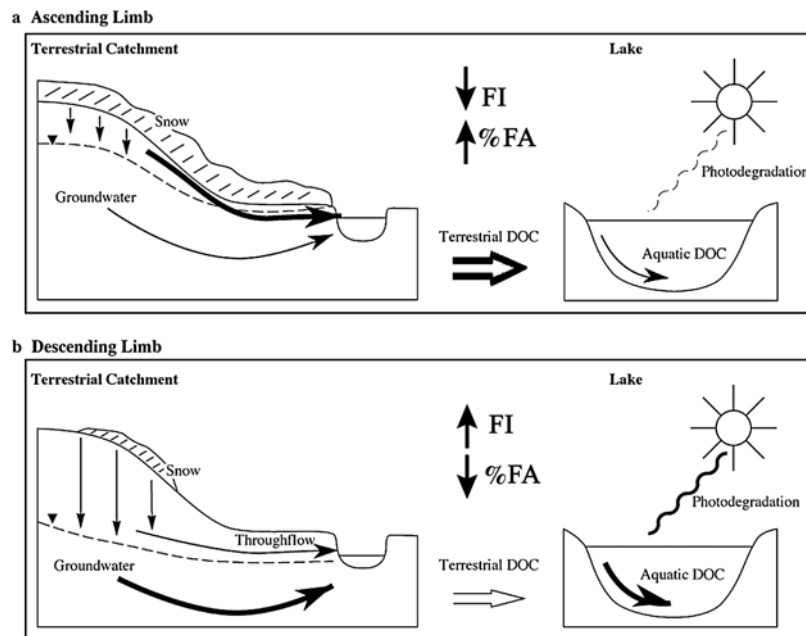
700 [35] The similarities between the FI values and the  
701 EEMs for fulvic acids collected in Green Lakes Valley  
702 and those of the reference fulvic acids suggest that the  
703 Suwannee River and Lake Fryxell fulvic acids are reason-  
704 able end-members for evaluating shifts in DOM precursor

material between terrestrial and aquatic sources. As such, 705  
the fluorescence properties of stream water fulvic acids 706  
provide a semiquantitative method for evaluating seasonal 707  
changes in the sources of DOM in surface waters. During 708  
peak snowmelt, the FI values of fulvic acids at all four sites 709  
converged on the value for the terrestrial end-member. This 710  
finding provides an independent line of evidence to cor- 711  
roborate the inferences from changes in the concentration 712  
and chemical composition of DOC that terrestrial precursor 713  
material is the dominant source of stream water DOC on 714  
the ascending limb of the hydrograph. At the GL4 site, 715  
elevated FI values both before the onset of snowmelt and 716  
on the descending limb of the hydrograph similarly agree 717  
with changes in DOC chemistry in suggesting that aquatic 718  
production can be an important source of stream water 719  
DOC in the alpine reach of the catchment. The likely 720  
source of this aquatic DOC is autochthonous algal and 721  
microbial production in alpine lakes. The importance of 722  
these lakes as a DOC source has been inferred previously 723  
based on downstream changes in particulate/dissolved 724  
organic carbon ratios, stable carbon isotope ratios, and 725  
the elemental composition of fulvic acids [Baron *et al.*, 726  
1991; McKnight *et al.*, 1997]. Moreover, the timing of 727  
shifts in the FI is consistent with phytoplankton studies in 728  
Front Range alpine lakes showing that algal growth is 729  
substantial during winter and spring ice cover [Spaulding *et al.*, 730  
1993] and during late season base flow [McKnight *et al.*, 731  
1990; Waters, 2003]. 732

[36] Over the entire study period, FI values for fulvic 733  
acids showed a relatively consistent decrease moving from 734  
the alpine to the subalpine. This trend is again consistent 735  
with the downstream increase in the fulvic acid content of 736  
DOC in suggesting that there is an increase in the propor- 737  
tion of DOC derived from terrestrial material in the lower 738  
reaches of the catchment. However, because DOC from 739  
algal/microbial precursor material is predominantly non- 740  
humic material, it is a more efficient substrate for bacterial 741  
growth [Moran and Hodson, 1990]. Thus it is alternatively 742  
possible that the longitudinal trend in FI values is due in 743  
some part to the depletion of aquatic DOC as a result of 744  
metabolism in the water column and hyporheic zone. 745  
Interestingly, the FI values at SLP, the forested site on the 746  
North Boulder Creek transect, were consistently higher than 747  
FI values at CC, the forested control catchment at the same 748  
elevation. This finding suggests that stream water from the 749  
high-elevation lakes in the North Boulder Creek catchment 750  
may be altering the composition of DOC in downstream 751  
aquatic systems by acting as a source of aquatic DOC that is 752  
lacking in catchments without lakes. 753

### 754 5.4. Conceptual Model of DOC Production 755 in High-Elevation Catchments 756

[37] The evidence from the FA and FI data allow us to 757  
develop a conceptual model of DOM dynamics in high- 758  
elevation catchments. The focus of this model is the alpine 759  
reach of the catchment above the ALB site where lakes 760  
appear to play a substantial role in influencing both the 761  
amount and chemistry of DOC being exported from the 762  
catchment. On the ascending limb of the hydrograph, our 763  
data suggest that DOC inputs to the aquatic system are 764  
dominated by flushing of soluble organic carbon from catch- 765  
ment soils via relatively shallow flow paths (Figure 7a). The 766



**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.

767 affect of this is an increase in the fulvic acid content of DOC  
 768 and a concomitant decrease in the FI values of fulvic acids. At  
 769 this time, the lakes in the alpine function almost as wide  
 770 points in the stream with high flushing rates and very low  
 771 water residence times. As a result, we hypothesize that there  
 772 is a high import of allochthonous DOC but little net produc-  
 773 tion of autochthonous DOC and small losses of DOC through  
 774 photodegradation within the lakes. These processes are  
 775 similarly consistent with a high fulvic acid content of DOC  
 776 and low FI values.

777 [38] On the descending limb of the hydrograph, our data  
 778 are consistent with several processes that could occur  
 779 simultaneously and affect the concentrations and chemistry  
 780 of stream water DOC (Figure 7b). In the terrestrial system,  
 781 lower DOC concentrations are consistent with both the  
 782 depletion of the reservoir of soluble organic carbon in  
 783 near-surface soils and increased sorption of DOC in mineral  
 784 soils as a result of deeper flow paths to the stream channel.  
 785 Further, soil sorption would alter DOC chemistry by prefer-  
 786 entially removing fulvic acids. The net effect of these  
 787 processes would be to lower the fulvic acid content of DOC  
 788 and to potentially increase the FI value of fulvic acids by  
 789 decreasing terrestrial inputs to lakes and streams. In the  
 790 alpine lakes, we hypothesize that longer water residence  
 791 times result in increased net production of aquatic DOC as  
 792 well as increased photodegradation of DOC. Photodegrada-  
 793 tion has previously been hypothesized not to be important in  
 794 alpine lakes because of low residence times and suspended  
 795 material loads [Baron *et al.*, 1991]. However, recent  
 796 research has shown that colored fulvic acid DOC is lost

797 more rapidly than uncolored DOC [Curtis and Schindler, 797  
 798 1997] and further that substantial DOC losses via photo- 798  
 799 degradation can occur on the timescale of a day or less 799  
 [Bertilsson and Tranvik, 2000]. The net result of these lake 800  
 processes would be a seasonal decrease in the fulvic acid 801  
 content of DOC and an increase in the FI of fulvic acids, 802  
 both of which were observed at GL4 and ALB. 803

804 [39] Over the entire season, the fact that the FI values for 804  
 fulvic acids were significantly correlated with the fulvic 805  
 acid content of DOC at the GL4 site suggests that observed 806  
 changes in DOC chemistry are linked with changes in DOC 807  
 precursor material in the alpine reach of the catchment. 808  
 Moreover, the lack of correlation between indices of DOC 809  
 chemistry and precursor material at the other sites is likely 810  
 a result of the smaller range in the indices at the forested sites. 811  
 One potentially important implication of this conceptual 812  
 model is that autochthonous production may exert substan- 813  
 tial influence on the amount and chemical character of DOC 814  
 in high-elevation catchments with appreciable lake area. To 815  
 illustrate this point, a simple end-member mixing analysis 816  
 using the fluorescence index to apportion the seasonal yield 817  
 of DOC at GL4 to terrestrial and aquatic sources suggests 818  
 that between 30 and 40% of the seasonal DOC yield is 819  
 derived from net production in lakes. Care must be taken in 820  
 interpreting these yields because they are based on the 821  
 assumptions that the fluorescence index can be used in a 822  
 quantitative manner and that the Lake Fryxell and Suwan- 823  
 nee River fulvic acids are valid end-members for net 824  
 production of autochthonous and allochthonous DOC in 825  
 our study catchment. However, even with these limitations, 826



827 these calculations strongly suggest that the alpine lakes in  
828 the upper Green Lakes Valley, which account for less than  
829 5% of the total catchment area, act as centers of DOC  
830 production in a relatively unproductive landscape and there-  
831 fore have disproportionately high area-weighted yields of  
832 DOC compared to the terrestrial portion of the catchment.

833 [40] In the Colorado Front Range, developing a better  
834 understanding of the role of lakes in the DOC yield of high-  
835 elevation catchments is important in light of recent studies  
836 showing that the provenance of sediment organic matter in  
837 the lakes has changed markedly since the midtwentieth  
838 century. Stratigraphic records from sediment cores in Green  
839 Lake 4 as well as several high-elevation lakes in Rocky  
840 Mountain National Park in Colorado indicate that diatom  
841 assemblages have changed in concert with an increase in  
842 carbon storage in sediments and a decrease in sediment C:N  
843 ratios [Waters, 2003; Wolfe et al., 2002]. At the same time,  
844 the FI values of organic material in sediments have  
845 increased, which is consistent with an increase in inputs  
846 of autochthonous organic material to sediments. These  
847 findings indicate that algal production in alpine lakes is  
848 increasing, likely as a result of nutrient enrichment from  
849 anthropogenic N emissions and a decrease in ice-cover  
850 thickness and duration during the last several decades  
851 [Sommaruga-Wogratz et al., 1997; Waters, 2003; Wolfe et  
852 al., 2001, 2002]. In relation to our study, these findings  
853 suggest that changes in chemical inputs and climate in the  
854 high-elevation reaches of the Green Lakes Valley are  
855 increasing the net production of autochthonous organic  
856 material in alpine lakes. This, in turn, has the potential to  
857 alter both the amount and chemical character of DOC  
858 exported to downstream aquatic systems. Moreover, recent  
859 reports of elevated concentrations of inorganic N in high-  
860 elevation lakes in both the western United States [Campbell  
861 et al., 1995; Williams and Tonnessen, 2000] and Europe  
862 [Psenner, 1989; Kopacek et al., 1995] suggest that a wide  
863 range of high-elevation ecosystems may be susceptible to  
864 shifts in DOC dynamics similar to those that appear to be  
865 occurring in Green Lakes Valley.

866

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