

A model of degradation and production of three pools of dissolved organic matter in an alpine lake

Matthew P. Miller,^{a,1,*} Diane M. McKnight,^a Steven C. Chapra,^b and Mark W. Williams^c

^aDepartment of Civil, Environmental, and Architectural Engineering, Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado

^bDepartment of Civil and Environmental Engineering, Tufts University, Medford, Massachusetts

^cDepartment of Geography, Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado

Abstract

We investigated the transport and production of dissolved organic matter (DOM) in an alpine lake in the Colorado Front Range during snowmelt and the summer ice-free season by employing a new approach for distinguishing between three pools of DOM based on fractionation and spectroscopic characterization. Reactive transport modeling results confirm that terrestrially derived sources of humic DOM are dominant during snowmelt and that microbially derived humic and nonhumic DOM are produced in the lake in the summer, when rates of primary productivity are highest. DOM characterization and modeling results support the interpretation that losses of terrestrially derived humic DOM are dependent on photochemistry and indicate that the decay of nonhumic and microbially derived humic DOM is more influenced by heterotrophic degradation. Results suggest that production of nonhumic DOM can be directly related to chlorophyll *a* concentrations and that microbially derived humic DOM can be produced through condensation reactions. Furthermore, fluorescence and parallel factor analysis (PARAFAC) of DOM suggest that the rate of decay of microbially derived humic DOM decreases as the redox state of quinone-like moieties of the DOM becomes more oxidized. This study quantifies the influence of DOM source on the chemical and biological reactivity of DOM in lakes. The methods presented in this study provide a framework for testing hypotheses related to the effects of a changing climate on lake ecosystem structure and function.

Recently, increases in dissolved organic carbon (DOC) concentrations in surface waters have been documented in many north temperate regions (de Wit et al. 2007; Monteith et al. 2007). These trends have raised concerns because the underlying processes are not fully understood and because of the affects of increasing DOC on aquatic ecosystems and drinking water quality (Reckhow et al. 1990). To resolve among potential drivers, it is important to consider that the quality and reactivity of dissolved organic matter (DOM) is dependent on its source (Hood et al. 2003; Mladenov et al. 2007; Gondar et al. 2008). For example, humic DOM of terrestrial origin generally has a higher content of aromatic groups than does humic DOM of microbial origin (McKnight et al. 1994; Mladenov et al. 2005; Jaffe et al. 2008). Additionally, the presence of lakes in catchments has been shown to influence the quantity and quality of DOM at downstream sites (Larson et al. 2007). Sources of DOM to surface waters include (1) the flushing of humic DOM from catchment soils and vegetation (Thurman 1985), (2) the release of nonhumic microbial exudates and other nonhumic plant and soil products (Giroldo and Vieira 2005; Kawasaki and Benner 2006), and (3) the production of microbially derived humic DOM from biomass (McKnight et al. 1994). Furthermore, it is anticipated that the relative contribution of DOM from these different sources will change in response to a changing climate (L. J. Tranvik et al. unpubl. data).

In the Green Lakes Valley in the Front Range of the Colorado Rocky Mountains, yearly monitoring has shown that a pulse of terrestrially derived, aromatic humic DOM is transported into alpine and subalpine lakes during snowmelt (Hood et al. 2003). This pulse is characterized by a low fluorescence index (FI) and high specific ultraviolet absorbance (SUVA). Later in the summer, during the annual phytoplankton bloom, microbial sources contribute humic DOM with a high FI and low SUVA and the percentage of humic DOM decreases. Based on these results, Hood et al. (2003) proposed a conceptual model of DOM cycling in the Green Lakes Valley in which the alpine lakes function as wide points in the stream during snowmelt, with minimal in-lake modification of the DOM pool. In contrast, later in summer, on the descending limb of the snowmelt hydrograph, alpine lakes provide autochthonous DOM to the lower stream reaches. Using the FI in an end-member mixing analysis, they calculated that 30–40% of the DOC yield at the outlet of an alpine lake was derived from in-lake production.

The conceptual model of Hood et al. (2003) provides a framework for understanding future changes in these lakes but requires quantification of the biogeochemical reactivity of DOM to be useful in predicting the extent of changes in DOM quality that may occur. Several trends observed in the Colorado Front Range may be drivers of change in algal production and in-lake DOM quality, including decreasing lake ice thickness, earlier occurrence of ice out and snowmelt, and increasing atmospheric nitrogen deposition (Williams and Tonnesen 2000; Caine 2002). These changes will likely result in greater phytoplankton and

*Corresponding author: mpm18@psu.edu

¹Present address: School of Forest Resources, Pennsylvania State University, University Park, Pennsylvania

benthic algal production and therefore greater autochthonous production of nonhumic and microbially derived humic DOM in lakes. Terrestrially derived DOM inputs may also change with the eventual arrival of the mountain pine beetle (*Dendroctonus ponderosae*). Quantitative analysis of the potential changes in DOM quality requires a reactive transport model that considers allochthonous sources of DOM and the decay and production of DOM within the lake. Recently there have been advances in the reactive transport modeling of DOM of varying source and quality in wetlands (Mladenov et al. 2007), streams (Miller et al. 2006), and lakes (Hanson et al. 2004). In some of these studies, DOM has been separated into pools based on source and/or lability; however, information gained from chemical characterization of DOM quality was not used as a basis to perform the separation.

This study focuses on quantitatively evaluating and extending the hypotheses put forward in the conceptual model of Hood et al. (2003) for an alpine lake in the Colorado Front Range. A lake model was developed that accounts for DOM in three pools of differing source entering the epilimnion via surface water runoff and precipitation, as well as lake stratification, and time-variable water residence times. This model allows for comparison of measured values for the three DOM pools with simulated values at the lake's outlet, assuming conservative transport. Additionally, the development of a reactive transport model has allowed for a more detailed investigation into the biological and chemical conditions that drive the reactivity of the three pools of DOM in the lake.

Methods

Site description—The research site is the Green Lakes Valley, which is described elsewhere (Williams et al. 2001; Hood et al. 2003). Beginning in May 2006 and ending in September 2006 samples were collected on a weekly basis from the inlet and outlet of Green Lake 4, an oligotrophic alpine lake in the Green Lakes Valley (Fig. 1; Table 1). The watershed above Green Lake 4 drains approximately 2.2 km² and has steep talus slopes. About 20% of the valley floor is covered by vegetation with well-developed soils, and the rest of the valley floor is glaciated bedrock (Williams et al. 2001). The inlet to Green Lake 4 is braided and divides into multiple channels, while the outlet is a well-defined channel. Water level at the lake outlet is monitored continuously with a pressure transducer, and discharge is calculated using a rating curve.

The Green Lakes Valley receives the majority of its precipitation as winter snowfall, and the hydrology is dominated by spring snowmelt. An annual peak in the hydrograph occurs in late May or early June. As the snow melts, primary productivity is generally low, with chlorophyll *a* (Chl *a*) concentrations <1 µg L⁻¹ (Gardner et al. 2008). After snowmelt, residence time in the lake gradually returns to baseflow conditions (~30 d). Monitoring of Green Lake 4 shows that as snowmelt ends, the percentage contribution of fulvic acids decreases, nitrate (NO₃⁻) concentrations decrease, total dissolved phosphorus (TDP) concentrations are consistently low, and primary

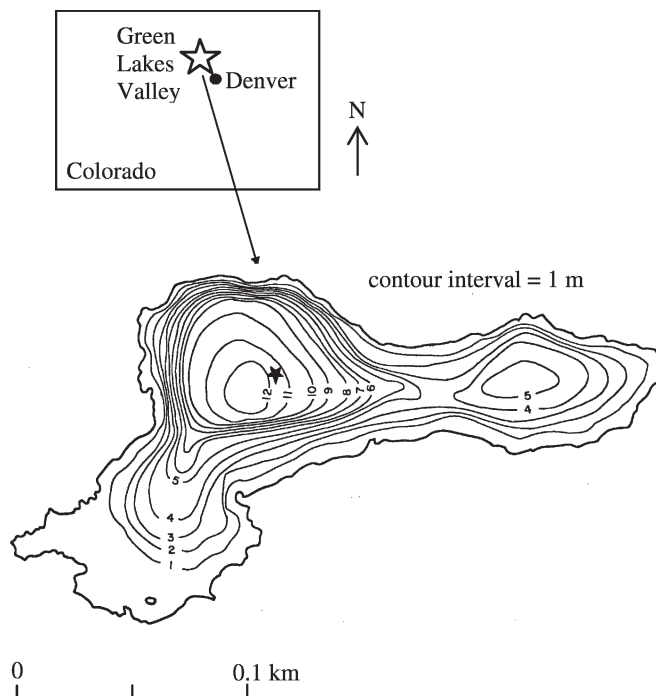


Fig. 1. Map of Colorado showing the location of the Green Lakes Valley. The inset shows a bathymetric map of Green Lake 4, and the solid star represents the sampling location for collection of water column samples.

productivity increases (peak Chl *a* concentrations of ~8 µg L⁻¹; Gardner et al. 2008). Conservative transport simulations have shown that nitrate and total dissolved phosphorus are consumed in the lake coincident with a peak in phytoplankton productivity (Miller 2008).

Field sampling—Water samples were collected from a representative inlet stream and the outlet of Green Lake 4. Samples were collected on 15 dates during the summer of 2006. The water column of Green Lake 4 was sampled at three depths (surface, 3 m, and 9 m) on 06 July 2006. A composite rainwater sample was collected as part of the National Atmospheric Deposition Program (<http://nadp.sws.uiuc.edu/>) during a rain event from 07 to 09 July 2006. Samples for analysis of DOC, percentage of fulvic acid content (%FA), Chl *a*, absorbance, oxygen isotopes (δ¹⁸O), and fluorescence spectroscopy were collected in precombusted 500-mL amber glass bottles and filtered within 4 h of collection with precombusted 0.7-µm, 47-mm Whatman GF/F glass-fiber filters with a hand-pump filtration system. The rainwater sample was collected in a 60-mL Nalgene high-density polyethylene bottle, filtered with a 1-µm, 47-mm Gelman A/E glass-fiber filter, and analyzed for DOC, absorbance, fluorescence, and δ¹⁸O. Table 2 lists the variables that were measured, calculated, or estimated in this study and their abbreviations.

Laboratory methods—Filters were immediately processed for analysis of Chl *a* concentrations following the methods of Marker et al. (1980). The filtrate was acidified to pH 2 and stored at 4°C. Within 1 week, samples were analyzed for

Table 1. Morphometric characteristics of Green Lake 4.

Characteristic	Green Lake 4
Elevation (m)	3550
Surface area (km ²)	0.05
Volume (m ³)	214,960
Maximum depth (m)	13.1
Depth of stratification (m)	8.0
Thickness of thermocline (m)	2.0
Approx. date of ice out	06 Jul 2006

DOC concentration, percentage of fulvic acid, absorbance, and fluorescence characteristics. DOC concentrations were measured by high temperature catalytic oxidation with a Shimadzu TOC-550A total organic carbon analyzer, with a confidence interval of 0.02 mg L⁻¹. Absorbance values for all whole water samples and humic fractions were obtained with an Agilent 8453 ultraviolet (UV)–visible spectroscopy system. A 3-mL quartz cuvette with a path length of 1 cm was used, and absorbance was measured at 1-nm intervals over a range of 190 nm to 1100 nm. Specific ultraviolet absorbance (SUVA₂₅₄; m² g⁻¹) of the humic fraction was calculated as the ratio of the decadic absorption coefficient at 254 nm (α) to the DOC concentration of the humic fraction. Analysis for $\delta^{18}\text{O}$ was done at the Stable Isotope Laboratory at the Institute of Arctic and Alpine Research (INSTAAR) (Epstein and Mayeda 1953). The 1- σ precision was $\pm 0.05\%$.

A 200-mL subsample of each 500-mL sample was fractionated into nonhumic and humic fractions using columns with a 10-mL bed volume packed with XAD-8 resin following the methods of Thurman and Malcolm (1981). The nonhumic fraction, which includes low molecular weight compounds such as carbohydrates, amino acids, and carboxylic acids (Thurman 1985), does not sorb to the XAD-8 resin at low pH and was collected as the effluent from the column. The humic fraction sorbs to the XAD-8 resin and was obtained by back elution with 20 mL of 0.1 NaOH. The humic fraction was immediately acidified to pH 2 with concentrated HCl. The percentage of the DOM that was humic was determined using the mass balance approach described by Hood et al. (2003), which typically yields near complete DOC recovery ($\pm 5\%$). Thurman (1985) reported that the majority of the humic DOM in surface waters is fulvic acid. Therefore, the percentage of humic DOM is referred to as the percentage of fulvic acid following the terminology of Baron et al. (1991) and Hood et al. (2003). It was not possible to fractionate the rainwater sample given the small sample volume.

All samples collected for fluorescence analysis were analyzed using a JY-Horiba/Spex Fluoromax-3 spectrofluorometer. To ensure stable instrument function, a lamp scan, cuvette check, and water raman scan were run daily. Scans collected every few months included a quinine sulfate scan and scans of Suwannee River fulvic acid (SRFA) and Pony Lake fulvic acid (PLFA). To correct for decay in the lamp output over time, the area underneath the water raman scan was calculated and used to normalize all sample intensities.

Table 2. Variables and their corresponding abbreviations that were used in the study. Also shown are the subscripts that were used in combination with a subset of the variables.

Variable	Abbreviation
Chlorophyll <i>a</i>	Chl <i>a</i>
Decadic absorption coefficient	α
Decay rate	<i>k</i>
Delta oxygen-18	$\delta^{18}\text{O}$
Dissolved organic carbon	DOC
Dissolved organic matter	DOM
Fluorescence index	FI
Percentage fulvic acid	%FA
Pony Lake fulvic acid	PLFA
Production rate	λ
Ratio of carbon to chlorophyll <i>a</i> in algae	r_{ca}
Reactive transformation	<i>S</i>
Redox index	RI
Specific ultraviolet absorbance	SUVA
Suwannee River fulvic acid	SRFA
Temperature	<i>T</i>
Thermocline area	A_t
Thermocline mixing rate	E'_t
Thermocline thickness	z_t
Vertical eddy diffusivity	E_t
Volume	<i>V</i>
Volumetric flow rate	<i>Q</i>
Subscript	
Epilimnion	<i>e</i>
Hypolimnion	<i>h</i>
Inflow stream	<i>in</i>
Microbially derived humic fraction	MH
Nonhumic fraction	NH
Precipitation	<i>p</i>
Terrestrially derived humic fraction	TH
Time	<i>t</i>
Total humic fraction	H
Whole water	WW

Three-dimensional fluorescence scans were run on all filtered whole water and humic samples. Scans were blank subtracted and corrected for excitation and emission in Matlab (Cory 2005) using the instrument specific excitation and emission correction files, and were corrected for the inner-filter effect. The FI for each sample was calculated as the ratio of intensity of emission at 470 nm to the intensity of emission at 520 nm for an excitation scan at 370 nm (McKnight et al. 2001; Cory 2005). The standard deviation associated with triplicate analyses was 0.01 (Cory 2005).

Corrected three-dimensional excitation-emission matrices (EEMs) were modeled using the parallel factor analysis (PARAFAC) model presented in Cory and McKnight (2005). PARAFAC corresponds to a three-way version of principal component analysis, and when applied to the EEMs of samples containing DOM, identifies different classes of fluorophores herein referred to as “components” (Stedmon et al. 2003). An EEM can be represented as the sum of the components. The redox state of the quinone-like fluorophores was determined using the redox index (RI; Miller et al. 2006).

Calculation of DOM source pools—For each sample collected at the inlet, outlet, and in the water column, the DOM was separated into three pools of differing source. The three source pools are (1) terrestrially derived humic DOM (DOC_{TH} ; mg L^{-1}), (2) nonhumic DOM (DOC_{NH} ; mg L^{-1}), and (3) microbially derived humic DOM (DOC_{MH} ; mg L^{-1}). Based on prior monitoring results, the three DOM pools were calculated using a mixing model approach similar to that of McKnight et al. (1992). The whole water DOC concentrations can be broken into two pools as follows:

$$\text{DOC}_{\text{WW}} = \text{DOC}_{\text{NH}} + \text{DOC}_{\text{H}} \quad (1)$$

where DOC_{WW} (mg L^{-1}) is the measured whole water DOC concentration and DOC_{H} (mg L^{-1}) is the measured humic fraction concentration. DOC_{H} can be separated further into the terrestrially derived and microbially derived humic pools described above by

$$\text{DOC}_{\text{H}} = \text{DOC}_{\text{TH}} + \text{DOC}_{\text{MH}} \quad (2)$$

Likewise, the decadic absorption coefficient balance is as follows:

$$\alpha_{\text{H}} = \alpha_{\text{TH}} + \alpha_{\text{MH}} \quad (3)$$

where α_{H} (m^{-1}), α_{TH} (m^{-1}), and α_{MH} (m^{-1}) represent the decadic absorption coefficients at 254 nm of the total humic fraction of the DOM, the terrestrially derived humic fraction, and the microbially derived humic fraction, respectively.

Because it is not possible to directly measure DOC_{TH} , DOC_{MH} , α_{TH} , or α_{MH} , end-member SUVA_{254} values can be used to rewrite Eq. 3, which can then be solved for DOC_{TH} and DOC_{MH} . Given that the SUVA_{254} value for a given sample is defined as the decadic absorption coefficient normalized to the DOC concentration, Eq. 3 can be rewritten as follows:

$$\text{SUVA}_{\text{H}}\text{DOC}_{\text{H}} = \text{SUVA}_{\text{TH}}\text{DOC}_{\text{TH}} + \text{SUVA}_{\text{MH}}\text{DOC}_{\text{MH}} \quad (4)$$

where SUVA_{H} ($\text{m}^2 \text{g}^{-1}$) is the measured SUVA_{254} value of the humic fraction, and SUVA_{TH} ($\text{m}^2 \text{g}^{-1}$) and SUVA_{MH} ($\text{m}^2 \text{g}^{-1}$) represent the SUVA_{254} values of terrestrially derived humic DOM and microbially derived humic DOM end members, respectively. The values of SUVA_{TH} and SUVA_{MH} end members are parameters of the model, and the expected ranges of both values are known from previous studies. SUVA_{TH} is expected to be similar to the SUVA_{254} of SRFA and SUVA_{MH} is expected to be similar to the SUVA_{254} of PLFA. SRFA and PLFA are end-member fulvic acids available from the International Humic Substances Society. The values of SUVA_{TH} and SUVA_{MH} were set based on comparison of the maximum and minimum humic SUVA_{254} values measured in this study with those of SRFA and PLFA, respectively, and to meet the requirement that

$$\text{SUVA}_{\text{MH}} \leq \text{SUVA}_{\text{H}} \leq \text{SUVA}_{\text{TH}} \quad (5)$$

It should be noted that SUVA_{TH} and SUVA_{MH} are constant parameters in the model, while DOC_{TH} , DOC_{MH} , α_{TH} , α_{MH} , and SUVA_{H} are all time-variable values. Therefore, each sample has unique DOC_{TH} and DOC_{MH}

concentrations. DOC_{TH} can be solved for any sample by combining Eqs. 2 and 4 as follows:

$$\text{DOC}_{\text{TH}} = \frac{\text{DOC}_{\text{H}}(\text{SUVA}_{\text{H}} - \text{SUVA}_{\text{MH}})}{(\text{SUVA}_{\text{TH}} - \text{SUVA}_{\text{MH}})} \quad (6)$$

It follows that

$$\text{DOC}_{\text{MH}} = \text{DOC}_{\text{H}} - \text{DOC}_{\text{TH}} \quad (7)$$

The DOM separation technique and the choice of SUVA_{TH} and SUVA_{MH} were evaluated by running a linear regression analysis between the ratio of $\text{DOC}_{\text{MH}}:\text{DOC}_{\text{H}}$ and the FI of the humic fraction of the samples collected at the outlet of the lake. Although FI and SUVA_{254} are generally inversely related, processes that may decrease SUVA_{TH} , such as photobleaching and sorption on iron oxides, do not cause an increase in FI, but may cause a slight decrease (McKnight et al. 2001; Cory et al. 2007). Thus, examination of the production and loss of DOC_{H} and temporal trends in the FI of the humic fraction is a robust test that differentiates between a decrease in SUVA_{H} resulting from addition of microbially derived humic DOM and a decrease resulting from a change in SUVA_{254} of the terrestrially derived humic end member.

Model development—A reactive transport model was developed to investigate hydrologic and in-lake biological controls on the three DOM pools described above. The lake was represented as two well-mixed constant-volume layers (epilimnion and hypolimnion) with one surface water inlet, a precipitation input, exchange between the epilimnion and hypolimnion, and one surface water outlet. Direct groundwater input to the lake and evaporative losses from the lake were not considered in the model.

Mass balance equations can be written for each of the DOM pools for the two layers as

$$\begin{aligned} V_e \frac{d\text{DOC}_{i,e}}{dt} = & Q_{in}(t)\text{DOC}_{i,in} + Q_p(t)\text{DOC}_{i,p} \\ & - (Q_{in}(t) + Q_p(t))\text{DOC}_{i,e} \\ & + E'_t(t)(\text{DOC}_{i,h} - \text{DOC}_{i,e}) + S_i V_e \end{aligned} \quad (8)$$

and

$$V_h \frac{d\text{DOC}_{i,h}}{dt} = E'_t(t)(\text{DOC}_{i,e} - \text{DOC}_{i,h}) + S_i V_h \quad (9)$$

where V = volume (m^3), DOC_i = DOC concentration (mg L^{-1}) for DOC species i , t = time (d), Q = volumetric flow rate ($\text{m}^3 \text{d}^{-1}$), E'_t = thermocline mixing rate ($\text{m}^3 \text{d}^{-1}$), and S_i = transformations ($\text{mg L}^{-1} \text{d}^{-1}$) for DOC species i . The (t) denotes that the parameter is a time-variable input function. The subscripts designate the epilimnion (e), hypolimnion (h), inflow stream (in), and precipitation (p). In addition to the three DOM pools, $\delta^{18}\text{O}$ was simulated as a conservative substance. That is, $\delta^{18}\text{O}$ was modeled using Eqs. 8 and 9 with transformations, S , set to zero.

The mixing rate, E' , quantifies mass transfer due to two-way flows across open boundaries (Chapra 1979). As applied to the thermocline, it is related to more fundamen-

Table 3. Parameters used in the lake model for values that were estimated.

Parameter	Units	Value	Source
Thermocline mixing coefficient	m ³ d ⁻¹	Time variable	Water column temperature profiles
Initial $\delta^{18}\text{O}$ value in hypolimnion	‰	-15.5	Value measured in hypolimnion during lake stratification on 06 July 2006
Humic DOC from terrestrial sources in precipitation	mg L ⁻¹	0.25	1/3 of whole water DOC
Nonhumic DOC in precipitation	mg L ⁻¹	0.25	1/3 of whole water DOC
Humic DOC from microbial sources in precipitation	mg L ⁻¹	0.25	1/3 of whole water DOC
Initial humic DOC from terrestrial sources in hypolimnion	mg L ⁻¹	0.11	Value measured from hypolimnion sample during lake stratification on 06 July 2006
Initial nonhumic DOC in hypolimnion	mg L ⁻¹	0.5	Value measured from hypolimnion sample during lake stratification on 06 July 2006
Initial humic DOC from microbial sources in hypolimnion	mg L ⁻¹	0.22	Value measured from hypolimnion sample during lake stratification on 06 July 2006

tal parameters by

$$E'_t = \frac{E_t A_t}{z_t} \quad (10)$$

where E_t = vertical eddy diffusivity across the thermocline (m² d⁻¹), A_t = thermocline area (m²), and z_t = the thermocline thickness (m).

Kinetic transformations for the DOM pools were developed to test specific hypotheses about the reactive transport of the three pools of DOM. First, to test the importance of photochemical and microbial decay of the terrestrially derived humic DOM pool, the following expression for reactive transformation was used:

$$S_{\text{TH}} = -k_{\text{DOC}_{\text{TH}}} 1.07^{T-20} \text{DOC}_{\text{TH}} \quad (11)$$

where T = layer temperature (°C) and k_i = the decay rate (d⁻¹) for DOC species i . The value of 1.07 is a constant that corresponds to a Q_{10} value of 2 (a doubling of the decay or production rate for an increase in water temperature from 10°C to 20°C) (Chapra 1997). Second, the dependence of the nonhumic DOM pool on primary productivity was tested with the transformation

$$S_{\text{NH}} = -k_{\text{DOC}_{\text{NH}}} 1.07^{(T-20)} \text{DOC}_{\text{NH}} + \lambda_{\text{DOC}_{\text{NH}}} 1.07^{(T-20)} r_{\text{ca}} \text{Chl } a \quad (12)$$

where λ_i = the production rate (d⁻¹) for DOC species i , r_{ca} is the ratio of carbon to Chl a in the algae (mg C μg Chl a ⁻¹), and Chl a is the Chl a concentration measured at the outlet (μg L⁻¹). Finally, the role of condensation reactions in the production of microbially derived humic DOM and redox-dependent decay of the microbially derived humic DOM pool were tested with the transformation

$$S_{\text{MH}} = -2k_{\text{DOC}_{\text{MH}}} 1.07^{(T-20)} \text{DOC}_{\text{MH}} \text{RI} + \lambda_{\text{DOC}_{\text{MH}}} 1.07^{(T-20)} \text{DOC}_{\text{NH}} \quad (13)$$

where RI is the unitless redox index of the whole water DOM.

The three DOM pools and $\delta^{18}\text{O}$ were modeled from 01 June 2006 through 07 September 2006. Initial conditions in the epilimnion were set as measured values from the outlet

to the lake on 01 June 2006. Discharge measured from the gage at the lake outlet, the volume of rainfall during the 07–09 July 2006 rain event, and knowledge of the mixing regime in the lake were used to estimate surface water flow at the inlet. Values for $E'_t(t)$ were based on water temperature data at the outlet to Green Lake 4 in concert with water column temperature profiles and knowledge of when the lake was ice covered and ice free.

All model parameters that were not measured directly were estimated (Table 3). The k_{DOC} (d⁻¹) terms are user-defined, first-order decay coefficients for the respective DOM pools and were obtained from the literature (Mladenov et al. 2007). The RI of the whole water DOM was scaled from 0 to 1, where 1 corresponded to the maximum value measured at the outlet during the course of the season (0.51 on 01 June 2006) and 0 corresponded to the minimum value measured at the outlet (0.27 on 17 August 2006). Values for the production coefficients, λ , for the DOC_{MH} and DOC_{NH} pools were determined by model calibration to fit the measured data. The sensitivity of the model to these assumptions was tested over the course of the season (Miller 2008). Forcing functions and parameters used in the reactive transport model are shown in Table 4.

Because the hypolimnion $\delta^{18}\text{O}$ and DOC concentrations were not measured over the course of the summer, they were modeled where the only sources to or from the hypolimnion were due to mixing with the epilimnion. The differential equations represented in Eqs. 8 and 9 were solved using the classical fourth-order Runge-Kutta method. For all model results the root mean square error (RMSE) between observed and simulated values was calculated.

Results

Hydrology—The hydrograph at the outlet to Green Lake 4 in early summer was characteristic of snowmelt dominated catchments (Fig. 2). Discharge began to increase in mid May and peaked in late May at just over 26,000 m³ d⁻¹, with a second peak in early June. As reported by Hood et al. (2003), this second peak may have been caused by failure of an upstream ice dam on Green Lake 5. Additionally, there was a peak in discharge in early July of approximately 60,000 m³ d⁻¹, which was over twice

Table 4. Forcing functions and parameters used in the reactive transport model.

Model inputs	Units	Value	Source
Forcing functions			
T_e	°C	Variable	Measured in field
Chl <i>a</i>	$\mu\text{g L}^{-1}$	Variable	Measured in field
RI	Unitless	0–1	Scaled from field measurements
Parameters			
k_{TH} , decay coefficient of DOC_{TH} pool	d^{-1}	0.045	Slowly decaying DOC pool value from Mladenov et al. (2007)
k_{NH} , decay coefficient of DOC_{NH} pool	d^{-1}	0.14	Rapidly decaying DOC pool value from Mladenov et al. (2007)
k_{MH} , decay coefficient of DOC_{MH} pool	d^{-1}	0.045	Slowly decaying DOC pool value from Mladenov et al. (2007)
λ_{NH} , production coefficient of DOC_{NH} pool	d^{-1}	0.85	Estimated by calibration
λ_{MH} , production coefficient of DOC_{MH} pool	d^{-1}	0.01	Estimated by calibration
r_{ca}	$\text{mg C } \mu\text{g Chl } a^{-1}$	0.03	Chapra (1997)

the peak during snowmelt. This peak resulted from an unusual 3-d midsummer rainstorm that produced 9 cm of precipitation. Following this peak, the flow from the lake quickly returned to pre-rain event conditions.

When the assumptions described in Table 3 were used, the conservative transport model results matched well with the measured $\delta^{18}\text{O}$ values (Fig. 3). Prior to the rain event, the simulated $\delta^{18}\text{O}$ values were essentially identical to the measured values. Following the rain event the model results deviated slightly from the measured values, with differences between the simulated and measured values being less than 2%. Late in the season the measured values were consistently more enriched than the modeled values. The greatest deviation of measured values from simulated values occurred at the end of the summer (1.7%) when the residence time, and subsequently the evaporation rate, was greatest. Moreover, sensitivity analyses showed that the model was not sensitive to the initial $\delta^{18}\text{O}$ values in the hypolimnion (Miller 2008).

Primary productivity—Chl *a* concentrations at the lake inlet were low ($\sim 1 \mu\text{g L}^{-1}$) throughout the summer (Fig. 4). In contrast, the Chl *a* concentrations at the lake outlet were low in May and then began to increase. Following the rain event, the Chl *a* concentration at the outlet decreased as the phytoplankton were flushed from the lake (Miller et al. 2009). Later in the summer, the Chl *a* concentration at the outlet rapidly increased and remained high ($5\text{--}6 \mu\text{g L}^{-1}$) for a period of 5 weeks.

The dominant phytoplankton found in Green Lake 4 during the monitoring period (06 July–10 August 2006) were of the divisions Cyanophyta and Chlorophyta. There were also species of Bacillariophyta, Dinophyta, Haptophyta, and Cryptophyta in lower abundances. The only noticeable shift in phytoplankton abundance occurred during the period of high Chl *a* concentrations, as species of Chlorophyta (*Chlamydomonas* sp. and *Chlorella* sp.) approximately doubled in abundance (www.culter.colorado.edu).

Dissolved organic matter chemistry—Figure 5 shows the biogeochemical characteristics of the DOM at the inlet and

outlet to Green Lake 4 during the summer. At both the inlet and outlet, DOC concentrations peaked during snowmelt (Fig. 5a,b) and then decreased and remained relatively steady ($0.5\text{--}1 \text{ mg L}^{-1}$). The percentage of fulvic acid at both sites was high during snowmelt ($\sim 80\%$) and decreased to approximately 20% during baseflow conditions (Fig. 5c,d). Immediately following the rain event, the percentage of fulvic acid increased.

The SUVA_{H} values of the humic fraction were high early in the summer at both sites, indicating that the humic fraction was more aromatic (Fig. 5e,f). Later in the season, during the phytoplankton bloom, the SUVA_{H} values decreased, indicating that the humic substances were less aromatic. The greatest SUVA_{H} value (SUVA_{TH} end member = $3.19 \text{ m}^2 \text{ g}^{-1}$; whole water FI = 1.42) was measured at the lake inlet on 06 July 2006. The lowest SUVA_{H} value (SUVA_{MH} end member = $1.66 \text{ m}^2 \text{ g}^{-1}$; whole water FI = 1.71) was measured at the lake outlet on 17 August 2006. These values are nearly identical to the SUVA_{254} values of SRFA ($3.2 \text{ m}^2 \text{ g}^{-1}$) and PLFA ($1.7 \text{ m}^2 \text{ g}^{-1}$) (Weishaar et al. 2003).

During snowmelt, the whole water FI values at both sites were low and similar to those of an adjacent wetland and to the SRFA end member, indicating a terrestrial source of DOM (Fig. 5g,h). Whole water FI values then increased as the summer progressed. This trend was more pronounced at the outlet than at the inlet. Following the rain event, the whole water FI decreased by approximately 0.1 units at the outlet to the lake but then rapidly increased, indicating a microbial source of DOM. The peak in whole water FI (1.71) occurred on 17 August 2006 at the outlet and was greater than the FI measured for the PLFA end member. After snowmelt, the FI values of the humic fraction increased consistently, but were lower than the whole water FI values by more than 0.1 units.

The RI at the inlet was about 0.5 during the entire summer, indicating that about half of the quinone-like fluorophores were in a reduced state (Fig. 5i). At the lake outlet, the RI was high early in the season, and then the quinone-like fluorophores became rapidly oxidized during the phytoplankton bloom late in the summer (Fig. 5j).

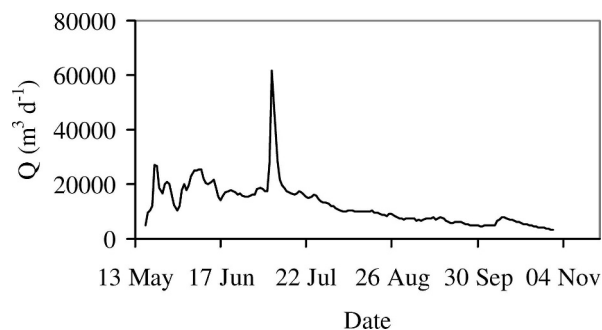


Fig. 2. Discharge at the outlet to Green Lake 4 during the summer of 2006. Following the snowmelt peak in late May the hydrograph peaked in early July in response to an unusual 3-d rain event.

The FI of the humic fraction for the samples from the lake outlet ranged from 1.24 on 01 June 2006 to 1.43 on 24 August 2006 (Fig. 5h). The percentage of humic DOM that was microbially derived ranged from 3% on 08 June 2006 to 100% on 17 August 2006. There was a significant positive relationship between the ratio of the microbially derived humic DOC concentration to total humic DOC concentration ($\text{DOC}_{\text{MH}}:\text{DOC}_{\text{H}}$) and the FI of the humic fraction of the DOM ($r^2 = 0.513$; $p < 0.01$) (Fig. 6). Furthermore, the two samples that had low RI values (Fig. 5j) and high concentrations of DOC_{MH} at the end of the summer (see Fig. 7c) had high $\text{DOC}_{\text{MH}}:\text{DOC}_{\text{H}}$ ratios and high humic FI values.

Conservative and reactive simulations of DOM pools— The measured concentrations of DOC_{H} and the three DOM pools (DOC_{TH} , DOC_{MH} , and DOC_{NH}) at the outlet to Green Lake 4 varied substantially over the course of the sampling period (Fig. 7). In general, the conservative transport simulation of the total humic pool (DOC_{H}) overestimated the measured concentrations, indicating that humic DOM was lost in the lake (Fig. 7a). However, the simulation underestimated the total humic DOM near the end of the phytoplankton bloom, indicating in-lake production of humic DOM.

The conservative transport simulation of the terrestrially derived humic pool (DOC_{TH}) overpredicted the measured concentrations at the outlet prior to the rain event (Fig. 7b). Addition of a decay term resulted in a better fit to the pre-rain event DOC_{TH} data. Both the conservative

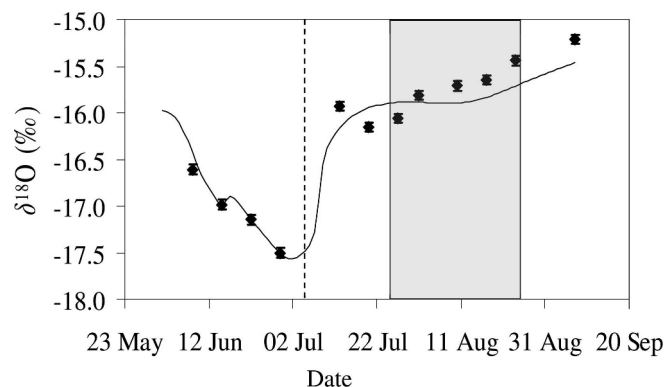


Fig. 3. Measured (points) and modeled (solid line) $\delta^{18}\text{O}$ content at the outlet to Green Lake 4. The vertical dashed line indicates the sustained rain event, and the shaded area represents the timing of the peak in Chl *a* at the outlet. Also shown are the $\pm 0.05\text{‰}$ 1- σ precision error bars. On all dates the error between the measured and modeled values is less than 2%.

and reactive simulations underpredicted the measured concentration directly following the rain event. Late in the summer, the measured DOC_{TH} concentrations were again overpredicted by the conservative transport simulation, and the addition of the decay term resulted in a more accurate simulation of the DOC_{TH} concentrations.

Generally, both the conservative and reactive transport simulations of the microbially derived humic pool (DOC_{MH}) overpredicted the measured concentrations prior to the rain event (Fig. 7c). On the other hand, following the rain event, the reactive transport simulation more accurately simulated the measured concentrations. The conservative simulation underpredicted the measured DOC_{MH} concentrations on two dates during the Chl *a* peak, when the quinone-like fluorophores were oxidized (see Fig. 5j), indicating that microbially derived humic DOM was produced in the lake. Addition of the first-order, redox-dependent decay term and the DOC_{NH} -dependent production term also resulted in an underprediction of DOC_{MH} on these two dates but provided a better fit than the conservative transport simulation.

The conservative transport simulation of the nonhumic pool (DOC_{NH}) overpredicted the measured DOC_{NH} concentrations prior to the Chl *a* peak and underpredicted the measured DOC_{NH} concentrations during the peak in Chl *a* (Fig. 7d). Addition of the first-order decay and Chl

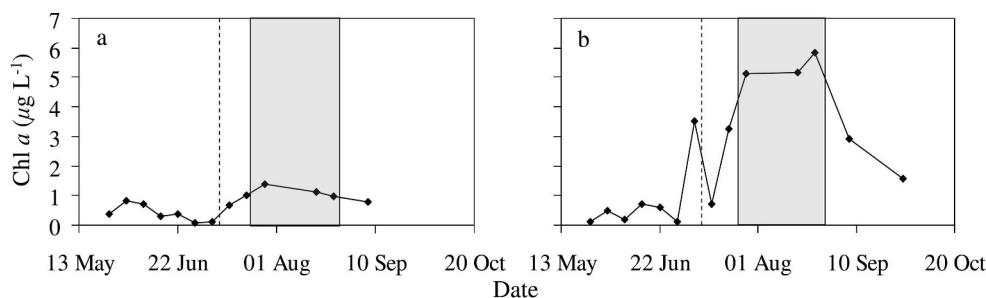


Fig. 4. Seasonal variation in Chl *a* at the (a) inlet and (b) outlet to Green Lake 4. The vertical dashed lines indicate the sustained rain event, and the shaded areas represent the timing of the peak in Chl *a* at the outlet.

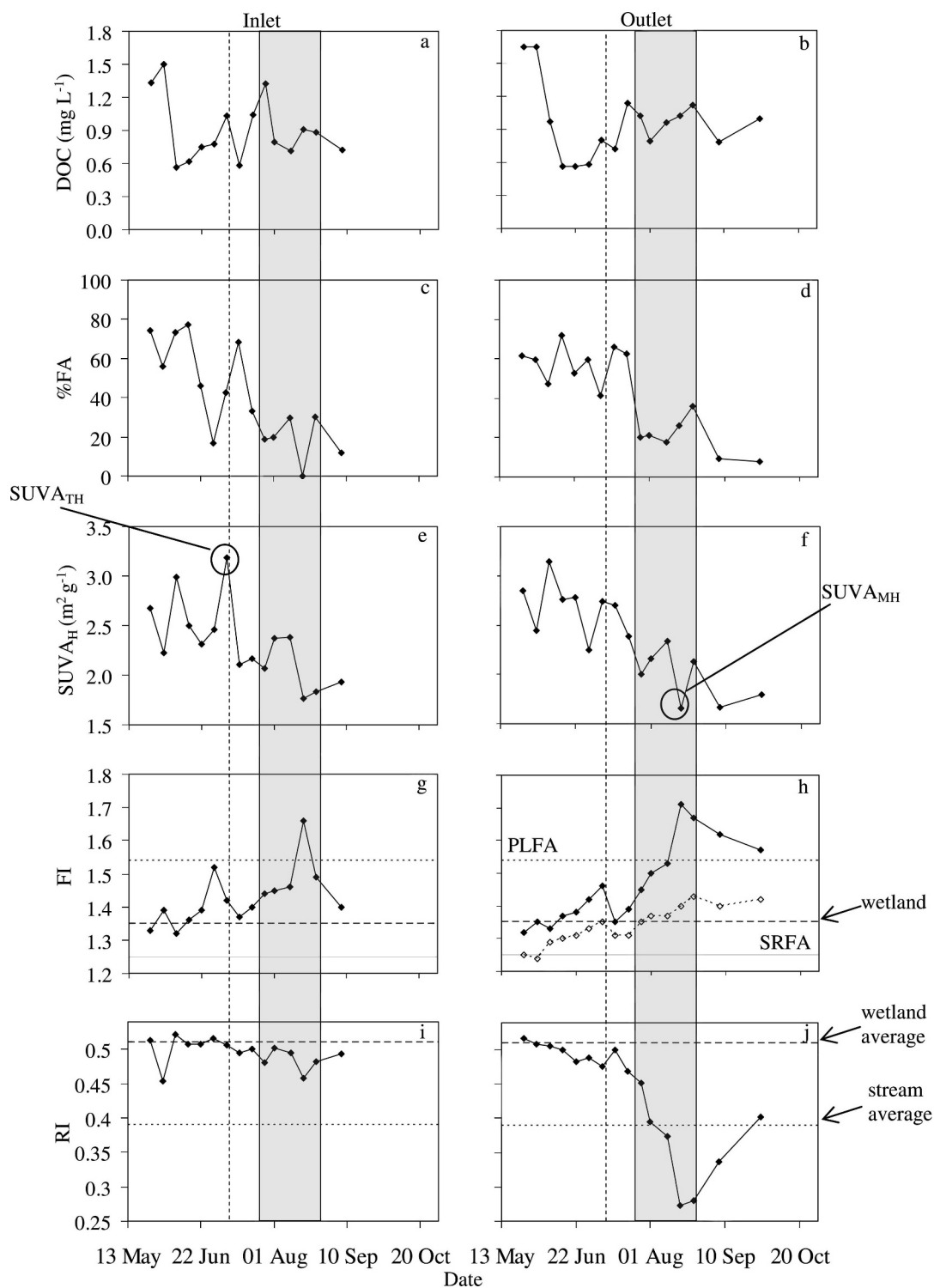


Fig. 5. Seasonal variation in (a, b) DOC, (c, d) percentage fulvic acid, (e, f) $SUVA_H$, (g, h) whole water FI, and (i, j) whole water RI at the inlet (left) and outlet (right) to Green Lake 4. Also shown in (h) is the FI of the humic fraction of the DOM at the outlet to Green Lake 4 (dashed line with open diamonds). The vertical dashed lines indicate the sustained rain event, and the shaded areas represent the timing of the peak in Chl *a* at the outlet. Also shown are the $SUVA_{TH}$ and $SUVA_{MH}$ end members that were used in the calculation of the three DOM pools. PLFA represents the FI of the Pony Lake fulvic acid end member, and SRFA represents the FI of the Suwannee River fulvic acid end member. The average FI and RI values from a wetland in the catchment as well as the average RI from an alpine stream site in the catchment are shown for reference.

α -dependent production terms improved the simulation both prior to and during the peak in Chl *a*. Sensitivity analyses for all assumptions (as described in Table 3) showed that the model was not sensitive to changes in the mixing regime in the lake, the initial DOC concentrations in the hypolimnion, or the biogeochemical characteristics of DOM in the precipitation (Miller 2008).

Sensitivity to photochemical degradation of DOC_{TH} —The sensitivity of the model to a time-variable decay coefficient for DOC_{TH} was used as a means to investigate the importance of photochemical degradation of the DOC_{TH} pool (Fig. 8). When it was assumed that there was a constant decay rate ($k_{TH} = 0.045 \text{ d}^{-1}$) regardless of whether the lake was ice covered or ice free and the effect of temperature was removed ($Q_{10} = 1.00$) the RMSE was 0.064. There was an improved fit to the measured DOC_{TH} concentrations when the terrestrially derived humic fraction was simulated with time-variable decay coefficients ($k_{TH} = 0.022 \text{ d}^{-1}$ under ice; $k_{TH} = 0.045 \text{ d}^{-1}$ when ice free) and $Q_{10} = 1.00$ (RMSE = 0.052).

Sensitivity to DOC_{NH} -dependent production of DOC_{MH} —There was little overall difference between the simulations of DOC_{MH} concentrations at the outlet to Green Lake 4 when the production of DOC_{MH} was modeled as being dependent on the concentration of the DOC_{NH} pool or the concentration of Chl *a* (Fig. 9). The deviation between the two simulations occurred at the end of the sampling period. The simulation in which the production of DOC_{MH} was dependent on $[DOC_{NH}]$ provided a better fit to the measured concentrations on 17 and 24 August 2006, while the simulations in which DOC_{MH} production was dependent on $[Chl \text{ } a]$ provided a better fit to the measured 07 September 2006 concentration.

Sensitivity to humic redox-dependent decay of DOC_{MH} —The model was somewhat sensitive to the dependence of the decay of the DOC_{MH} pool on the redox state of the quinone-like fluorophores (Fig. 10). The simulation in which the decay of DOC_{MH} was dependent on the scaled RI values (RMSE = 0.100) resulted in a better fit to the measured concentrations than did the simulation where the decay was not dependent on the RI (RMSE = 0.105). The simulations were essentially identical early in the season. The deviation between the two simulations occurred during the last three sampling dates of the season. On 17 and 24 August 2006, when the quinone-like fluorophores were oxidized (RI = 0.27 and 0.28, respectively), the simulation in which the decay of DOC_{MH} was dependent on the scaled RI provided a better fit to the measured concentrations. This simulation then deviated from the measured value on 07 September 2006 when the quinone-like fluorophores were in a moderately oxidized state (RI = 0.34).

Discussion

Hydrologic modeling—When modeling biogeochemical processes of reactive solutes such as DOM in aquatic systems, it is necessary to understand hydrologic controls

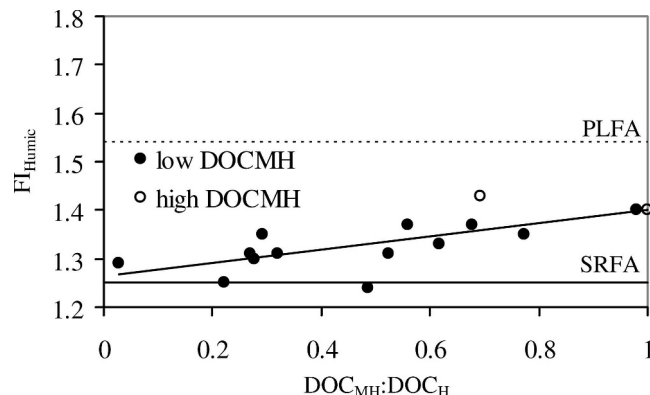


Fig. 6. Relationship between the ratio of microbially derived humic DOC and total humic DOC ($DOC_{MH}:DOC_H$) and the fluorescence index (FI) of the humic fraction of the DOC from samples collected at the outlet to Green Lake 4. There was a significant positive relationship between $DOC_{MH}:DOC_H$ and humic FI ($r^2 = 0.51$; $p < 0.01$) when considering all samples at the outlet. Also shown are the FI values of the Pony Lake fulvic acid (PLFA) and Suwannee River fulvic acid (SRFA) end members.

on the solutes of interest (Bencala 1983). The excellent fit between the measured $\delta^{18}O$ values at the outlet and those simulated assuming conservative transport (Fig. 3) indicates that the assumption that flow at the outlet is a function of flow at the inlet and precipitation is valid (e.g., direct groundwater input and evaporation can be ignored; as in Eq. 8). It follows that the change in the volume of the epilimnion is controlled by the degree of mixing with the hypolimnion. The fact that there was a good fit between the measured and modeled $\delta^{18}O$ without modeling direct groundwater input to the lake is not surprising. In the southern Sierra Nevada mountains of California, Williams et al. (1990) found that direct seepage of groundwater into an alpine lake was not an important source of water to the lake. Using the upper value for evaporative loss from mountain lakes reported by Gurrieri and Furniss (2004) (3.8 mm d^{-1}) for Green Lake 4 corresponds to an evaporative loss from the surface of Green Lake 4 of $203 \text{ m}^3 \text{ d}^{-1}$. This value is 2.1% of the average daily discharge at the outlet to Green Lake 4 measured during baseflow conditions in August 2006, when the residence time of the lake was high. This evaporative loss could explain the small (1.7%) deviation between the measured and modeled $\delta^{18}O$ values at this time. However, any potential evapo-concentration of DOC would not be expected to affect the interpretation of the DOM modeling results because the differences between measured and modeled DOC concentrations at this time of year were greater than 2%.

Separation of DOM into three pools of differing source—The partitioning of DOM into three pools used in this study was based on direct measurement of the total humic and nonhumic fractions and partitioning of the humic fraction based on measured humic $SUVA_{254}$ values. The results of the $SUVA$ -based partitioning and the choice of $SUVA_{TH}$ and $SUVA_{MH}$ were evaluated by comparing the DOC_{MH} concentrations with the measured FI of the humic

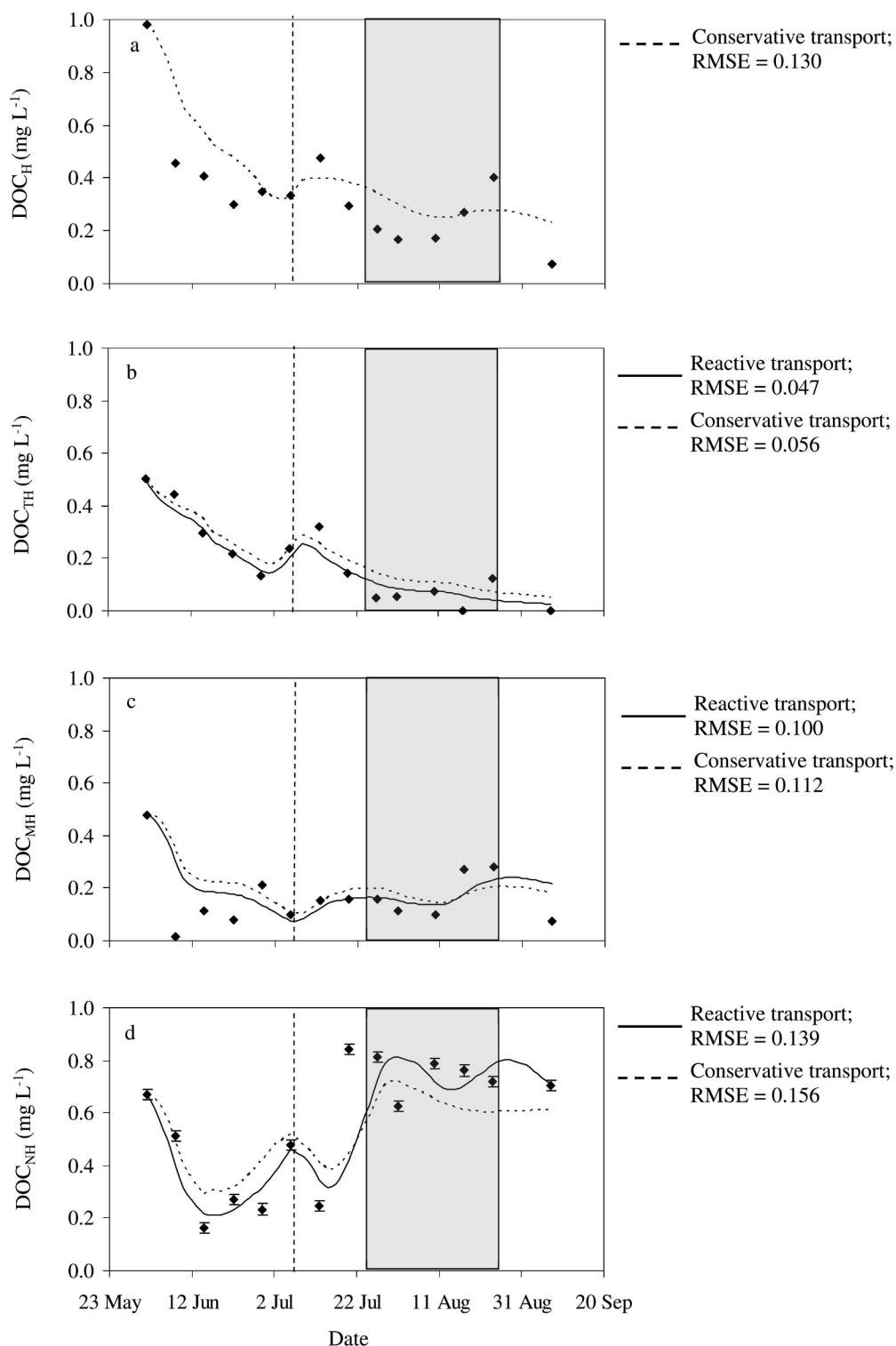


Fig. 7. Measured DOC concentrations (points), conservative transport simulation (dashed line), and reactive transport simulation (solid line) for (a) the total humic fraction, (b) the terrestrially derived humic fraction, (c) the microbially derived humic fraction, and (d) the nonhumic fraction at the outlet to Green Lake 4. Note that a reactive transport simulation was not run for the total humic fraction. The vertical dashed lines indicate the sustained rain event, and the shaded areas represent the timing of the peak in Chl *a* at the outlet. The $\pm 0.02\%$ confidence interval error bars are shown with the DOC_{NH} measured values. Also shown are the RMSE.

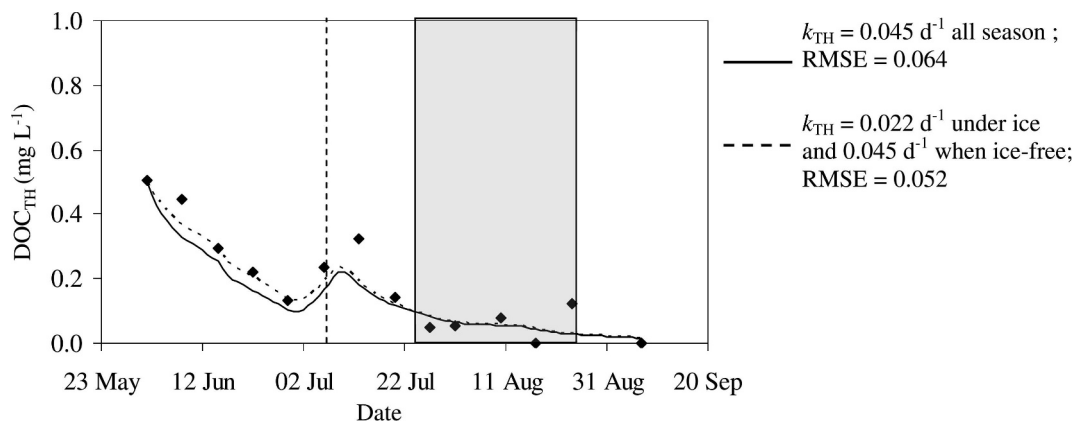


Fig. 8. Measured DOC_{TH} concentrations (points), simulation with a $k_{\text{TH}} = 0.045 \text{ d}^{-1}$ all season (solid line), and simulation with $k_{\text{TH}} = 0.022 \text{ d}^{-1}$ when the lake was ice covered and $k_{\text{TH}} = 0.045 \text{ d}^{-1}$ when the lake was ice free (dashed line) for the terrestrially derived humic fraction of the DOC at the outlet to Green Lake 4. Note that the temperature effect on the decay rate was removed for these simulations ($Q_{10} = 1.00$). The vertical dashed line indicates the sustained rain event, and the shaded area represents the timing of the peak in Chl *a* at the outlet. Also shown are the RMSE.

fraction. Indeed, the significant positive relationship between $\text{DOC}_{\text{MH}}:\text{DOC}_{\text{H}}$ and the FI of the humic fraction of the samples from the lake outlet provided additional spectroscopic support for the separation approach. The high $\text{DOC}_{\text{MH}}:\text{DOC}_{\text{H}}$ ratios and high humic FI values for the two samples collected at the end of the summer peak in Chl *a* supports the idea that the humic fraction of the DOM of these samples is from a microbial source.

The steady increase in the FI of the humic DOM (Fig. 5h) indicates a microbial source of humic DOM. Additionally, the observed production of total humic DOM in the lake near the end of the phytoplankton bloom (Fig. 7a) can be attributed primarily to in-lake production of microbially derived humic DOM (Fig. 7c). While the modeling results show that photochemical degradation is an important control on the quantity of terrestrially derived humic DOC (Fig. 8), the observed changes in quality of the humic DOM (e.g., decrease in SUVA_{H} and increase in FI) are not likely due to photochemical degradation. This is

supported by the finding that any photochemical alteration of the humic DOM pool would be expected to decrease the FI (Cory et al. 2007). Therefore, loss of DOC from the humic pool due to photochemical degradation can likely be attributed to conversion of humic DOM to nonhumic DOM or CO_2 , rather than an alteration of the quality of the humic DOM. Taken together, these results provide support for the idea that the decrease in SUVA_{H} is driven by the addition of microbially derived humic DOM instead of biogeochemical alteration of the SUVA end-member values.

The SUVA-based approach may be more robust than using the measured humic FI to partition the humic DOM because most humic molecules are likely to be chromophores and contribute to the SUVA_{254} of the humic fraction (Weishaar et al. 2003). Using FI would require some assumptions about fluorescence intensity per mass of humic DOM, which was found to vary by a factor of two or more for humic samples from similar sources (McKnight

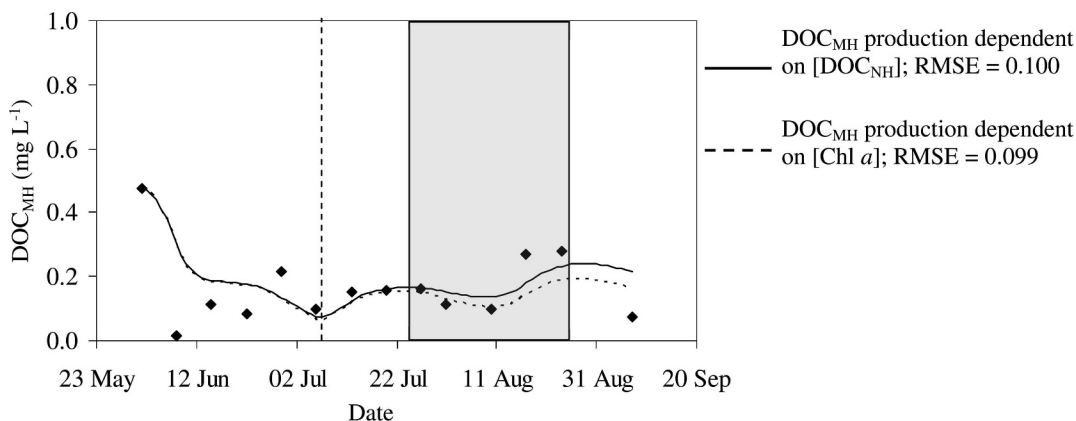


Fig. 9. Measured DOC_{MH} concentrations (points), simulation with DOC_{MH} production dependent on $[\text{DOC}_{\text{NH}}]$ (solid line), and simulation with DOC_{MH} production dependent on $[\text{Chl } a]$ (dashed line) for the microbially derived humic fraction of the DOC at the outlet to Green Lake 4. The vertical dashed line indicates the sustained rain event, and the shaded area represents the timing of the peak in Chl *a* at the outlet. Also shown are the RMSE.

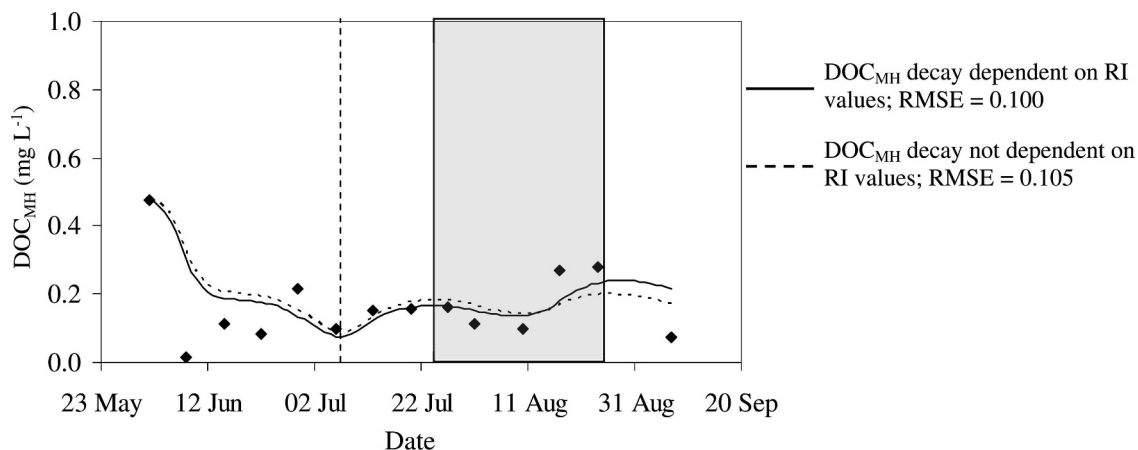


Fig. 10. Measured DOC_{MH} concentrations (points), simulation with DOC_{MH} decay dependent on scaled RI values (solid line), and simulation with DOC_{MH} decay not dependent on RI values (dashed line) for the microbially derived humic fraction of the DOC at the outlet to Green Lake 4. The vertical dashed line indicates the sustained rain event, and the shaded area represents the timing of the peak in Chl *a* at the outlet. Also shown are the RMSE.

et al. 2001). This variability may reflect a lack of fluorescent properties for some molecules in the humic fraction (McKnight et al. 2003).

Conservative and reactive transport modeling of DOM—The modeling results confirm that both in-lake decay and production of DOM from microbial sources are important processes influencing downstream transport of DOM. The validation of assumptions regarding mixing and distribution of the DOM pools in precipitation and the hypolimnion at the beginning of the season allows for deviations between conservative and reactive transport simulations of DOC and measured DOC to be interpreted with confidence. The addition of reactive transport terms to the transport equations resulted in improved simulations at the outlet to Green Lake 4 for all three DOM pools. This indicates that transport of the three DOM pools is not conservative. The nonconservative behavior of DOM in a wetland has been demonstrated previously (Mladenov et al. 2007). By using decay values for humic DOM from the literature (Mladenov et al. 2007), optimization of the model resulted in a large difference between the production coefficients of nonhumic DOM and microbially derived humic DOM (Table 4). The concentration of DOC_{NH} measured at the outlet was generally two to four times greater, and is more biologically labile, than DOC_{MH} . Therefore, it is not surprising that the coefficient for the production of DOC_{NH} is nearly two orders of magnitude greater than that for the production of DOC_{MH} .

Photochemical controls on terrestrially derived humic DOM—Degradation by both bacteria and UV light can be important controls on DOM quantity. Amado et al. (2006) showed that bacterial degradation is the main driver of decay of autochthonous DOM, while photochemical degradation plays a greater role in the decay of allochthonous DOM. Cory et al. (2007) showed that photodegrada-

tion effects on DOM increased with increasing residence time for fulvic acids isolated from arctic surface waters. This observation suggests that photodegradation may be more important in Green Lake 4 late in the season when the water residence time is two to four times greater than the water residence time during snowmelt.

The general overestimation of terrestrially derived humic DOC concentrations by the conservative transport model suggests that DOC_{TH} is degraded by microbes and/or UV light. Terrestrially derived humic DOM that enters surface waters during snowmelt has a high aromaticity (Weishaar et al. 2003). Therefore, this fraction absorbs more light than the other two DOM pools and may be more susceptible to photodegradation and more recalcitrant to microbial degradation as compared with the less aromatic, less conjugated DOC_{NH} and DOC_{MH} . The importance of photochemistry in controlling the concentrations of DOC_{TH} is further highlighted by the improved simulation when a lower decay coefficient was used when the lake was ice covered (microbial degradation only) and a higher decay coefficient was used when the lake was ice free (microbial degradation and UV degradation).

Chlorophyll *a*-dependent production of nonhumic DOM—In-lake primary production by phytoplankton can be a dominant source of autochthonous nonhumic DOM. This production is a critical link in the microbial loop of aquatic ecosystems. In a lake system that experiences a wide range of Chl *a* concentrations, Gondar et al. (2008) report that concentrations of autochthonous DOM are significantly correlated with Chl *a* concentrations (a proxy for primary production by phytoplankton). Likewise, in the Arctic Ocean, Davis and Benner (2007) have shown that there is a strong seasonal link between primary productivity and the production of labile DOM. The overestimation of DOC_{NH} early in the season and underestimation during the Chl *a* peak by the conservative transport model suggest a combination of microbial and UV degradation as well as

microbial production of DOC_{NH} . It is reasonable to assume that this production is dependent on the biomass (e.g., Chl *a* concentration) of the phytoplankton in the system. The addition of a Chl *a* dependent production term to the conservative transport model for the DOC_{NH} pool improved the simulation significantly. This result indicates that although nonhumic DOM comes from both allochthonous and autochthonous sources, the in-lake production is tightly coupled with the primary productivity of the system.

In-lake production and decay of microbially derived humic DOM—Lake and stream systems with terrestrial vegetation in the surrounding watershed receive inputs of humic DOM from the terrestrial environment. This is demonstrated by the pulse of DOC_{TH} to Green Lake 4 during snowmelt and following the rain event. However, during the late summer, at least 50% of the measured humic DOM at the outlet to Green Lake 4 was microbially derived, indicating an in-lake source of humic DOM. In-lake production of humic DOM during the phytoplankton bloom is also supported by the underestimation of the measured total humic DOC by the conservative transport model. The SUVA-based DOC separation and the conservative transport modeling of the DOC_{MH} fraction indicate that the in-lake production of humic DOC is microbially derived.

Autochthonous production of microbially derived humic DOM has been demonstrated to occur in oceans (Harvey et al. 1983) and lakes without terrestrial plants in the watershed (McKnight et al. 1994), but it is also likely to occur in freshwater ecosystems that receive inputs of terrestrially derived humic DOM. One potential mechanism of in-lake production of microbially derived humic DOM is condensation reactions, whereby nonhumic DOM condenses to form humic DOM (Harvey et al. 1983; Kieber et al. 1997). The fact that the production of DOC_{MH} at the end of the peak growing season corresponded with the timing of high concentrations of DOC_{NH} in the lake suggests condensation reactions as a possible mechanism for the observed production. However, this hypothesis was not directly supported by the model results over the course of the entire sampling season. When DOC_{MH} was modeled as having $[\text{DOC}_{\text{NH}}]$ -dependent production or as having $[\text{Chl } a]$ -dependent production, there was little overall difference in how well the simulations matched the data. The pronounced differences between these two simulations late in the summer indicate that condensation reactions may be driving DOC_{MH} production primarily when the quinone-like fluorophores in the lake become oxidized. It may be that any condensation reactions taking place to produce DOC_{MH} are masked by heterotrophic decay of DOC_{MH} during the rest of the summer when the quinone-like fluorophores are more reduced. It is worth noting that the treatment of the nonhumic DOM fraction as a single pool is a simplification. In actuality, the nonhumic fraction is composed of compounds of differing degrees of reactivity such as amino acids, carbohydrates, and carboxylic acids (Thurman 1985). It is possible that one or more of these subpools of nonhumic DOM could be driving any potential condensation reactions taking place to form DOC_{MH} .

The observed peak in DOC_{MH} late in the season, when the quinone-like fluorophores were oxidized, suggests that there may be an oxidation threshold whereby quinone-like fluorophores associated with microbially derived humic DOC become oxidized and are no longer readily decayed by microorganisms. This is further supported by the observation that the simulations of DOC_{MH} being redox-dependent or not redox-dependent deviate from one another during the late season. DOC_{MH} , which is at least in part produced in the lake, is less conjugated than DOC_{TH} and therefore more likely to be used as an electron donor by microorganisms, thereby becoming oxidized, than is DOC_{TH} . The oxidized quinone-like fluorophores associated with this humic DOM may be more processed than reduced DOM and are therefore more chemically stable and less susceptible to microbial degradation. Early in the season when the quinone-like fluorophores are reduced, heterotrophic decay may drive changes in DOC_{MH} . Later in the season, when oxidized, the DOC_{MH} may behave more like a large aromatic DOC_{TH} molecule that is difficult for organisms to use as an electron donor and is more dependent on UV degradation.

The results presented in this study suggest that separating DOM into pools of differing source and reactivity provides insight into DOM–biota interactions and potentially the trend of increasing DOC concentrations seen in north temperate surface waters around the world (Monteith et al. 2007). Through the use of a rigorous modeling approach, it was demonstrated that lakes in a catchment may themselves be sources of increases in DOC concentrations observed in downstream surface waters. The model results presented here provide quantitative support for the conceptual model put forward by Hood et al. (2003). Specifically, it has been demonstrated that lakes in the upper portion of the catchment are essentially wide points in the stream during snowmelt and do not contribute DOM to downstream surface waters. Later in the season during times of increased primary productivity, lakes act as a source of autochthonous DOM to downstream surface waters. Finally, three pools of DOM from different sources have been shown to behave differently in response to changes in biogeochemical conditions in the lake, such as the amount of primary productivity, UV light exposure, and the redox state of quinone-like fluorophores.

Acknowledgments

We thank B. Vaughn, for isotopic analyses and T. Bell for identification of phytoplankton. N. Caine and K. Alexander provided field assistance, and R. Runkel provided helpful comments. We are grateful to two anonymous reviewers for their comments on earlier versions of the manuscript. This work was funded by the National Science Foundation's Niwot Ridge Long Term Ecological Research Program (grant DEB-0423662) and Critical Zone Observatory project (grant EAR-0724960).

References

- AMADO, A. A., V. F. FARJALLA, F. A. ESTEVES, R. L. BOZELLI, F. ROAND, AND A. ENRICH-PRAST. 2006. Complementary pathways of dissolved organic carbon removal pathways in clear-water Amazonian ecosystems: Photochemical degradation and bacterial uptake. *Fems. Microbol. Ecol.* **56**: 8–17.

- BARON, J., D. M. MCKNIGHT, AND A. S. DENNING. 1991. Sources of dissolved and particulate organic material in Loch Vale Watershed, Rocky-Mountain National-Park, Colorado, USA. *Biogeochemistry*. **15**: 89–110.
- BENCALA, K. E. 1983. Simulation of solute transport in a mountain pool-and-riffle stream with a kinetic mass transfer model for sorption. *Water Resour. Res.* **19**: 732–738.
- CAINE, N. 2002. Declining ice thickness on an alpine lake is generated by increased winter precipitation. *Clim. Chang.* **54**: 463–470.
- CHAPRA, S. C. 1979. Applying phosphorus loading models to embayments. *Limnol. Oceanogr.* **24**: 163–168.
- . 1997. *Surface water-quality modeling*. McGraw-Hill.
- CORY, R. M. 2005. Redox and photochemical reactivity of dissolved organic matter in surface waters. Ph.D. thesis. Univ. of Colorado.
- , AND D. M. MCKNIGHT. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ. Sci. Technol.* **39**: 8142–8149.
- , ———, Y. P. CHIN, P. MILLER, AND C. L. JAROS. 2007. Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations. *J. Geophys. Res.* **112**: G04S51, doi: 10.1029/2006JG000343.
- DAVIS, J., AND R. BENNER. 2007. Quantitative estimates of labile and semi-labile dissolved organic carbon in the western Arctic Ocean: A molecular approach. *Limnol. Oceanogr.* **52**: 2434–2444.
- DE WITT, H. A., J. MULDER, A. HINDAR, AND L. HOLE. 2007. Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environ. Sci. Technol.* **41**: 7706–7713.
- EPSTEIN, S., AND T. MAYEDA. 1953. Variations of the $\delta^{18}\text{O}$ content of waters from natural sources. *Geochim. Cosmochim. Acta* **4**: 213–224.
- GARDNER, E. M., D. M. MCKNIGHT, W. M. LEWIS, AND M. P. MILLER. 2008. Effects of nutrient enrichment on phytoplankton in an alpine lake, Colorado, USA. *Arct. Antarct. Alp. Res.* **40**: 55–64.
- GIROLDO, D., AND A. A. H. VIEIRA. 2005. Polymeric and free sugars released by three phytoplanktonic species from a freshwater tropical eutrophic reservoir. *J. Plankton Res.* **27**: 695–705.
- GONDAR, D., S. A. THACKER, E. TIPPING, AND A. BAKER. 2008. Functional variability of dissolved organic matter from the surface water of a productive lake. *Water Res.* **42**: 81–90.
- GURRIER, J. T., AND G. FURNISS. 2004. Estimation of groundwater exchange in alpine lakes using non-steady mass-balance methods. *J. Hydrol.* **297**: 187–208.
- HANSON, P. C., A. I. POLLARD, D. L. BADE, K. PREDICK, S. R. CARPENTER, AND J. A. FOLEY. 2004. A model of carbon evasion and sedimentation in temperate lakes. *Glob. Chang. Biol.* **10**: 1285–1298.
- HARVEY, G. R., D. A. BORAN, L. A. CHESAL, AND J. M. TOKAR. 1983. The structure of marine fulvic and humic acids. *Mar. Chem.* **12**: 119–132.
- HOOD, E. W., D. M. MCKNIGHT, AND M. W. WILLIAMS. 2003. Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States. *Water Resour. Res.* **39**: 118, doi: 10.1029/2002WR001738.
- JAFFE, R., D. MCKNIGHT, N. MAIE, R. CORY, W. H. McDOWELL, AND J. L. CAMPBELL. 2008. Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *J. Geophys. Res.* **113**: G04032, doi: 10.1029/2008JG000683.
- KAWASAKI, N., AND R. BENNER. 2006. Bacterial release of dissolved organic matter during cell growth and decline: Molecular origin and composition. *Limnol. Oceanogr.* **51**: 2170–2180.
- KIEBER, R. J., L. H. HYDRO, AND P. J. SEATON. 1997. Photooxidation of triglycerides and fatty acids in seawater: Implication toward the formation of marine humic substances. *Limnol. Oceanogr.* **42**: 1454–1462.
- LARSON, J. H., P. C. FROST, Z. ZHENG, C. A. JOHNSTON, S. D. BRIDGHAM, D. M. LODGE, AND G. A. LAMBERTI. 2007. Effects of upstream lakes on dissolved organic matter in streams. *Limnol. Oceanogr.* **52**: 60–69.
- MARKER, A. F., E. A. NUSCH, H. RAI, AND B. REIMANN. 1980. The measurement of photosynthetic pigments in freshwaters and standardization of methods: Conclusions and recommendations. *Arch. Hydrobiol. Beih.* **14**: 91–106.
- MCKNIGHT, D. M., E. D. ANDREWS, S. A. SPAULDING, AND G. R. AIKEN. 1994. Aquatic fulvic acids in algal-rich Antarctic ponds. *Limnol. Oceanogr.* **39**: 1972–1979.
- , K. E. BENCALA, G. W. ZELLWEGER, G. R. AIKEN, G. L. FEDER, AND K. A. THORN. 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. *Environ. Sci. Technol.* **26**: 1388–1396.
- , E. W. BOYER, P. K. WESTERHOFF, P. T. DORAN, T. KULBE, AND D. T. ANDERSEN. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* **46**: 38–48.
- , E. HOOD, AND L. KLAPPER. 2003. Trace organic moieties of dissolved organic material in natural waters, p. 71–96. *In* E. C. Stuart and R. L. Sinsabaugh [eds.], *Aquatic ecosystems: Interactivity of dissolved organic matter*. Academic Press.
- MILLER, M. P. 2008. Interactions between hydrology, dissolved organic matter, and algal populations in the headwaters of Boulder Creek. Ph.D. thesis. Univ. of Colorado.
- , D. M. MCKNIGHT, AND S. C. CHAPRA. 2009. Production of microbially derived fulvic acid from photolysis of quinone-containing extracellular products of phytoplankton. *Aquat. Sci.* **71**: 170–178.
- , ———, R. M. CORY, M. W. WILLIAMS, AND R. L. RUNKEL. 2006. Hyporheic exchange and fulvic acid redox reactions in an alpine stream/wetland ecosystems, Colorado Front Range. *Environ. Sci. Technol.* **40**: 5943–5949.
- MLADENOV, N., D. M. MCKNIGHT, P. WOLSKI, AND M. MURRAY-HUDSON. 2007. Simulation of DOM fluxes in a seasonal floodplain of the Okavango Delta, Botswana. *Ecol. Model.* **205**: 181–195.
- , ———, ———, AND L. RAMBERG. 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango Delta, Botswana. *Wetlands* **25**: 622–638.
- MONTEITH, D. T., AND OTHERS. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* **450**: 537–540.
- RECKHOW, D. A., P. C. SINGER, AND R. L. MALCOLM. 1990. Chlorination of humic materials: Byproduct formation and chemical interpretations. *Environ. Sci. Technol.* **24**: 1655–1664.
- STEDMON, C. A., S. MARKAGER, AND R. BRO. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **82**: 239–254.
- THURMAN, E. M. 1985. *Organic geochemistry of natural waters*. Dr. W. Junk Publishers.

- , AND R. L. MALCOLM. 1981. Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15**: 463–466.
- WEISHAAR, J. L., G. R. AIKEN, B. A. BERGAMASHI, M. S. FRAM, R. FUJI, AND K. MOPPER. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**: 4702–2708.
- WILLIAMS, M. W., E. HOOD, AND N. CAINE. 2001. Role of organic nitrogen in the nitrogen cycle of a high elevation catchment, Colorado Front Range. *Water Resour. Res.* **37**: 2569–2581.
- , R. KATTELMANN, AND J. MELACK. 1990. Groundwater contributions to the hydrochemistry of an alpine basin. *Int. Assoc. Hydrol. Sci.* **193**: 741–748.
- , AND K. A. TONNESSEN. 2000. Critical loads for inorganic nitrogen deposition in the Colorado Front Range, USA. *Ecol. Appl.* **10**: 1648–1665.

Associate editor: Stephen P. Opsahl

Received: 01 October 2008

Accepted: 20 July 2009

Amended: 04 August 2009