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The Effect of In-Line Lakes on Dissolved Organic Matter Dynamics in Mountain Streams

Keli J. Goodman

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ABSTRACT

The Effect of In-line Lakes on Dissolved Organic Matter Dynamics in Mountain Streams

by

Keli J. Goodman, Doctor of Philosophy
Utah State University, 2010

Major Professor: Michelle Baker
Department: Biology

This research combines observation, experimentation, and modeling to evaluate the influence of lakes on dissolved organic matter (DOM) quantity, quality and export in subalpine watersheds of the Sawtooth Mountain Lake District, central Idaho.

First, I conducted an empirical study of the hydrologic and biogeochemical controls on DOM dynamics in stream-lake fluvial networks. I hypothesized that lakes would decrease temporal variability (i.e., buffer) and alter the characteristics of DOM from inflow to outflow. I tested these hypotheses by evaluating DOM temporal patterns and measuring annual export in seven-paired lake inflows and outflows. I then evaluated how ultraviolet (UV) exposure affected DOM characteristics during snowmelt and baseflow, and how UV alters baseflow DOM bioavailability and nutrient limitation. Given that increased water residence time increases UV exposure, I hypothesized that lake outflow DOM would be more photorecalcitrant than DOM from lake inflows. I
further hypothesized that UV exposure would increase DOM quality, heterotrophic processing, and nutrient demand.

Results indicate that lakes can buffer stream temporal variability by acting as a DOM sink during snowmelt and a DOM source during baseflow. Lake outflow DOM photodegradation was similar to lake inflows during snowmelt (p=0.66). Conversely, outflow DOM was 2X more photorecalcitrant than inflow DOM during baseflow (ANOVA, p=0.03) and was strongly related to water residence time (WRT). During baseflow, light exposure increased inflow and outflow DOM bioavailability (p=0.059 and 0.024, respectively) and nutrient limitation (p=0.03 and 0.09, respectively). Combined, these results indicate that WRT in subalpine lakes strongly influences DOM temporal variability and DOM degradation and processing. Thus, lakes can provide temporal stability of DOM and potentially increase both carbon and nutrient uptake by heterotrophs in lake outflows.

I then evaluated how global changes could alter hydrologic and nutrient dynamics in a subalpine lake. Model results indicate that the magnitude and timing of snowmelt runoff can have a substantial effect on water and nutrient exports. In phosphorus (P)-limited lakes, increases in inorganic N concentrations within and exported from lakes are likely to occur with increased temperatures and lake WRT. Increases in atmospheric N deposition will further enhance inorganic N exports in P-limited subalpine lakes.
DEDICATION

For my family, who has been incredible supportive.
ACKNOWLEDGMENTS

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Hydrology data was core to addressing the questions presented in this dissertation, which could not have been answered without the work of Tim Covino and Caleb Izdepski. I thank Dave Epstein for being a fantastic colleague and for his constant support and constructive criticisms. I thank Nora Burbank and John Olsen for GIS work. I thank Ian Washbourne and Angie Benedetto for help in the laboratory and with chemical analysis. Past students Sam Hochholter, Chris Arp, and Andrew Myers were wonderful colleagues and I would not be where I am today without them.

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Keli J. Goodman
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RATIONALE FOR THE STUDY OF DISSOLVED ORGANIC MATTER IN FLUVIAL NETWORKS CONTAINING LAKES</td>
<td>1-13</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>LAKES AS BUFFERS OF STREAM DISSOLVED ORGANIC MATTER [DOM] VARIABILITY: TEMPORAL PATTERNS OF DOM CHARACTERISTICS IN MOUNTAIN STREAM-LAKE SYSTEMS</td>
<td>21-73</td>
</tr>
<tr>
<td></td>
<td>Abstract</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Methods</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Results</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Discussion</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Conclusion</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>DISSOLVED ORGANIC MATTER (DOM) PHOTOBLEACHING IN SUBALPINE OLIGOTROPHIC STREAM-LAKE SYSTEMS: IMPLICATIONS FOR DOM BIOAVAILABILITY AND HETEROTROPHIC PROCESSING</td>
<td>73-111</td>
</tr>
<tr>
<td></td>
<td>Abstract</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Methods</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Results</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Discussion</td>
<td>89</td>
</tr>
</tbody>
</table>
Conclusion…………………………………………………………………………………………96
References…………………………………………………………………………………………96

4. PREDICTING THE EFFECTS OF ENVIRONMENTAL CHANGE ON AN Oligotrophic SUBALPINE LAKE: BULL TROUT LAKE, BOISE NATIONAL FOREST, IDAHO………………113

Abstract…………………………………………………………………………………………113
Introduction……………………………………………………………………………………114
Methods…………………………………………………………………………………………119
Results…………………………………………………………………………………………126
Discussion……………………………………………………………………………………132
Conclusion……………………………………………………………………………………139
References……………………………………………………………………………………139

5. SUMMARY AND CONCLUSIONS…………………………………………………………155

APPENDIX………………………………………………………………………………………161

CURRICULUM VITAE……………………………………………………………………………165
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Lake and watershed characteristics of seven study lake inflows and outflows in the Sawtooth Mountain Lake District, central Idaho. WS is watershed. BF ( R_t ) is lake residence time, calculated as lake volume/average baseflow discharge. SM ( R_t ) is lake residence time during snowmelt, calculated as lake volume/peak daily discharge assuming a 12% increase in lake volume [Arp et al., 2006]. ( R_t ) calculations assume a completely mixed lake. NA – Not applicable as a result of no upstream lakes or upstream lakes that are too far and small to influence the study locations.</td>
</tr>
<tr>
<td>2.2</td>
<td>Day of the year when 50% of the total annual discharge (Q) and DOC mass had been exported during the 2008 water year for seven lake inflows and outflows in the Sawtooth Mountains, central Idaho. Q-DOC lag is the difference between the center of mass for discharge and DOC in the inflows and outflows. Outflow – Inflow DOC lag is the difference, in days, that the outflow and inflow DOC Center of Mass occurred.</td>
</tr>
<tr>
<td>2.3</td>
<td>Means and coefficients of variations (CV, ( % )) for DOM concentration (DOC) and characteristics for seven lake inflows and outflows of the Sawtooth Mountain Lake District in central Idaho, throughout the entire 2008 sampling season from early spring (pre-snowmelt) to early fall. DOC is mg C L(^{-1}) and SUVA is L mg(^{-1}) C m(^{-1}). Note ( \delta^{13}C_{DOC} ) has different sample number (n) than all other DOM attributes.</td>
</tr>
<tr>
<td>2.4</td>
<td>Correlation coefficients (r) and significance (p) between inflow and outflow coefficients of variations (CV) and watershed variables during the 2008 sampling season and watershed variables. DOC is mg C L(^{-1}) and SUVA is L mg(^{-1}) C m(^{-1}). Note ( \delta^{13}C_{DOC} ) has different sample number (n) than all other DOM characteristics. Significant correlations are highlighted in bold font.</td>
</tr>
<tr>
<td>2.5</td>
<td>Nonparametric ANCOVA results comparing equality of temporal patterns of DOM characteristics between seven lake inflows and outflows of the Sawtooth Mountains, central Idaho, from May to October, 2008. HR1 and HR2 represent two different inflows to HR Lake. 'h' is the smoothing parameter. p-value &lt;0.05 indicates inflow and outflow patterns that are statistically different.</td>
</tr>
<tr>
<td>2.6</td>
<td>DOC export (kg C ha(^{-1})) during high flow (92 days), low flow (273 days) and total annual (365 days) for seven lake inflows and outflows of the Sawtooth Mountains, central Idaho during the 2008 water year. High flow conditions</td>
</tr>
</tbody>
</table>
occur from 1 May 2008 to 30 July 2008 and low flow is from 1 October 2007 to 30 April 2008 and 1 August 2008 to 30 September 2008. % High flow export is the % of annual flow exported during high flows

3.1 Physical characteristics of four study lakes and their associated watersheds in the Sawtooth Mountain Lake District, central Idaho, USA during 2008. Q is discharge at the time of water collection for snowmelt and baseflow 2008 experiments. Water residence time (WRT) is calculated as lake volume/Q. Snowmelt WRT was estimated assuming a 12% increase in lake area

3.2 Summary of dissolved organic matter characteristics from four lake inflows and outflows during snowmelt (June) and baseflow (August) 2008. DOC is dissolved organic carbon concentration (mg C L⁻¹), A is absorbance at 254 nm, %R is reduction in absorbance as percent of dark control after 30 h of sunlight incubation. Data are presented as mean ± SE

3.3 Effects of full-spectrum sunlight and no-UVB sunlight on DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) after 30 h exposure to radiation. DOM source waters were collected from the inflow and outflow of Bull Trout Lake, central Idaho, USA during snowmelt (June) and baseflow (August). Data are means ±SE of three samples; significant differences (ANOVA df=1,4 p<0.02) between radiation treatments are indicated by *

3.4 Effect of microbes and light exposure on dissolved organic carbon (DOC) loss during 55-d incubation of inflow water in Bull Trout Lake. DOC loss due to microbes was calculated as the percent difference between sterilized (no-microbe) and microbe treatments

3.5 DOM quantity (as dissolved organic carbon, DOC), Absorbance (A) at 254 nm, quality as specific ultra violet absorbance at 254 nm (SUVA_{254}), and bioavailability (%BDOC) under ambient nutrients and nutrient-amended conditions. DOM quality and quantity are reported as initial conditions (±0.038 mg C L⁻¹ analytical error), and bioavailability is reported as mean ±SE of four replicate bioassays. %BDOC nutrient response is calculated as the log_{10}(+ nutrient %BDOC/ mean control %BDOC)

4.1 Calibration parameter values for the Bull Trout Lake model. Highlighted values indicate parameters that were adjusted to calibrate the Bull Trout Lake model. Low and high values are the parameter ranges suggested by the EPA (Bowie et al. 1985)

4.2 Summary table of water and nutrient flux from Bull Trout Lake outflow, Boise National Forest, central Idaho for different model scenarios. Total represents 1 June to 1 October, high flow represents 1 June to 31 July, and low
flow represents 1 August to 1 October. In the warming scenario, air
temperature was increased by 2°C. In the snowpack decline scenario, inputs to
the lake were decreased by 20% during high flows. In the hydrograph advance
scenario, the snowmelt hydrograph and associated nutrient concentrations
were advanced by seven days. The combination scenario is a combination of
three hydrophysical model scenarios. The N deposition scenario increases
inorganic inputs to the lake 4-fold, while the interaction scenario is the
interaction of the hydrophysical scenarios and the N deposition increase
scenario.................................................................148
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Conceptual diagram for the hypothesized effects of lakes on stream DOM quantity and quality during a) spring snowmelt and b) summer baseflow</td>
<td>20</td>
</tr>
<tr>
<td>2.1</td>
<td>Map of study area of in the Sawtooth Mountain Lake District</td>
<td>65</td>
</tr>
<tr>
<td>2.2</td>
<td>Hydrographs from late April to early October 2008 (lines) and DOC concentrations in seven lake inflows and outflows of the Sawtooth Mountain Lake District</td>
<td>66</td>
</tr>
<tr>
<td>2.3</td>
<td>Hysteresis plots of DOC concentration versus discharge for seven study lake inflows and outflows in the Sawtooth Mountain lake district from April to October 2008</td>
<td>68</td>
</tr>
<tr>
<td>2.4</td>
<td>Relationship between time of year and two metrics of dissolved organic carbon from forest soils, specific ultraviolet absorbance (SUVA\textsubscript{254}) and $\delta^{13}\text{C}_{\text{DOC}}$, in the inflows and outflows of two lakes</td>
<td>70</td>
</tr>
<tr>
<td>2.5</td>
<td>Mean ($\pm$SE) DOC concentrations during 2008 baseflow conditions (August to October) for seven lake inflows (white bars) and outflows (black bars) in the Sawtooth Mountains, central Idaho</td>
<td>71</td>
</tr>
<tr>
<td>2.6</td>
<td>% DOC production calculated as the difference in DOC loads (concentration * discharge) between each inflow and outflow pair relative to the respective inflow load for seven lakes in the Sawtooth Mountains, central Idaho from April to October 2008</td>
<td>72</td>
</tr>
<tr>
<td>3.1</td>
<td>Map of study area in the Sawtooth Mountain Lake District (44° 89 10' N, 114 ° 56' W), central Idaho, USA</td>
<td>108</td>
</tr>
<tr>
<td>3.2</td>
<td>Seasonal variation in DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) after 30 h exposure to sunlight</td>
<td>109</td>
</tr>
<tr>
<td>3.3</td>
<td>DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) as a function of sunlight exposure time for samples collected from four lake inflows and outflows during snowmelt</td>
<td>110</td>
</tr>
<tr>
<td>3.4</td>
<td>Temporal changes in A) SUVA and B) Fluorescence Index (FI) during a 55-d incubation of Bull Trout inflow stream water in Bull Trout Lake throughout the summer of 2007</td>
<td>111</td>
</tr>
</tbody>
</table>
3.5 Relationship between DOC-Specific Ultraviolet Absorbance at 254 nm (SUVA_{254}) and % preincubation bioavailable DOC (%BDOC)…………112

4.1 Schematic of the kinetics and interactions from LAKE2K that were the focus of the Bull Trout Lake model calibration………………………………………150

4.2 Measured data for A) Bull Trout Lake outflow discharge during 2008. The arrow indicates start of modeled time period on 1 June, B) Bull Trout Lake inflow and outflow mean daily temperature, C) Bull Trout Lake inflow and outflow NO_{3}-N concentrations. …………………………………………………151

4.3 Epilimnetic A) Temperature, B) Chlorophyll a, C) TN and D) TP measured (points) and predicted (line) from the Base Case model for Bull Trout Lake, Boise National Forest, Idaho……………………………………………………………152

4.4 Epilimnetic A) Temperature, B) Chlorophyll a, C) TN and D) TP results from different model scenarios for the Base Case Bull Trout Lake model……153

4.5 Epilimnetic A) Chlorophyll a, B) TN and C) TP results for different model scenarios from the Base Case Bull Trout Lake model……………………………154

5.1 Conceptual diagram of lake influence on mountain stream DOC variability, quantity and quality…………………………………………………………………160
CHAPTER 1
RATIONALE FOR THE STUDY OF DISSOLVED ORGANIC MATTER IN FLUVIAL NETWORKS CONTAINING LAKES

This research combines observation, experimentation and modeling to evaluate the effect of lakes on stream dissolved organic matter (DOM) quantity, quality and export in subalpine watersheds of the Sawtooth Mountain Lake District, central Idaho. DOM is the most abundant form of organic matter across aquatic ecosystems (Findlay and Sinsabaugh, 2003). However, the processing and production of DOM in different aquatic ecosystems (i.e., streams and lakes) may influence DOM concentration and characteristics differently (Kling et al. 2000). The main objective of this research was to elucidate the hydrologic and biogeochemical controls on DOM dynamics in stream-lake networks of oligotrophic mountain watersheds, and to evaluate how global change issues may influence hydrological and nutrient dynamics in subalpine lakes. The results of this research will be applicable to studies of DOM dynamics in high elevation mountain networks, as well as other watersheds containing lakes and ponds.

Background

Dissolved organic matter is a heterogeneous mixture of organic compounds ranging in size, structure and chemical composition, from simple carbohydrates to complex aromatics (Thurman 1985). Additionally, DOM is one of the largest and most bioavailable carbon sources on Earth, and thus is an important energy source for heterotrophic organisms, subsequently impacting energy flow in aquatic ecosystems (Schiff et al. 1990). The chemical and physical properties of DOM can have a large
influence on the mobility and transport of contaminants and heavy metals (McKnight et al. 1992, Breault et al. 1996), pH buffering capacity (McKnight et al. 1985) and light attenuation (Scully and Lean 1994, Laurion et al. 1997), ultimately influencing aquatic ecosystem function. The extent to which DOM can affect ecosystem functioning depends on DOM concentration, origin, age, structure and chemical composition (Benner 2003). Thus, a better understanding of the controls on the temporal and spatial patterns of DOM characteristics is necessary for understanding controls on ecosystem functioning and predicting how these ecosystems will respond to environmental changes.

Dissolved organic matter is comprised of dissolved organic carbon, nitrogen and phosphorus (DOC, DON, and DOP, respectively). Dissolved organic carbon, operationally defined in this dissertation as organic carbon that passes through a 0.7-μm filter (Kaplan 1994), is the primary component of DOM. Given that DOC is the major constituent of the DOM molecule, DOC is often the constituent used when discussing DOM characteristics. Throughout this dissertation, the term DOM will be used when discussing the entire dissolved organic matter molecule including chemical attributes, while the term DOC will be used when discussing concentrations and bioavailability since DOC is the element measured.

Organic matter dynamics in headwater streams are closely linked to the surrounding terrestrial landscape (Hynes 1975, Vannote et al. 1980). The majority of stream organic matter studies have been conducted in eastern U.S. mountain streams, while the number of studies on DOM in subalpine and alpine western U.S. streams is much smaller. Differences between eastern and western U.S. mountain streams include timing of organic matter inputs, source of organic matter, and flow regimes (Webster and
Meyer 1997). For example, in eastern mountain systems, the majority of organic matter enters the stream as leaf fall during autumn when flows are low. Conversely, in the western US, conifers are the dominant vegetation, and the majority of organic matter enters the streams in dissolved form during snowmelt when water infiltrates the upper soil horizon and soluble organic carbon is flushed to the streams (Hornberger et al. 1994, Boyer et al. 1997). Thus, during spring snowmelt these mountain stream systems both receive and export a large pulse of nutrients, organic matter and water.

In alpine and subalpine aquatic systems, snowmelt delivers 60 to 70% of the annual nutrient loads (Lewis and Grant 1979, Kaushal and Lewis 2005), and the ability of stream networks to retain these nutrients and DOM may be important to aquatic system productivity. Many studies have evaluated the hydrologic linkages between terrestrial and freshwater ecosystems that control DOC export (Lewis and Grant 1979, Hornberger et al. 1994, Boyer et al. 1997, McGlynn and McDonnell 2003, Hood et al. 2005, Inamdar and Mitchell 2006). However, little is known about how linkages within aquatic systems can influence the fate of DOC once it enters the stream network or how hydrologic linkages between streams and lakes can alter DOM characteristics.

Lakes and small ponds are common across many landscapes (Downing et al. 2006), yet traditionally lakes and streams have been viewed as separate entities (but see Kling et al. 2000). Given that lakes can store water and nutrients, lakes within mountain stream networks may act to mediate the snowmelt DOM flushing response by storing some of this allochthonous (i.e., terrestrially derived) DOM. Furthermore, in oligotrophic systems lakes may play a critical role in providing autochthonous (i.e., aquatically derived) DOM to downstream locations later in the season when nutrient availability is
low (Fig 1.1). However, given the small body of literature on mountain DOM dynamics, and even smaller body of literature on stream-lake linkages, we do not fully understand the relative role of stream-lake interactions on DOM dynamics.

**DOM photodegradation and bioavailability in stream-lake systems**

In addition to altering DOM export, lakes may alter DOM bioavailability, which is controlled by DOM origin, age and chemical composition (Benner 2003). Lakes receive large amounts of allochthonous DOM, and these inputs are regulated by catchment and lake characteristics (Sobek et al. 2007). However, lakes may modify the DOM bioavailability of this allochthonous DOM to downstream locations through DOM production, processing and transformation. Low molecular weight DOM, such as DOM created by autochthonous production (Wetzel 1983) is generally considered to be easier for heterotrophic bacteria to utilize compared to complex aromatic DOM (Chrost and Faust 1983), which is typical of terrestrial organic matter compounds (Malcolm 1990). The presence of lakes within stream networks may increase the prevalence of low molecular weight compounds through photodegradation and autochthonous production, and thus increase the bioavailability, by creating a new source of DOM (i.e., autochthonous) or through DOM breakdown by UV photodegradation and/or microbial processing.

During hydrologic retention within a lake, DOM is exposed to ultraviolet (UV) radiation for extended time periods, which can alter both the chemical structure and the bioavailability of DOM (Moran and Covert 2003). The key to understanding DOM photodegradation in aquatic systems is to understand DOM characteristics (Sulzberger
and Durisch-Kaiser 2009). Photochemical degradation of chemically complex (i.e., allochthonous) DOM results in the production of less aromatic, more bioavailable DOM (Bertilsson and Tranvik 1998). Conversely, low-molecular weight DOM may become less bioavailable following UV exposure and DOM complexation (Benner and Biddanda 1998, Obernosterer et al. 1999, Tranvik and Bertilsson 2001). Hydrologic connections between streams and lakes leads to a mixture of DOM sources and characteristics (Benner 2003), and photo-induced changes in lake water and streams draining lakes may result in increased chemical complexity of microbially derived DOM (Kieber et al. 1997, Obernosterer et al. 2001) or decreased chemical complexity of terrestrially derived DOM (Wetzel et al. 1995, Bertilsson and Tranvik 2000). Furthermore, high-elevation, shallow lakes with low DOC concentrations may be particularly susceptible to UV radiation, due to the high doses of UV radiation received at high-elevations and to the low light-absorbing capacity of these ecosystems (Morris et al. 1995, Williamson 1995). Thus, the presence of lakes within fluvial networks has the potential to increase the susceptibility of DOM to UV photodegradation (Frost et al. 2005, Larson et al. 2007), as well as alter the bioavailability, yet little is known about how lakes alter stream DOM photodegradation and bioavailability.

**Study area**

The study area was located in the Sawtooth Mountain Lake District of central Idaho. This area consists of many high-elevation tarn and lower-elevation moraine-dammed lakes within the stream networks. The study watersheds lie within the Sawtooth National Recreation or Wilderness Area and drain into the Salmon River, as well as
within the Boise National Forest and drain into the South Fork Payette River. Watershed uplands are comprised of Cretaceous granodiorite from the Idaho Batholith, while the valley bottom consists of till, alluvium and colluvium from the Pleistocene and Holocene (Kiilsgaard et al. 2003). These watersheds are >70% vegetated, and barren land ranges from 0 to 27.5%. Upland vegetation is dominated by lodgepole pine (Pinus contorta), while sedges (Carex sp.), willows (Salix sp.) and grasses dominate riparian areas (Arp et al. 2006).

These subalpine and alpine watersheds are typically snow covered from November to May, and 60 to 80% of the total annual discharge is exported during spring snowmelt. These watersheds have low human impact, limited recreational land use, and wet atmospheric nitrogen (N) deposition is low (~1.0 kg ha\(^{-1}\) yr\(^{-1}\)) (NADP 2001). Aquatic systems within the watersheds are oligotrophic and microbial processes are phosphorus (P)-limited or co-limited by N and P (Marcarelli and Wurtsbaugh 2007).

The focus of this dissertation was on moraine-dammed lakes at the base of seven different watersheds, which are fed by 2\(^{nd}\) or 3\(^{rd}\) order streams. Study lake surface areas range from 0.28 to 3.34 km\(^2\) and watershed areas range from 10 to 111 km\(^2\). The main study lakes are formed behind terminal moraines deposited ca. 13 kya at the base of their respective watersheds at 1978 to 2258 m elevation (Borgert et al. 1999); some watersheds also have upstream lakes behind younger moraines and/or tarns formed in high-elevation cirque basins. Upstream lake area ranges from 0 to 6.1 km\(^2\). Baseflow lake residence times of the study lakes range from 0.05 to 6.4 yrs.
Tools to evaluate DOM characteristics

Aquatic DOM is a heterogeneous mixture of molecules differing in origin, age, and state of processing (Thurman 1985, Moran and Covert 2003). Given the inherently difficult nature of quantifying DOM characteristics, the majority of studies on DOM have focused on measurements of bulk DOC. More recently, studies have begun to characterize DOM chemical and optical properties, following the development of simpler techniques to classify DOM, and to focus on a better understanding of how DOM characteristics, rather than concentration alone, may play a large role in controlling ecosystem functioning. In this dissertation, DOM characteristics include chemical composition, isotopic composition, and optical properties.

The elemental composition of DOM may be useful to determine both DOM quality and state of degradation. Organic matter quality has often been evaluated with metrics of chemical make-up (e.g., ratios of carbon, nitrogen, lignin, etc.) (Joffre et al. 2001). C:N ratios reflect organic matter N availability and can thus provide useful information on organic matter bioavailability. Isotopic composition of DOC (δ^{13}C_{DOC}) may be useful at distinguishing between DOM from freshly leached organic matter and microbially-degraded DOM (Schiff et al. 1990), and at providing insight into changing DOM source pools (Hood, 2005, Sebestyen, 2008), since ^{12}C is preferentially taken up by consumers (Andreux et al., 1990).

In addition to organic matter composition, optical properties (i.e., ultraviolet absorbance and fluorescence) of DOM, which are dependent on chemical characteristics, have been shown to be useful tools in evaluating DOM source and quality across many different ecoregions, such as in tropical (Roelke et al. 2006), xeric (Hood et al. 2006),
alpine and subalpine (Hood et al. 2005) and high-latitude ecosystems (McKnight et al. 2001). Specific ultraviolet absorbance at 254 nm (SUVA$_{254}$) relative to the DOC concentration is an indicator of average UV absorbance and DOM aromaticity (Westerhoff et al. 1999), with greater absorbance indicating greater DOM aromaticity. Since SUVA$_{254}$ is strongly related to the percentage of aromatics in DOM compounds (Weishaar et al. 2003), UV absorbance can be useful in distinguishing between mineral and organic flowpaths, as DOC flushed from organic soils has higher aromatic content than mineral soils that can adsorb DOM (Hood et al. 2006). Furthermore, DOM compounds with less aromatics are easier for heterotrophic bacteria to utilize (Chrost and Faust 1983), and SUVA$_{254}$ can therefore be an indicator of DOC bioavailability (Marschner and Kalbitz 2003).

While SUVA$_{254}$ provides a more qualitative indication of aromaticity, fluorescence may be a more reliable tool when attempting to discriminate between aquatic and terrestrial DOM source pools (Hood et al. 2006). Fulvic acids from terrestrial and aquatic sources make up a large portion (45 to 65% and 10 to 30%, respectively; Thurman 1985) of DOM and are a main fluorophore in natural waters (Stewart and Wetzel 1980). McKnight et al. (2001) developed a fluorescence index (FI) to differentiate precursor DOM sources (i.e., aquatic vs. terrestrial). The index, calculated as the ratio of emission intensity at 450 and 500 nm with an excitation at 370 nm, provides a measure of the steepness and shape of the emission intensity peak. This index has been successfully applied to streams, lakes and river systems around the U.S., as well as lakes in Antarctica. Headwater catchments (terrestrially derived DOM) in both Georgia and Colorado had FIs of 1.4 to 1.5. Lakes in Antarctica (aquatically derived
DOM) had Fls ranging from 1.7 to 2.0. Larger rivers across the U.S. had Fl values 1.4 to 1.5, indicating the dominance of terrestrial derived DOM, while lakes within the U.S. had values ranging from 1.6 to 1.9 (McKnight et al. 2001). Standard deviation of samples analyzed in triplicate has been shown to be less than 0.01 (Hood et al. 2005).

Since the aforementioned DOM characteristics are based on chemical properties, they are not necessarily independent. For example, changes in DOC:DON ratios of fulvic acid fractions have been shown to be highly correlated with changing SUVA	extsubscript{254} values, which indicates that DOM chemical structure changes along with chemical (i.e., elemental) make-up (Hood et al. 2005). Despite some correlation and overlap between metrics of DOM character, each technique provides unique and useful information. In situations were photobreakdown occurs (e.g., lakes), absorption (i.e., SUVA	extsubscript{254}) will decrease (Sulzberger and Durisch-Kaiser 2009), while DOM fluorophores will retain precursory material signature (McKnight et al. 2001). While Fl is extremely useful in differentiating between aquatic and terrestrial organic matter source material (McKnight et al. 2001, Hood et al. 2005), it does not respond strongly to changes among terrestrial source pools (Hood et al. 2006, Roelke et al. 2006). In contrast, SUVA	extsubscript{254} increases as the proportion of DOC derived from organic flowpaths increases, and thus can provide information regarding shifts in terrestrial source pools (i.e., organic vs. mineral flowpaths) (Hood et al. 2006). Used together, DOC:DON, δ\textsuperscript{13}C\textsubscript{DOC}, Fl and SUVA\textsubscript{254} have the potential to provide considerable information about DOM structure, source and bioavailability.
Stream-lake systems in a changing environment

As human activity changes the environment, it subsequently influences hydrological and nutrient dynamics, which may have large effects on lake water residence times and biogeochemical cycles. Given the rate of change, understanding how a shifting environment may affect these cycles is imperative. Global climate change, including shifts in temperature and hydrologic processes, may have profound effects on carbon cycling (Zepp et al. 2007) and warrant further investigation. For example, increasing temperature and the resulting change in hydrologic flows can alter the amount, timing and quality of terrestrial DOM flux into aquatic systems (Freeman et al. 2001). Additionally, changes in temperature and nutrient availability may alter primary production, thus altering aquatically-derived DOM concentrations and characteristics. These changes may lead to altered DOM concentration, characteristics and UV-induced changes on DOM (Zepp et al. 2007).

Global climate change is predicted to modify precipitation patterns in the western U.S. such that snowfall will decrease, while precipitation in the form of rain will increase and snowmelt will occur earlier (Stewart et al. 2004). However, regional climate models indicate that a large portion of the areas in the Intermountain West are so cold, that warming of a few degrees will do little to change the depth and duration of snowpack of these subalpine and alpine areas (Mote 2006).

In contrast to climate warming, increases in N deposition may have a sizable effect on these high elevation ecosystems. Human modifications (i.e., fossil fuel burning, agricultural fertilizers, urbanization) across the landscape have increased the rate of
nitrogen (N) supplied to the atmosphere two-fold (Vitousek 1994), resulting in terrestrial N saturation in many regions (Aber et al. 1998). As a consequence of N saturation in terrestrial systems, terrestrial N export to aquatic systems can increase (Aber et al. 1998). The Intermountain West receives less N deposition than many other regions of the US (NADP 2001), however high-elevation mountain systems in the Colorado Front Range are already exhibiting signs of N saturation (Williams et al. 1996, Williams and Tonnessen 2000). While the Front Range response to N deposition has received considerable attention, less research has been done in other high-elevation areas of the Intermountain West (but see Kaushal and Lewis 2005), which are predicted to be impacted by N deposition in the future (Burns 2004).

Given the high proportion of shallow soils and barren land, and thus a low ability to retain nutrients, high elevation alpine and subalpine aquatic ecosystems may be particularly sensitive to terrestrial N deposition, because short growing seasons typical of these ecoregions limit the potential for biotic N uptake. Increased N deposition to the terrestrial environment has been shown to result in higher N concentration in high-elevation lakes (Baron et al. 2000), as well as shifts in lake biological community biomass and composition (Baron et al. 2000, Wolfe et al. 2001). Changes in inorganic N concentration in aquatic systems, biological uptake and biological community composition may lead to changes in organic matter pool size and process rates (Clair et al. 1999, Grimm et al. 2003, Manabe et al. 2004, Kaushal and Lewis 2005).

Concerns about the effect of increased nutrient supply on water quality has lead to a greater understanding of the importance of headwater streams (Mulholland et al. 2000, Peterson et al. 2001), as well as the hyporheic zone (Valett et al. 1996), at processing and
retaining N, thereby decreasing N export downstream. Additionally, oligotrophic lakes may also serve to retain nutrients within mountain stream-lake systems and decrease N export (Kling et al. 2000, Kaste et al. 2003). Therefore, N limited lakes may act to buffer the predicted changes in N availability through in-lake uptake and retention, thereby altering organic matter dynamics. However, the response of subalpine lakes to changes in hydrologic and nutrient inputs have received little attention.

**Organization of dissertation**

The following chapters describe results of research conducted from June 2006 to October 2008 in the Sawtooth Mountain Lake District, central Idaho. Chapter 2 describes temporal patterns of DOM characteristics in stream-lake subalpine systems. The hypothesis of chapter 2 was that lakes buffer temporal patterns of stream DOM, and I specifically address how the presence of lakes, both immediate and upstream, in mountain stream networks alters the timing, temporal patterns and export of DOM. Chapter 3 evaluates the ability of lakes to modify stream DOM characteristics and bioavailability. The hypothesis was that lakes enhance DOM photodegradation and bioavailability, since longer water residence time increases UV photodegradation, microbial processing and in-lake production of DOM. Chapter 4 combines extensive field-collected data from one stream-lake system with a modeling framework to predict how aspects of global change may alter the biogeochemistry of mountain lake districts. In particular, I evaluate how changes in hydrologic regime and increased atmospheric N deposition may alter aquatic biogeochemical cycling and increase DOM source pools in these oligotrophic subalpine fluvial networks. Combined, this research provides insight
to how lakes affect temporal patterns of DOM quantity, quality and export in stream networks, and provides a means of relating hydrology to biogeochemical cycling (Fig. 1.1).

References


Figure 1.1. Conceptual diagram for the hypothesized effects of lakes on stream DOM quantity and quality during a) spring snowmelt and b) summer baseflow. Thickness of arrow indicates the magnitude of stream flow. Terrestrially derived DOM is represented by a “T,” and aquatically derived DOM is represented by an “A.” The size of the letter indicates the magnitude of DOM inputs.
CHAPTER 2
LAKES AS BUFFERS OF STREAM DISSOLVED ORGANIC
MATTER [DOM] VARIABILITY: TEMPORAL PATTERNS
OF DOM CHARACTERISTICS IN MOUNTAIN
STREAM-LAKE SYSTEMS¹,²

Abstract

Material fluxes in mountain systems are driven by snowmelt. Lakes within fluvial networks may dampen the effect of hydrologic transport on stream dissolved organic matter (DOM) dynamics by increasing water residence time, and can alter DOM concentration [DOC] through processing and production of DOM. We evaluate how lakes alter temporal variability of [DOC] and DOM characteristics (specific ultraviolet absorbance (SUVA$_{254}$), DOC: Dissolved Organic Nitrogen (DON) ratio and δ$^{13}$C$_{DOC}$), as well as DOC export in seven-paired lake inflows and outflows in the Sawtooth Mountain lake district, Idaho. We hypothesized that lakes would decrease stream DOM temporal variability (i.e., buffer), as measured by coefficients of variation (CV), and increase DOM export as a result of autotrophic production. We correlated DOM variability with landscape factors to evaluate potential drivers of DOM temporal patterns. CVs were 40 to 90% higher in lake inflows than outflows for [DOC], SUVA, and DOC:DON, and were related to both lake and land cover variables. The magnitude of [DOC] increase on the ascending limb of the snowmelt hydrograph was greater in lake inflows than outflows, and the mean center of mass export was 5.4 days earlier for inflows. During baseflow,

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² Coauthored by KJ Goodman, MA Baker, and WA Wurtsbaugh.
lake outflow [DOC] was 1.7X greater than lake inflow concentrations, and five lake outflows had higher annual export than inflows. Combined, these results illustrate that lakes can alter the magnitude, timing and temporal variation in the quality and quantity of DOM exported from subalpine watersheds. The extent of this buffering effect is related to water residence time in these lakes.

Introduction

Chemical and physical properties of dissolved organic matter (DOM) alter physicochemical properties of water, such as the mobility and transport of contaminants and heavy metals [McKnight et al., 1992; Breault et al., 1996], pH buffering capacity [McKnight et al., 1985], and light attenuation [Scully and Lean, 1994; Laurion et al., 1997; Williamson and Rose, 2009]. Additionally, DOM is typically the greatest bioavailable carbon pool across the Earth’s aquatic ecosystems [Benner, 2003], and thus is an important energy source for heterotrophic organisms, subsequently impacting energy flow in aquatic systems [Schiff et al., 1990; Cole et al., 2006]. The extent to which DOM can affect ecosystem functioning depends on DOM concentration, origin, age, structure, and chemical composition [Benner, 2003].

DOM, operationally defined here as organic matter that passes through a 0.7-µm filter [Kaplan, 1994], includes dissolved organic carbon, nitrogen and phosphorus (DOC, DON and DOP, respectively). DOC is both the primary component of DOM and the constituent most directly measured. Hereafter, the term DOC will be used when discussing concentrations since carbon is the element measured, while the term DOM will be used when discussing the entire molecule including chemical attributes.
DOM chemical attributes, such as chemical composition (i.e., DOC:DON ratios, lignin etc.), isotopic composition and optical properties, have been used successfully to provide information on hydrologic flowpaths (i.e., mineral vs. organic) [Hood et al., 2006], source material [McKnight et al., 1997; Hood et al., 2005], quality (i.e., bioavailability) [Joffre et al., 2001] and microbial degradation [Schiff et al., 1990; Sebestyen et al., 2008]. For example, DOC specific ultraviolet absorbance (SUVA\textsubscript{254}) measures average UV absorbance, and is an indicator of DOM aromaticity [Westerhoff et al., 1999] and has been used successfully to determine water flowpaths through organic versus mineral materials [Hood et al., 2006]. DOC:DON ratios reflect organic matter nitrogen (N) quantity and are inversely related to organic matter bioavailability [Hunt et al., 2000]. Carbon isotopic composition of DOC ($\delta^{13}$C\textsubscript{DOC}) can be used to discriminate between fresh and microbially-degraded DOM [Schiff et al., 1990; Sebestyen et al., 2008], since $^{12}$C is preferentially taken up by consumers [Andreux et al., 1990].

Together, DOM characteristics can provide considerable information regarding chemical and physical changes to DOM, which over time, affect ecosystem functioning.

DOC export from watersheds is a significant part of the global carbon cycle [Battin et al., 2009], and in most aquatic systems, this flux is driven by hydrologic processes [Schlesinger and Melack, 1981]. In arctic [Finlay et al., 2006], alpine [Boyer et al., 1997] and mountain [Baker et al., 2000] ecosystems, the majority of annual DOC flux is transported to streams during snowmelt runoff, when DOC concentrations peak prior to, or during, peak stream discharge and decline rapidly [Lewis and Grant, 1979; Boyer et al., 1997; Sebestyen et al., 2008]. This temporal pattern of DOC concentration in snowmelt-dominated systems is attributed to flushing of pore water from the upper soil
horizons as the water table rises [Hornberger et al., 1994] and depends on connectivity to source pools [Boyer et al., 2000; McGlynn and McDonnell, 2003], soil microbial processes [Brooks et al., 1999], topography, groundwater dilution, and landscape-scale patterns of snow accumulation and melt [Boyer et al., 1997, 2000]. Regardless, the snowmelt period represents the major source of DOM to alpine and subalpine stream systems and typically exhausts the terrestrial DOM pool [Boyer et al., 1997].

Despite the fact that lakes are present and common across many landscapes [Downing et al., 2006], lakes and streams have traditionally been studied as separate entities [but see Essington and Carpenter, 2000; Kling et al., 2000], and lakes have received little attention as a landscape control on stream DOM characteristics [Hood et al., 2003; Larson et al., 2007]. Lakes within fluvial networks are known to incorporate inorganic nutrients into organic matter [Kling et al., 2000] and may be a source of organic nitrogen during baseflow [Brown et al., 2008]. Similarly, lakes may functionally retain some of the spring-snowmelt pulse of terrestrially-derived (i.e., allochthonous) DOM, while at the same time provide an aquatically-derived (i.e., autochthonous) DOM source to downstream ecosystems.

Different landscape factors have been identified as good predictors of lake and stream DOC concentrations. For example, landscape position [Martin and Soranno, 2006], lake-order [Riera et al., 2000], spatial extent of land cover [Dillon and Molot, 1997; Gergel et al., 1999], and spatial configuration of lakes [Soranno et al., 1999; Riera et al., 2000; Martin and Soranno, 2006] have been shown to be good predictors of lake DOC concentrations. In streams, DOC concentrations are affected by precipitation [Meybeck, 1982], hydrologic events [Hornberger et al., 1994; Boyer et al., 1997],
hydrologic flowpaths [Mulholland and Hill, 1997], and vegetation type [Dillon and Molot, 1997; Gergel et al., 1999]. Thus, DOC dynamics in lakes appear to be largely controlled by watershed characteristics related to landscape position, while DOC dynamics in streams are attributed to hydrologic processes and connectivity to terrestrial DOC sources.

Since lake DOC concentrations appear to be less affected by hydrologic transport than stream DOC concentrations, streams with upstream lakes may also be less affected by changes in discharge as water is first routed through a lake, where both water and nutrients may be stored [Kaste et al., 2003]. For example, Ito et al. [2007] observed that nitrate (NO$_3^-$) concentrations in two Adirondack mountain lake inlets were strongly affected by hydrologic processes, mainly groundwater inputs, while in-lake processing influenced NO$_3^-$ dynamics at the lake outlets. These studies suggests that lakes may act to decrease the temporal variability of, hereafter referred to as buffer, stream solute dynamics associated with hydrologic processes, and the extent of this effect may be related to water residence time [Kaste et al., 2003; Ito et al., 2007].

Despite the large effect lakes may have on nutrient dynamics, few studies have evaluated how lakes can alter DOM characteristics in streams [Hood et al., 2003; Frost et al., 2006; Larson et al., 2007]. Hydrologic controls, such as those acting upon streams, are temporally dynamic, while watershed position controls, such as those acting upon lake DOM, are static. In the past, temporal variability in aquatic systems has been evaluated using mean-variance relationships [Downing, 1979; Morin, 1985; Cattaneo and Prairie, 1995], coefficients of variation (CV) [Palmer and Poff, 1997; Hutchens et al., 1998], and temporal coherence [Magnuson et al., 1990; Soranno et al., 1999]. These
techniques are useful at providing insight into sampling strategies, evaluating temporal variability, and analyzing the extent to which paired study locations are similar over time in relation to spatial structure (i.e., distance between locations, watershed position, etc.). For example, temporal coherence evaluates if one study location is more similar to a study site that is close in proximity or one that is close in size, providing insight into the drivers of temporal dynamics. However, none of the above methods provides a means to directly test equality of temporal patterns between study locations. In fact, the majority of DOM studies use visual assessment of temporal data to evaluate trends over time [Hood et al., 2006; Inamdar and Mitchell, 2006; Hood and Scott, 2008; Sebestyen et al., 2008].

Here, we use nonparametric ANCOVA [Young and Bowman, 1995] to test equality in temporal patterns between paired lake inflows and outflows in order to directly evaluate the effect of lakes on stream DOM over time.

The objectives of this research were to evaluate the effects of lakes on temporal patterns of DOM characteristics and annual export of DOC within mountain stream networks. We hypothesized that the presence of lakes within mountain stream networks would act to buffer temporal variability of stream DOM characteristics by altering hydrologic transport (i.e., water retention time) and organic carbon source pools. To test this hypothesis we compared paired lake inflow and outflow streams in seven mountain watersheds. We quantified the timing of water and DOC center of mass export for the 2008 water year, evaluated relationships between DOC concentration and discharge in lake inflows and outflows, as well as analyzed the intra-annual variability and temporal patterns of DOM characteristics (light absorbing capacity, DOC:DON ratios and δ$^{13}$C$_{DOC}$ signatures). We then correlated the variability of DOM characteristics to watershed
characteristics to elucidate the drivers of lake inflow and outflow temporal variability. Given that lakes can store both water and nutrients, we predicted that lakes would dampen snowmelt DOC flushing responses in lake outflows, thereby decreasing temporal variability of DOM characteristics in comparison to lake inflows. Further, we predicted that the extent of this buffering effect would be related to lake area (i.e., storage capacity, an indirect metric of lake water retention time). Finally, we evaluated the extent to which lakes alter baseflow DOC quantity and annual DOC export. Since lakes can act as a source of autochthonous DOM, we predicted that in-lake production would increase outflow DOC concentrations during baseflow and increase annual DOC export, relative to the lake inflow.

Study Sites

This study was conducted in paired lake inflows and outflows in seven catchments of the Sawtooth Mountain Lake District of central Idaho: Alturus, (ALT), Bull Trout (BT), Hell Roaring (HR), Little Redfish (LRF), Pettit (PET), Stanley (ST), and Yellow Belly (YB) in 2008 (Figure 2.1, Table 2.1). HR Lake has two main inflows, hereafter referred to as HR1 and HR2. Additionally, four of the stream-lake systems (ALT, BT, PET, ST) were studied during the summer and fall of 2007. The lakes are fed by second or third order streams [Arp et al., 2007]. Inflow and outflow sampling locations were located within 20 to 550 m of the lakes.

All of the lakes are formed behind terminal moraines deposited ca. 13 kya at the base of their respective watersheds at 1978 to 2258 m elevation [Borgert et al., 1999]; some watersheds also have upstream lakes behind younger moraines and/or tarns formed
in high-elevation cirque basins (Fig. 2.1). Six (ALT, HR, LRF, PET, ST, YB) of the seven-study watersheds lie within the Sawtooth National Recreation or Wilderness Area and drain into the Salmon River. ALT, HR, LRF, PET, YB watersheds lie on the east side of the Sawtooth Mountain range, while ST lies on the northern edge of the Sawtooth Mountains. BT watershed lies 20 km northwest of ST watershed within the Boise National Forest and drains into the South Fork Payette River.

This area is typically snow-covered for seven to eight months, and spring snowmelt, occurring in May or June, represents the dominant hydrologic flux in these systems. Watershed vegetation cover ranges from 70 to 100% (Table 2.1). Upland vegetation is dominated by lodgepole pine (*Pinus contorta*), while sedges (*Carex* sp.), willows (*Salix* sp.) and grasses dominate riparian areas [Arp et al., 2006]. All watersheds are relatively pristine with limited recreational land use and low wet atmospheric nitrogen (N) deposition (~1.0 kg ha\(^{-1}\) yr\(^{-2}\)) [NADP, 2001]. Lakes and streams are typically oligotrophic with co-limitation of primary production by phosphorus (P) and N availability [Wurtsbaugh et al., 1997].

**Methods**

**Sample Collection and Chemical Analysis**

To evaluate the temporal patterns of DOM characteristics in subalpine stream-lake systems, we collected stream-water samples at gauging stations located at inflows and outflows of seven lakes every two-to-three days throughout the peak of the 2008 snowmelt hydrograph and weekly following peak discharge throughout summer.
baseflow. Additionally, in 2007 we sampled the inflows and outflows of four lakes (ALT, BT, PET, and ST) weekly following spring snowmelt through the fall. DOM characteristics were evaluated as DOC concentration, DOC: dissolved organic nitrogen (DON) ratio, DOC specific ultraviolet absorbance (SUVA\textsubscript{254}) and $\delta^{13}$C\textsubscript{DOC}.

We filtered replicate stream-water samples through ashed 0.7-µm glass-fiber filters (Whatman GFF, Maidstone, UK). Filtered stream water samples for analysis of DOC concentration and SUVA\textsubscript{254} were acidified with HCl to pH 2 and stored in the dark until analysis, while filtered stream-water samples for $\delta^{13}$C\textsubscript{DOC} and DON were frozen until analysis.

We measured DOC concentrations on a Oceanography International TOC analyzer (OI Corporation model 700, College Station, TX) using wet persulfate oxidation [Menzel and Vacarro, 1964]. DON was measured as total dissolved N (TDN) [Valderrama, 1981] minus dissolved inorganic N (NO\textsubscript{3} and NH\textsubscript{4}). We measured NO\textsubscript{3}-N by colorimetric analysis via cadmium reduction on an automated analyzer (Astoria Pacific International, Portland, OR). We measured NH\textsubscript{4}-N concentrations for a subset of samples using the phenolhypochlorite colorimetric method [Solorazo, 1969] and found NH\textsubscript{4}-N concentrations to be near or below the detection limit (3.95 µg L\textsuperscript{-1}). Therefore, NH\textsubscript{4}-N was considered to be 0 µg N L\textsuperscript{-1} in the calculation of DON.

We measured ultraviolet (UV) absorbance using a 1-cm path length quartz cell on a Genesys 10 UV spectrophotometer (Thermo Fisher Scientific, Waltham, MA) at 254 nm using acidified double-deionized (DDI) water as a blank [Weishaar et al., 2003]. We then calculated SUVA\textsubscript{254} by dividing the UV absorbance at 254 nm by the respective DOC concentration and reported data as L mg\textsuperscript{-1} C m\textsuperscript{-1}. 
A subset of 7 to 12 samples collected in 2008 from each of ALT, BT, and ST lake inflow and outflow were analyzed for $\delta^{13}$C$_{\text{DOC}}$ at the Stable Isotope Facility at the University of California, Davis, using an Oceanography International Analytical Model 1010 TOC Analyzer (OI Analytical, College Station, TX) connected to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). We evaluated the potential sources of DOM by analyzing samples of water-soluble soil organic carbon and groundwater in the BT watershed. Water-soluble soil organic carbon was collected by extracting 50 g of the top 10 cm of BT lodgepole forest soil in 100 mL of DDI and shaken for 30 min. We collected groundwater samples from hillside springs in BT watershed. Both water-soluble soil organic carbon and groundwater samples were filtered as described above, acidified to pH 2, and analyzed for $\delta^{13}$C$_{\text{DOC}}$.

**Hydrologic Measurements and Watershed Characteristics**

We measured stream discharge ($Q$) weekly, using a flow meter and top-setting wading rod (Flo-mate 2000, Marsh-McBirney Inc., Frederick, MD). Stream stage was recorded at hourly intervals using capacitance rods (Tru-Track, Inc., Christchurch, New Zealand) at all lake inflows and outflows, except for YB, which was instrumented with pressure transducers (Global Water Instrumentation, Inc., Gold River, CA). Such data were collected from April 2007 through October 2008 for ALT, BT, PET and ST inflows and outflows, while HR, LRF, and YB inflows and outflow stage was recorded from April 2008 through October 2008. We developed stream stage-discharge relationships and used the curves to estimate continuous stream discharge for the period of record. Because of ice-damaged stage recorders, discharge data were unavailable for ALT inflow.
and outflow from 1 January to 28 May 2008 and PET inflow and outflow from 31 January to 29 May 2008. To estimate the missing ALT inflow and outflow discharge, we regressed data from 1 October 2007 to 31 December 2007 and 30 May 2008 to 22 September 2008 against the respective discharges for ST. For PET inflow and outflow, we regressed data from 1 October 2007 to 30 January 2008 and 30 May 2008 to 22 September 2008 against ST inflow and outflow data to estimate the missing PET discharge. The $R^2$ was above 0.95 for all relationships.

Watershed area was calculated using the multi-watershed delineation tool (MWD) from a 30-m digital elevation model (http://seamless.usgs.gov/) (Table 2.1). Lake areas and stream lengths were calculated from digital hydrography layers (National Hydrology Dataset, 1:100,000) using ARC/INFO (Environmental Systems Research Institute, Inc., Redlands, CA). Lake area in the Sawtooth Mountains is highly correlated with lake volume measured bathymetrically. Lake volume was calculated using a lake area-volume log-log regression developed from twelve lakes in the Sawtooth Mountains with areas ranging from 0.04 to 6.15 km$^2$ following (Wurtsbaugh, unpublished data, $R^2 = 0.995$, $p<0.0001$):

$$\text{(1)} \quad Volume = 0.0175 \times Area^{1.517}$$

where volume is in units of km$^3$ and area is in km$^2$.

For baseflow conditions, assuming lake hydrologic steady state and complete mixing, maximum water residence time for the seven lakes was calculated as:

$$\text{(2)} \quad R_t = \frac{V}{Q},$$

where $R_t$ is water residence time (years) within the lake, $V$ is lake volume (km$^3$) and $Q$ is mean outflow discharge (L yr$^{-1}$) during baseflow (Table 2.1). During snowmelt, lake
residence time was estimated, using equation 2, assuming a 12% increase in lake
volume, typical of an average water year [Arp et al., 2006], and the peak snowmelt
discharge.

**Analysis of Temporal Variability and Patterns**

First, we assessed if our sampling design was sufficient to characterize temporal
patterns in DOM characteristics by evaluating mean-variance relationships, as log-log
plots [Cattaneo and Prairie, 1995]. Mean-variance plots provide insight into the
magnitude of temporal variation relative to the mean. Following Cattaneo and Prairie
[1995], slopes of two indicate constant variability relative to means (i.e., constant
coefficients of variation; CVs). Slopes greater than two indicate increasing variability
with increasing means, and signify a need for more frequent samples to capture this
variability. In the latter case, an estimate of sampling size, assuming a 20% error,
required to accurately capture the temporal variability was obtained following Downing
[1979].

We found a strong positive relationship between the means and temporal
variances of DOC:DON ratios across our fifteen study sites ($R^2 = 0.80$, $F_{1,13} = 51.70$, $p < 0.0001$), which indicated an increasing CV with increasing mean. This strong positive
relationship for DOC:DON was statistically indistinguishable for inflows and outflows,
separately (ANCOVA, $p = 0.78$). Despite these strong relationships for DOC:DON ratios
in inflows and outflows, we did not observe strong mean-variance relationships for DOC
or DON alone. We estimate that 1.8 times the number of samples we analyzed would
have been required to adequately assess temporal variation in DOC:DON. Thus,
DOC:DON ratio results will be evaluated in terms of the magnitude of variability in these systems and will not be evaluated for temporal patterns and landscape controls. We return to the implications of this variability in the discussion.

In contrast, we found no significant mean-variance relationship for DOC concentration over time across our fifteen study sites ($F_{1,13} = 2.28$, $R^2 = 0.15$, $p = 0.16$), $SUVA_{254}$ ($F_{1,13} = 0.063$, $R^2 = 0.005$, $p = 0.81$), or $\delta^{13}C_{DOC}$ ($F_{1,13} = 0.5026$, $R^2 = 0.091$, $p = 0.51$), as evaluated by log-log plots, which indicated a consistent variance relative to the respective means and adequate sample size.

**DOM flushing and intra-annual buffering**

To evaluate if lakes act to buffer DOC snowmelt flushing, we compared the timing at which the water and DOC center of mass (i.e., 50% of the cumulative mass) was exported during the 2008 water year for the seven study lake inflows and outflows, similar to Sebestyen et al. [2008] and Hodgkins et al. [2003]. Additionally, we evaluated the timing of DOC flushing relative to changes in discharge in inflows and outflows by comparing patterns of hysteresis in DOC concentration by discharge ($C\text{-}Q$) plots from April to October 2008. $C\text{-}Q$ plots provide visual analysis of concentrations during the rising and falling limb of the hydrograph, with greater concentrations on the rising limb than the falling limb indicating greater hysteresis, which is typical of a slowly renewed source pool (e.g., terrestrial organic carbon in mountain ecosystems). Given that lakes may act to buffer snowmelt flushing of terrestrial DOM, as well as provide an additional source of DOM, we predicted that lake inflows will exhibit greater hysteresis than lake outflows.
To test the hypothesis that lakes buffer stream DOM temporal variability across the sampling season, we calculated means and coefficients of variation (CVs) for DOC concentration, SUVA$_{254}$, DOC:DON ratio and $\delta^{13}$C$_{DOC}$ from April to October 2008, and CVs were compared between all lake inflows and outflows using analysis of variance (ANOVA, JMP 7.0.1, SAS Institute, Cary, NC). Alpha value was set to 0.05. If lakes act to buffer snowmelt flushing and stream temporal variability, we predicted that the lake outflow DOC center of mass export will occur after the inflow center of mass export. Further, we predicted that DOM temporal variation (measured as CV) would be less in lake outflows than lake inflows. We then evaluated the relationships between the temporal variability of DOM characteristics and potential environmental drivers by calculating Pearson correlation coefficients between CVs and watershed characteristics (e.g., % upstream lake area, % barren area, distance to the closest upstream lake, area of the closest upstream lake, study lake area, study lake:watershed area, combined water residence time in upstream lakes; Table 2.1) thought to impact temporal DOM variability.

Equality of Temporal Patterns

Nonparametric analysis of covariance (ANCOVA) was conducted to test equality of temporal patterns of DOM characteristics between all seven pairs of lake inflows and outflows during the 2008 sampling season [Young and Bowman, 1995] with lake position (i.e., inflow and outflow) as the grouping variable and time as the covariate. Given that lakes may buffer temporal changes in DOM in outflow streams by temporarily storing DOC and providing an additional source of DOC, we predicted that temporal patterns of DOM characteristics would not be equal in inflows and outflows. Nonparametric models
were fit using the ‘sm’ package, version 2.2-3 [Bowman and Azzalini, 2007] in R version 2.9.1 (R Development Core Team, Vienna, Austria). This model uses cross-validation to select the best smoothing parameter \( h \) for each pair (i.e., lake inflow and outflow) of regression curves. Adjusting \( h \) did not significantly alter the results of the nonparametric ANCOVA. The model compares curves to a reference band, which indicates the acceptance region for the null hypothesis (i.e., the two curves are equal). The width of the reference band is directly related to the difference between the actual data and the modeled curve. For example, when the actual data points do not fit the modeled curve well, the width of the reference band increases, and thus there is a larger probability of accepting the null hypothesis. ANCOVA alpha was 0.05.

**Annual Export Estimates**

To evaluate if lakes alter DOC export, we compared high flow, low flow and total annual DOC loads for seven lake inflows and outflows. We interpolated DOC concentrations between sampling events as the mean DOC concentration of the two samples spanning each modeled period. Daily flux \( F_d \) of DOC (kg C d\(^{-1}\)) was calculated as:

\[
F_d = Q * [DOC]
\]

where \( Q \) is mean daily discharge (L d\(^{-1}\)) and \( [DOC] \) is the DOC concentration (kg C L\(^{-1}\)).

The annual DOC load for all inflows and outflows was calculated as the sum of the daily DOC flux for the 2008 water year (1 October 2007 to 30 September 2008). April (pre-snowmelt) 2008 and October 2008 discharge for HR, LRF, and YB were similar, therefore we used the mean as the discharge from October 2007 to April 2008.
Mean baseflow DOC concentrations were used as an estimate of DOC concentration from October 2007 to April 2008. Annual DOC export from each watershed, above and below the study lakes was calculated by dividing the annual DOC load by the respective watershed area (Table 1). For the 2008 water year, DOC export for inflows and outflows was calculated, as above, for the time period of high (1 May to 31 July 2008) and low flows (1 October 2007 to 30 April 2008 and 1 August 2008 to 30 September 2008).

**DOC Production**

To evaluate if lakes act as a source of DOC in mountain fluvial networks, during 2008 (seven lakes) and 2007 (four lakes) baseflow conditions, inflow and outflow mean DOC concentrations were compared using an ANOVA.

In order to better understand if lakes can shift from a DOC sink to a DOC source throughout a sampling season, we calculated in-lake DOC production from April to October 2008. In-lake DOC production was calculated as:

(4) \[
\% \text{ DOC production} = \left( \frac{F_{d(\text{outflow})} - F_{d(\text{inflow})}}{F_{d(\text{inflow})}} \right) \times 100
\]

Lake inflow DOC load calculations were corrected for by adding non-channelized hillslope runoff as the product of the inflow load and the proportion of additional catchment area draining directly into the lake relative to the inflow area. This approach allows comparison across our seven study watersheds, which differ considerably in watershed areas and inflow DOC concentrations [Fairchild and Velinsky, 2006]. Negative values signify that the lake was acting as a DOC sink, while positive values signify the lake was acting as a DOC source (i.e., DOC production). To examine relationships between in-lake DOC production and watershed characteristics, correlation
coefficients were calculated between maximum DOC production values and watershed characteristics (Table 2.1).

Results

Temporal Variability and Patterns

DOM flushing and intra-annual buffering

Our results support the hypothesis that lakes alter the timing of DOC but not water export during snowmelt. From 60 to 80% of the total water export from these watersheds occurred during elevated snowmelt flows (Figure 2.2). Timing of peak daily discharge was similar between lake inflow and outflow pairs. Additionally, peak DOC concentrations were generally higher in lake inflows than lake outflows (Figure 2.2). Following snowmelt flushing, inflow DOC concentrations decreased to pre-snowmelt values and ranged from 0.5 to 1.0 mg C L\(^{-1}\). On the contrary, outflow DOC concentrations remained elevated after snowmelt and ranged from 1.0 to 2.0 mg C L\(^{-1}\).

Inflow DOC center of mass occurred, on average, 5.1 \(\pm\) 1.3 (SE) days before the water center of mass (Table 2.2). Conversely, in most lakes the outflow DOC center of mass occurred at approximately the same time (0.1 \(\pm\) 1.9 days) as the water center of mass. The HR watershed was the only drainage where the outflow DOC center of mass export occurred before the water center of mass export. Despite similarities between inflows and outflows in discharge flux patterns, the DOC center of mass occurred, on average, 5.4 \(\pm\) 1.4 (SE) days earlier in seven lake inflows relative to their respective outflows, and ranged from -1 to 11 days (Table 2.2).
In addition to a lag in DOC export in outflows relative to inflows, we observed greater DOC hysteresis in lake inflows (i.e., lake inflow DOC concentrations increased at a faster rate with increasing discharge) than in lake outflows (Figure 2.3). Six of the seven lake inflows showed clockwise hysteresis, with rapid increases in DOC concentration on the ascending limb of the hydrograph and lower concentrations on the descending limb of the hydrograph (Figure 2.3). The hydrograph in all watersheds except BT was bimodal (Figure 2.2), with the first peak in discharge associated with higher DOC concentrations (Figure 2.3). The only lake inflow that did not have a rapid DOC increase with increasing discharge was LRF, which is directly downstream of a large (6 km²) lake (Figure 2.1; Table 2.1). In contrast to lake inflows, DOC concentration in lake outflows did not increase as rapidly on the ascending limb of the hydrograph. Instead, lake outflow DOC concentrations tended to increase after discharge had increased (Figure 2.3).

As we hypothesized, DOM in lake outflows was less variable, as measured by coefficients of variation (CV), than in lake inflows. Throughout the 2008 sampling season, inflow CVs were 1.9 times greater for DOC concentration ($F_{1,13} = 34.64$, $p < 0.0001$), 1.6 times greater for SUVA$_{254}$ values ($F_{1,13} = 5.24$, $p = 0.039$) and 1.4 times greater for DOC:DON ratio values ($F_{1,13} = 13.72$, $p = 0.0026$; Table 2.3) than outflow CVs. For the three watersheds where $\delta^{13}$C$_{DOC}$ was evaluated, we observed no difference between inflow and outflow CV ($F_{1,4} = 0.78$, $p = 0.427$). However, two of the three inflows had higher CVs than outflows (Table 2.3).

DOM temporal variability was related to watershed attributes. For both the inflows and outflows, the CVs for DOC concentration were negatively correlated with
the percentage of upstream area occupied by lakes ($r = -0.578, p = 0.024$) and, for inflows alone, the area of the closest upstream lake ($r = -0.900, p = 0.037$; Table 2.4). CVs for SUVA$_{254}$ and $\delta^{13}$C$_{DOC}$ were positively correlated to the percentage of upstream barren area ($r = 0.653, p = 0.008$ and $r = 0.819, p = 0.046$, respectively) and negatively correlated to the % of upstream area covered by vegetation ($r = -0.677, p = 0.006$ and $r = -0.814, p = 0.049$, respectively). Percent barren area and % vegetated area were, not surprisingly, highly negatively correlated with each other ($r = 0.861, p < 0.0001$).

Equality of DOM temporal patterns

Temporal patterns of DOC concentration differed significantly between inflows and outflows for five of the seven study watersheds (ANCOVA, $p < 0.03$; Table 2.5). This resulted from higher DOC peaks in the inflow during snowmelt and higher DOC concentrations in outflows during baseflow (Figure 2.2).

SUVA$_{254}$ values pre-snowmelt in all study watersheds were approximately 1.5 to 2.0 L mg$^{-1}$ C m$^{-1}$. During peak snowmelt (day of the 140 to 142), SUVA$_{254}$ values were approximately 2.5 to 3.0 L mg$^{-1}$ C m$^{-1}$ and were the highest values (i.e., greatest aromatic compounds) observed throughout the sampling season. Following peak snowmelt, SUVA$_{254}$ values decreased to 0.5 to 1.0 L mg$^{-1}$ C m$^{-1}$ in all seven lake inflows and outflows until early August (approximate day of the year 214), when the SUVA$_{254}$ values increased again towards pre-snowmelt values (Figure 2.4, BT and ALT inflow and outflow data shown). Temporal patterns in SUVA$_{254}$ differed between inflows and outflows at ALT, BT, HR1, HR2 and PET, but not at LRF, ST, or YB (Table 2.5).
Mean (+SE) groundwater and soil extract $\delta^{13}C_{DOC}$ values were -25.5‰ (0.54) and -28.3‰ (0.66), respectively (Figure 2.4). In April (i.e., pre-snowmelt), BT inflow had a $\delta^{13}C_{DOC}$ value of -21‰, which was dissimilar to both groundwater and soil extract $\delta^{13}C_{DOC}$. In May, during the ascending limb of the snowmelt hydrograph (day of the year 135), ALT, BT and ST Lake inflow and outflow had similar $\delta^{13}C_{DOC}$ values (~24 to -24.5‰) that approximated that of groundwater and soil extracts (Figure 2.4, Bull Trout and Alturas inflow and outflow data shown). During the peak of the snowmelt hydrograph (approximate day of the year 141), all three inflows became even more depleted in $\delta^{13}C_{DOC}$ (-25 to -25.5‰) and shifted towards a $\delta^{13}C_{DOC}$ signature closer to those of groundwater and soil extract. Following peak snowmelt discharge, all inflow $\delta^{13}C_{DOC}$ values increased to ~22‰, and then decreased again in early August (approximate day of the year 214; Figure 2.4). Lake outflow $\delta^{13}C_{DOC}$ values increased across the summer and early fall and ranged from -27 (BT) and -25 (ALT and ST) to -24 %‰ $\delta^{13}C_{DOC}$. BT and ST inflow and outflow had marginally different $\delta^{13}C_{DOC}$ temporal patterns (ANCOVA, $p = 0.053$ and 0.089, respectively), while ALT inflow and outflow $\delta^{13}C_{DOC}$ patterns were not significantly different (ANCOVA, $p = 0.11$; Table 2.5).

**Lakes as a DOC Source**

Annual DOC export ranged from 10.2 to 14.6 kg C ha$^{-1}$ yr$^{-1}$ for inflows and from 11.7 to 14.7 kg C ha$^{-1}$ yr$^{-1}$ for outflows (Table 2.6). Annual export increased below five (BT, HR, LRF, PET and ST) of the seven study lakes. During high flows, inflows exported between 75 to 93% of their total annual DOC load to lakes, while lake outflows exported from 70 to 82% of the total annual DOC export. During low flow periods, DOC
export was 1.2 to 2.4 times greater in lake outflows than their respective inflows (Table 2.6).

Results supported our hypothesis that lake outflows would have higher DOC concentrations than lake inflows during summer baseflow. Mean baseflow DOC concentrations in 2008 were 1.7 times greater in the lake outflows than inflows ($F_{1,12} = 18.32; p = 0.0011$; Figure 2.5) for the seven watersheds. During 2008 baseflow, lake outflow DOC concentrations were significantly greater than inflows in ALT ($F_{1,8} = 26.8136, p = 0.0008$), BT ($F_{1,11} = 29.2093, p = 0.0002$), LRF ($F_{1,11} = 5.5135, p = 0.0386$), PET ($F_{1,7} = 38.6448, p = 0.0004$), and ST ($F_{1,9} = 64.9571, p < 0.0001$) and marginally significant in YB ($F_{1,10} = 4.263, p = 0.066$) and HR ($F_{1,10} = 3.8321, p = 0.0788$, Figure 2.5). Similarly, outflow DOC concentrations were two times greater than inflows during baseflow in 2007 ($F_{1,6} = 17.66; p = 0.0057$) in four study watersheds (ALT, BT, PET and ST).

The percentage (%) of in-lake DOC production varied temporally and spatially. From April through early June 2008 (pre-peak snowmelt), % DOC production in all lakes was at or below 0 (Figure 2.6), indicating that lakes were DOC sinks. Following spring snowmelt in early to mid-June, net DOC production increased in all lakes and the lakes became a source of DOC to outflow streams. % DOC production in LRF and YB had lower peaks (<65%), which occurred in early August before they declined to <30%. Conversely, in the other five study lakes the % DOC production peaked at 170 to 250% of inflow values in mid-late August before they declined (Figure 2.6). Maximum % DOC production was strongly negatively correlated with % total upstream lake area ($r = -0.74, F_{1,5} = 6.07; p = 0.057$) and was not correlated to any other watershed characteristics.
Discussion

Our results support the hypothesis that the presence of lakes within mountain stream networks can alter DOM temporal patterns. First, we show that lakes can dampen DOC snowmelt flushing from mountain watersheds and alter the timing of DOC export to downstream locations. Second, subalpine lakes decreased temporal variability of lake-outflow stream DOC concentration and characteristics compared to lake inflows. Finally, subalpine lakes acted as a sink of DOC during spring snowmelt and as a DOC source throughout baseflow conditions.

DOM Temporal Variability and Patterns

Our DOC:DON results illustrate the high temporal variability of DOC:DON ratios, which may be a result high variability of DON analytical measurements, of differences in flushing rates [Kaiser and Zech, 2000; Kaushal and Lewis, 2003] and cycling [Wiegner and Seitzinger, 2001; Caraco and Cole, 2003; Kaushal and Lewis, 2005]. Additionally, rapid uptake of DON can occur in N-limited systems [Stepanauskas et al., 2000; Kaushal and Lewis, 2005], such as the Sawtooth Mountains, which further obscures the usefulness of DOC:DON ratios as an indicator of source DOM quality and bioavailability. Kaushal and Lewis [2005] found DOC bioavailability to be related to the non-humic (i.e., carbohydrates) fraction C:N ratio, yet a substantial portion of DOC is humic substances [Hood et al., 2003; Kaushal and Lewis, 2005]. Similarly, DOC:DON ratios of DOM isolates, such as fulvic and transphilic acids, may be a more reliable indicator of DOM temporal variability in chemical characteristics Hood et al. [2005]. Therefore, we suggest care should be taken when evaluating DOC:DON ratios as an
indicator of DOM bioavailability, and further suggest the use of DOM chemical isolates or a large sample size when attempting to evaluate DOM characteristics using DOC:DON ratio.

Our results indicate that inflows had more rapid and larger increases in DOC concentration, and higher snowmelt peak concentrations than outflows, indicating in-lake DOC retention during snowmelt. LRF inflow was the only lake inflow that did not exhibit a rapid increase in DOC concentration on the ascending limb of the snowmelt hydrograph. LRF is only 2.6 km downstream of a large (6 km²) lake, likely causing LRF inflow to behave more like lake outflows. In contrast, lakes do not appear to buffer peak stream water discharge, consistent with data from Bull Trout presented by Arp et al. [2006]. The inability of lakes to buffer spring snowmelt flows is likely a result of low in-lake storage capacity as lake water levels rise [Arp et al., 2006]. These results indicate that the differences observed between inflow and outflow DOC concentrations during snowmelt were a result of biogeochemical, rather than hydrological, processes.

Our inflow DOC flushing responses were similar to other snowmelt-dominated systems, where snowmelt represents a flushing of a finite terrestrial DOC source in soil pore water [Hornberger et al., 1994; Boyer et al., 1997; Brooks et al., 1999; Hood et al., 2003]. However, our results indicate that lakes can dampen this flushing response in lake outflows. The ability of lakes to dampen this DOC flushing pulse was variable across watersheds and is likely related to an interaction of many factors including terrestrial connectivity [McGlynn and McDonnell, 2003], topography, elevation and patterns of snowmelt and accumulation [Hornberger et al., 1994; Boyer et al., 1997], lake residence time [Arp et al., 2006] and microbial processing [Crump et al., 2003].
Pace and Cole [2002] hypothesized that DOC may build up in lakes during times of ice-cover due to a lack of light, and hence a lack of photodegradation. If lakes did build up DOC during ice-cover, we would expect lake outflows to exhibit high DOC concentrations during spring snowmelt flushing. However, pre-ice-out DOC concentrations were not above baseflow concentrations, and during peak snowmelt flows DOC concentrations were lower than inflows. The fact that we did not observe a build up DOC in lakes during ice-cover may be a result of the oligotrophic nature, and hence low productivity, of these systems [Budy et al., 1995] relative to the forest’s productivity and DOC export.

As we hypothesized, we observed significantly lower CVs for DOM concentrations and characteristics in lake outflows than inflows. These results illustrate the ability of lakes to buffer stream DOM temporal variability. In contrast, Cattaneo and Prairie [1995] did not observe a dampening effect of lakes on lake outlet stream chemistry (DOC concentration was not included) in a low-gradient Canadian stream, which they attribute to the relatively small lake size (0.03 to 5.29 km$^2$) and rapid flushing (not reported) of their study lakes. However, their sampling began following spring runoff, and therefore may not have captured the period when stream chemical concentrations and characteristics are changing drastically in snowmelt-dominated systems [Lewis and Grant, 1979; Boyer et al., 1997].

We observed an inverse relationship between lake outflow DOC temporal variability and the size of the study lake, suggesting that the extent to which lakes can stabilize temporal variability in DOC concentrations in mountain landscapes is related to their storage capacity. Furthermore, we observed an inverse relationship between inflow
DOC variability and the area of the closest upstream lake, indicating that upstream water residence time can regulate downstream DOC temporal variability. Longitudinal changes in DOC concentration and SUVA\textsubscript{254} indicate that a 10 to 25% change in these DOM characteristics occur for every kilometer downstream of a lake outlet (K. Goodman, unpublished data). Thus, we would predict a 50 to 100% change in DOM characteristics 4 to 5 km downstream of a lake outlet.

Arnott \textit{et al.} [2003] evaluated lake temporal variability of four chemical variables related to acidification and found, during ice-free periods, the variability was inversely related to lake flushing rates. Water residence time and flushing rates are related to both watershed and lake size. Lake:watershed area ratios (i.e., drainage ratio) provide insight into the amount of water being routed from the surrounding landscape to a lake of a known size. Thus, drainage ratio can provide considerable information on lake storage capacity and flushing rates [Canham \textit{et al.}, 2004] and DOC concentration [Sobek \textit{et al.}, 2007]. Our results support the hypothesis of Arnott \textit{et al.} [2003]. We observed negative relationships between drainage ratio and DOM variability. We also observed a negative correlation, albeit not as strong for DOM characteristics, between DOM variability and the study lake area. These results illustrate that both lake area and watershed area influence DOM temporal variability.

Upstream watershed characteristics also appear to influence DOM temporal variability. Upstream lake area appears to be a good predictor of temporal variability in DOM (specifically DOC concentration and $\delta^{13}$C\textsubscript{DOC}). Additionally, we observed strong relationships between the temporal variability of DOM characteristics (SUVA\textsubscript{254} and $\delta^{13}$C\textsubscript{DOC}) and watershed land cover characteristics, where the greater the % barren area
and lower the % vegetated area, the greater the variability. Similar to our results, Little et al. [2008] found the proportion of barren land to be a significant predictor of N export during baseflow conditions in Chilean watersheds, and attributed this result to a low capacity for water and nutrient retention.

As we hypothesized, DOM temporal patterns were different between most lake inflows and outflows. However, two (HR and LRF) of our seven study watersheds did not exhibit a significant difference in DOC temporal patterns between inflow and outflow streams. These two watersheds have extremely low residence times during snowmelt (0.02 and 0.01 yrs, respectively) and baseflow (0.31 and 0.05 yrs, respectively) conditions. Therefore, high flushing rates likely resulted in the decreased buffering capacity of these lakes [Arnott et al., 2003]. Additionally, both of these lakes are strongly influenced by relatively close upstream lakes.

Similarly, DOM characteristics in lake inflow streams were more temporally dynamic than lake outflow streams. During spring snowmelt, when the stream is hydrologically connected to the surrounding terrestrial environment and the soil pore water is flushed to the stream [Hornberger et al., 1994], we would expect a large proportion of terrestrial aromatic compounds in the stream. Accordingly, we observed higher SUVA$_{254}$ (i.e., greater aromatics), and $\delta^{13}$C$_{\text{DOC}}$ values shifted towards the $\delta^{13}$C$_{\text{DOC}}$ value of groundwater and soil extract. Following snowmelt, SUVA$_{254}$ values decreased (i.e., less aromatics) and $\delta^{13}$C$_{\text{DOC}}$ values became less depleted as the stream became less connected to the surrounding landscape [McGlynn and McDonnell, 2003] and microbial processing increased [Schiff et al., 1990]. Surprisingly, in late July and early August (approximate days of the year 200 to 214), SUVA$_{254}$ values increased again and $\delta^{13}$C$_{\text{DOC}}$
values became more depleted in lake inflows compared to outflows. This shift in
DOM characteristics was most dramatic in lake inflows, and may be a result of decreased
soil water inputs as the water table falls [Baker et al., 2000; Hood et al., 2003] and/or
decreased microbial DOM production and processing.

Interestingly, Bull Trout outflow $\delta^{13}$C$_{\text{DOC}}$ increased throughout the summer,
which was an opposite trend from that of lake seston $\delta^{13}$C$_{\text{DOC}}$, which declined from -28 to
-30 ‰. This increase in $\delta^{13}$C$_{\text{DOC}}$ in Bull Trout outflow may be a result of increased
DOM inputs from macrophytes ($\delta^{13}$C$_{\text{DOC}}$ ranged from -21 to -24 ‰; D. Epstein and W.
Wurtsbaugh, unpublished data) in Bull Trout Lake. Furthermore, SUVA$_{254}$ values were
higher in BT and ST outflow relative to their respective inflow, which is opposite the
anticipated shifts in aromaticity within a lake following production of aquatically-
derived, as well as photodegraded aromatic DOM [McKnight et al. 1994; Allard et al.
1994]. The observed increase in SUVA$_{254}$ in ST and BT may be a result of large
macrophyte beds within these lakes (K. Goodman, manuscript in preparation, 2010), as
submerged macrophytes can contribute DOM to the lake pelagic zone during summer and
fall senescence [Carpenter 1980; Janse et al. 1998]. Our results indicate that
macrophytes can increase DOM aromaticity in high-elevation oligotrophic lakes, as well
as downstream locations. Macrophyte-derived DOM influence on ecosystem functioning
has received little attention, however the quantity of quality of macrophyte-derived DOM
is likely to differ from other aquatically-derived DOM and warrants further study.
Lakes as Sink/Source of DOC

Annual export from our study watersheds was similar to those reported from Colorado Front Range systems (10 to 11 kg C ha\(^{-1}\)), [Hood et al., 2003]), albeit in the low range of DOC yields across the United States, 7 to 74 kg C ha\(^{-1}\) [Tate and Meyer, 1983; Aitkenhead and McDowell, 2000]. Similar to other studies, DOC export in our systems was driven by spring snowmelt runoff [Boyer et al., 1997; Schindler et al., 1997; Baker et al., 2000]. Despite increased Q in the outflow compared to the inflow during high flows, only three lake outflows had higher DOC export during high flows (BT, HR and ST), indicating biological or chemical DOC retention in the lake during snowmelt.

Recent studies have shown that lakes can be a sink for inorganic nutrients [Kling et al., 2000; Robinson and Matthaei, 2007; Brown et al., 2008], and may be a source of particulate and dissolved organic nutrients [Robinson and Matthaei, 2007; Brown et al., 2008]. Furthermore, Brown et al. [2008] suggested that lakes may switch from sinks to sources of nitrogen from spring snowmelt to summer baseflow. Our results support this hypothesis. We observed a shift in the role of lakes from a DOC sink to a source (i.e., in-lake DOC production increased) throughout the summer, as evaluated by differences in DOC loads between lake inflows and outflows.

Following peak snowmelt discharge in early June, lake % DOC production increased for approximately two months, which may be related to increased primary production [Crump et al., 2003], and both DOC and DON production in lakes has been observed in small oligotrophic [Kling et al., 2000; Lockwood, 2009] and eutrophic [Fairchild and Velinsky, 2006] lakes and ponds. Our prediction that larger lakes would have greater DOC production due to longer residence time was not supported by the data...
and may be a result of the inherently low pelagic primary production of these systems [Budy et al., 1995].

The fact that % DOC production declined dramatically in all lakes by mid-August, coincident with shifts in SUVA\textsubscript{254} (i.e., aromaticity increased, lower quality carbon) and \(\delta^{13}\text{C}_{\text{DOC}}\) signature (i.e., more depleted, less microbial processing) suggests a shift in DOM source and/or decreased microbial processing rates. Previous work in these systems indicates that in July and August, nutrients (i.e., N and P) become limiting to autotrophic [Spaulding, 1992; Marcarelli and Wurtsbaugh, 2007] and heterotrophic (K. Goodman, manuscript in preparation, 2010) production and processing. Thus, decreased microbial processes due to nutrient limitation may have altered inflow DOM characteristics. Additionally, the strong negative correlation between % upstream lake area and % DOC production may be a result of upstream lakes retaining inorganic nutrients [Kling et al., 2000; Ito et al., 2007; Robinson and Matthaei, 2007; Brown et al., 2008] and increasing organic nutrient export [Brown et al., 2008]. In contrast, while lake outflow DOM characteristics exhibit a shift towards terrestrial sources during snowmelt, we did not observe as dramatic a shift in outflow DOM characteristics in late July and early August. This buffering in temporal patterns of DOM characteristics may be a result of lake DOM storage capacity, as well as continued in-lake DOM production, albeit low [Budy et al., 1995].

While the presence of lakes in the watershed decreased DOC export during high flows in four of seven study watersheds, on an annual basis lakes in five of the seven study watershed increased DOC export. This increase in annual DOC export is driven by higher DOC exports during baseflow conditions, and may provide an important DOC
source to downstream locations at a time when the terrestrial DOC supply has been exhausted [Hornberger et al., 1994; Bayer et al., 1997; Brooks et al., 1999; Hood et al., 2003].

Conclusion

Watershed export of DOC to the oceans is an important flux in the global carbon cycle and landscape patterns play a large role in dictating flows and DOC export [Cole et al., 2007]. DOC concentration and export has been shown to be controlled by runoff [Schlesinger and Melack, 1981], vegetation [Dillon and Molot, 1997; Gergel et al., 1999], and landscape C:N ratios [Aitkenhead and McDowell, 2000; Aitkenhead-Peterson et al., 2007]. Our data demonstrates that mountain lakes can also regulate DOC concentration and export at landscape scale.

To our knowledge, this is the only study that attempts to characterize the ability of lakes to buffer DOM temporal patterns in mountain streams. Our results illustrate that lakes within high-elevation ecosystems can buffer DOC temporal patterns in streams, by acting as a DOC sink during snowmelt and a DOC source during baseflow. The fact that lake inflow variability was strongly related to upstream lake area further illustrates the ability of lakes to reduce the control of hydrologic transport on stream DOM dynamics. Our results suggest that lakes within mountain fluvial networks may provide an important energy source to downstream locations when terrestrial supplies have been exhausted. We further suggest that mountain lakes provide stability to surface stream networks.
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Table 2.1. Lake and watershed characteristics of seven study lake inflows and outflows in the Sawtooth Mountain Lake District, central Idaho. WS is watershed. BF $R_t$ is lake residence time, calculated as lake volume/average baseflow discharge. SM $R_t$ is lake residence time during snowmelt, calculated as lake volume/peak daily discharge assuming a 12% increase in lake volume [Arp et al., 2006]. $R_t$ calculations assume a completely mixed lake. NA – Not applicable as a result of no upstream lakes or upstream lakes that are too far and small to influence the study locations.

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<th>Outflow WS Area (km$^2$)</th>
<th>Lake Area (km$^2$)</th>
<th>Lake/WS Area</th>
<th>Lake Volume (km$^3$)</th>
<th>BF $R_t$ (yrs)</th>
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<th>Elev. (m)</th>
<th>Distance to closest upstream lake (km)</th>
<th>Area of closest upstream lake (km$^2$)</th>
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<td>YB</td>
<td>26.28</td>
<td>30.03</td>
<td>0.79</td>
<td>0.030</td>
<td>0.012</td>
<td>1.12</td>
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<td>34.2</td>
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</table>
Table 2.2. Day of the year when 50% of the total annual discharge (Q) and DOC mass had been exported during the 2008 water year for seven lake inflows and outflows in the Sawtooth Mountains, central Idaho. Q-DOC lag is the difference between the Center of Mass for discharge and DOC in the inflows and outflows. Outflow – Inflow DOC lag is the difference, in days, that the outflow and inflow DOC Center of Mass occurred.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Inflow Q</th>
<th>DOC</th>
<th>Q-DOC Lag (days)</th>
<th>Outflow Q</th>
<th>DOC</th>
<th>Q-DOC Lag (days)</th>
<th>Outflow – Inflow DOC Lag (days)</th>
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<td>154</td>
<td>-4</td>
<td>159</td>
<td>160</td>
<td>1</td>
<td>6</td>
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<td>BT</td>
<td>153</td>
<td>150</td>
<td>-3</td>
<td>153</td>
<td>153</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>HR</td>
<td>164</td>
<td>156</td>
<td>-8</td>
<td>169</td>
<td>161</td>
<td>-8</td>
<td>5</td>
</tr>
<tr>
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<td>170</td>
<td>158</td>
<td>-12</td>
<td>169</td>
<td>161</td>
<td>-8</td>
<td>3</td>
</tr>
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<td>1</td>
<td>163</td>
<td>168</td>
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<td>11</td>
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<td>5</td>
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<tr>
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<td>157</td>
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Table 2.3. Means and coefficients of variations (CV, %) for DOM concentration (DOC) and characteristics for seven lake inflows and outflows of the Sawtooth Mountain Lake District in central Idaho, throughout the entire 2008 sampling season from early spring (pre-snowmelt) to early fall. DOC is mg C L\(^{-1}\) and SUVA is L mg\(^{-1}\) C m\(^{-1}\). Note \(\delta^{13}\)C\(_{DOC}\) has different sample number (n) than all other DOM attributes.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Position</th>
<th>n</th>
<th>Mean</th>
<th>CV</th>
<th>Mean</th>
<th>CV</th>
<th>Mean</th>
<th>CV</th>
<th>n</th>
<th>Mean</th>
<th>CV</th>
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<tr>
<td>BT</td>
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<td>60.2</td>
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<td>Inflow 2</td>
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<td>1.56</td>
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<td>75.1</td>
<td>41.3</td>
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<td>40.5</td>
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<tr>
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<td>1.52</td>
<td>37.1</td>
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<td>1.63</td>
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<td>Inflow</td>
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<td>60.5</td>
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<tr>
<td>YB</td>
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<td>43.5</td>
<td>33.8</td>
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</table>
Table 2.4. Correlation coefficients (r) and significance (p) between inflow and outflow coefficients of variations (CV) and watershed variables during the 2008 sampling season and watershed variables. DOC is mg C L$^{-1}$ and SUVA is L mg$^{-1}$ C m$^{-1}$. Note $\delta^{13}$C$_{\text{DOC}}$ has different sample number (n) than all other DOM characteristics. Significant correlations are highlighted in bold font.

<table>
<thead>
<tr>
<th></th>
<th>DOC</th>
<th>SUVA</th>
<th>$\delta^{13}$C-DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>r</td>
<td>p</td>
</tr>
<tr>
<td>% Upstream lake area</td>
<td>15</td>
<td>-0.578</td>
<td><strong>0.024</strong></td>
</tr>
<tr>
<td>% Barren area</td>
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<td>0.406</td>
<td>0.133</td>
</tr>
<tr>
<td>% Vegetated area</td>
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<td>0.267</td>
</tr>
<tr>
<td>Dist. to closest upstream lake$^a$</td>
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<td>0.657</td>
</tr>
<tr>
<td>Area of closest upstream lake$^a$</td>
<td>5</td>
<td>-0.900</td>
<td><strong>0.037</strong></td>
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<tr>
<td>Study lake area$^b$</td>
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<td>0.120</td>
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<tr>
<td>Study lake: Watershed area$^b$</td>
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<td>-0.574</td>
<td>0.178</td>
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</table>

$^a$ Analyzed only with study lake inflows.

$^b$ Analyzed only with study lake outflows.
Table 2.5. Nonparametric ANCOVA results comparing equality of temporal patterns of DOM characteristics between seven lake inflows and outflows of the Sawtooth Mountains, central Idaho, from May to October, 2008. HR1 and HR2 represent two different inflows to HR Lake. ‘h’ is the smoothing parameter. p-value <0.05 indicates inflow and outflow patterns are statistically different.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>DOC</th>
<th>SUVA</th>
<th>δ\textsuperscript{13}C-DOC</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>h</td>
<td>p</td>
<td>h</td>
</tr>
<tr>
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<td>30.6 0.018</td>
<td>20.0 0.110</td>
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<td>19.5 0.012</td>
<td>20.4 0.053</td>
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<td>HR2</td>
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<td>12.4 0.050</td>
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<td>15.0 0.048</td>
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<td>YB</td>
<td>31.3 0.030</td>
<td>25.0 0.176</td>
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</table>
Table 2.6. DOC export (kg C ha\(^{-1}\)) during high flow (92 days), low flow (273 days) and total annual (365 days) for seven lake inflows and outflows of the Sawtooth Mountains, central Idaho during the 2008 water year. High flow conditions occur from 1 May 2008 to 30 July 2008 and low flow is from 1 October 2007 to 30 April 2008 and 1 August 2008 to 30 September 2008. % High flow export is the % of annual flow exported during high flows.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>High</th>
<th>Low</th>
<th>Total</th>
<th>% High Flow Export</th>
<th>High</th>
<th>Low</th>
<th>Total</th>
<th>% High Flow Export</th>
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<tr>
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<td>10.8</td>
<td>2.5</td>
<td>13.3</td>
<td>81.3</td>
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<td>2.4</td>
<td>10.2</td>
<td>76.1</td>
<td>10.6</td>
<td>4.1</td>
<td>14.7</td>
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<td>1.7</td>
<td>10.9</td>
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<td>2.7</td>
<td>14.5</td>
<td>81.7</td>
</tr>
<tr>
<td>LRF</td>
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<td>11.1</td>
<td>75.0</td>
<td>8.3</td>
<td>3.4</td>
<td>11.7</td>
<td>70.7</td>
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<tr>
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<td>9.7</td>
<td>1.3</td>
<td>11.1</td>
<td>87.9</td>
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<td>2.4</td>
<td>11.8</td>
<td>79.6</td>
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<tr>
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<td>12.5</td>
<td>82.5</td>
<td>11.3</td>
<td>3.6</td>
<td>14.9</td>
<td>75.8</td>
</tr>
<tr>
<td>YB</td>
<td>12.1</td>
<td>2.5</td>
<td>14.6</td>
<td>82.8</td>
<td>9.7</td>
<td>3.0</td>
<td>12.7</td>
<td>76.4</td>
</tr>
</tbody>
</table>
Figure 2.1. Map of study area of in the Sawtooth Mountain lake district. Seven study lakes (ALT – Alturas, BT- Bull Trout, HR – Hell Roaring, LRF – Little Redfish, PET – Pettit, ST – Stanley, YB – Yellow Belly) are indicated by arrows. Inflow and outflow sampling stations were located within 550 stream meters of the study lakes and usually within 200 m.
Figure 2.2. Hydrographs from late April to early October 2008 (lines) and DOC concentrations in seven lake inflows and outflows of the Sawtooth Mountain Lake District. Open triangles indicate inflow DOC concentration (mg C L⁻¹) and closed squares indicate outflow DOC concentrations.
Discharge (L s\(^{-1}\))
Figure 2.3. Hysteresis plots of DOC concentration versus discharge for seven study lake inflows and outflows in the Sawtooth Mountain Lake District from April to October 2008. HR1 is inflow plotted in the HR graph.
Figure 2.4. Relationship between time of year and two metrics of dissolved organic carbon from forest soils, specific ultraviolet absorbance (SUVA$_{254}$) and $\delta^{13}$C$_{\text{DOC}}$, in the inflows and outflows of two lakes. Lines fitted by nonparametric analysis of covariance for BT (left panels) and ALT (right panels) lake inflow (circles) and outflow (triangles). * Indicates inflow (solid) and outflow (dashed) curves are not equal, $p < 0.05$ for SUVA and $< 0.10$ for $\delta^{13}$C$_{\text{DOC}}$. Arrows indicate the time of peak snowmelt discharge occurred between Day of Year 140 and 143. In the lower frames, the horizontal lines show $^{13}$C$_{\text{DOC}}$ of groundwater (GW; -25.5 ‰) and soil extract (SE; -28.3 ‰).
Figure 2.5. Mean (±SE) DOC concentrations during 2008 baseflow conditions (August to October) for seven lake inflows (white bars) and outflows (black bars) in the Sawtooth Mountains, central Idaho. Lakes are plotted in order of increasing distance to an upstream lake. ** indicate p<0.04. * indicate p<0.08.
Figure 2.6. % DOC production calculated as the difference in DOC loads (concentration * discharge) between each inflow and outflow pair relative to the respective inflow load for seven lakes in the Sawtooth Mountains, central Idaho from April to October 2008.
Abstract

Dissolved organic matter (DOM) is an important energy source for heterotrophic microbes in aquatic systems, however not all DOM is readily bioavailable. Ultraviolet (UV) radiation can alter the chemical characteristics of DOM, potentially affecting its bioavailability. Lakes and streams are hydrologically linked in many mountain catchments, and we hypothesized that routing of water through lakes would alter chemical properties and bioavailability of DOM via increased UV exposure. We measured seasonal changes in DOM photodegradation (defined as % reduction (%R) in UV absorbance of samples exposed to sunlight for 30 h relative to dark controls) in four-paired lake inflow and outflow streams; and used field and laboratory experiments to evaluate the effects of UV light on DOM bioavailability. DOM from lake inflow and outflow streams showed similar amounts of photodegradation during spring snowmelt. In contrast, during baseflow, outflow DOM photodegradation was half that of inflows and was inversely related to lake water residence time. Exposure to sunlight also affected DOM quality: aquatically-derived DOM (measured as fluorescence index) and DOM uptake both increased during a 55-d field experiment in light treatments relative to dark controls.

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1 To be submitted for publication in the journal *Limnology and Oceanography.*
2 Coauthored by KJ Goodman, AR Benedetto, and MA Baker
controls. Furthermore, exposure to sunlight during a laboratory bioassay increased the bioavailability of lake inflow and outflow DOM, 1.6X and 1.2X, respectively (p<0.01). Together, our results support the hypothesis that routing of water through lakes alters the chemical complexity of DOM via photodegradation, which increases the bioavailable DOM pool in surface waters.

Introduction

Dissolved organic matter (DOM) plays a major role in the chemical and physical properties of aquatic ecosystems, such as the transport of contaminants and heavy metals (Breault et al. 1996), pH buffering capacity (McKnight et al. 1985), and light attenuation (Laurion et al. 1997). Further, it is one of the largest and most bioavailable carbon sources on Earth, and thus is an important energy source for heterotrophic organisms, subsequently impacting energy flow in aquatic ecosystems (Pomeroy 1974; Azam et al. 1983; Schiff et al. 1990). The extent to which DOM is bioavailable depends, in large part, on its chemical composition (Tranvik 1998).

Aquatic DOM is a heterogeneous mixture of molecules differing in origin, age, and state of processing (Thurman 1985; Moran and Covert 2003). Organic matter pools in headwater streams are derived primarily from terrestrial sources (Vannote et al. 1980), the leaching of which (Dahm 1981) results in relatively refractory, complex aromatic organic molecules (Tranvik 1998). In contrast to headwater streams, clear-water lake DOM typically consists of lower molecular weight compounds that can be created photochemically, following DOM degradation from UV exposure (Allard et al. 1994; Salonen and Vahatalo 1994) or biologically, following microbial processing (Amon and
Benner 1996) and autochthonous production (McKnight et al. 1994). Additionally, in nutrient limited lakes, primary producers can exude photosynthate, further increasing the presence of high quality, low molecular weight DOM (Reynolds 2001).

DOM origin, age and chemical composition are controlling factors of DOM bioavailability (Benner 2003), and exposure to UV radiation can alter both the chemical structure and the bioavailability of DOM (Moran and Covert 2003). Lower molecular weight DOM is generally considered to be easier for heterotrophic bacteria to utilize compared to complex aromatic DOM (Chrost and Faust 1983). Photochemical degradation of chemically complex DOM results in the production of less aromatic, more bioavailable DOM, predominantly carboxylic acids, that can provide an important carbon source for heterotrophic bacteria (Bertilsson and Tranvik 1998). In contrast, Tranvik and Bertilsson (2001) showed that low-molecular weight DOM derived from lake phytoplankton was made less bioavailable after UV exposure. This reversal of DOM bioavailability has also been observed in ocean waters (Benner and Biddanda 1998; Obernosterer et al. 1999). These results indicate that DOM source may play a role in determining the bacterial response to irradiated DOM (Moran and Covert 2003).

In alpine and subalpine watersheds, hydrologic connections between streams and lakes leads to a mixture of DOM sources and characteristics (Benner 2003). Given the heterogeneous nature of the DOM source pool, photo-induced changes in lake water and streams draining lakes may result in increased chemical complexity of microbially-derived DOM (Kieber et al. 1997; Obernosterer et al. 2001) or decreased chemical complexity of terrestrially derived DOM (Wetzel et al. 1995; Bertilsson and Tranvik 2000). Furthermore, high-elevation, shallow lakes with low DOC concentrations, may be
particularly susceptible to UV, mainly UVB, radiation (Morris et al. 1995). Thus, the presence of lakes within fluvial networks has the potential to alter DOM characteristics to outlet streams, yet has received little study (but see Frost et al. 2006; Larson et al. 2007b).

DOM dynamics in alpine and subalpine systems are further complicated by strong seasonal patterns resulting from a flush of terrestrial DOM during spring snowmelt (Boyer et al. 1997; Brooks et al. 1999). During peak snowmelt, lakes are unable to store the large amounts of water being delivered to them (Arp et al. 2006). Hence lake residence times are short and outflow stream chemistry may be very similar to that of lake inflows. In contrast, during baseflow conditions when water residence times and lake storage capacities are greater (Arp et al. 2006), DOM source and chemical characteristics of streams draining lakes may differ from that of lake inflows (Brown et al. 2008) because of autochthonous production and/or light exposure during in-lake retention (Biddanda and Cotner 2003; Frost et al. 2005). Thus, seasonal shifts in hydrology and DOM source pools may result in seasonal variability in DOM photodegradation (Amado et al. 2006; Suhett et al. 2007).

We hypothesized that the presence of lakes in mountain surface water networks changes the chemical character and bioavailability of DOM because longer water residence times enhance photodegradation, microbial processing and in-lake production of DOM. To test this hypothesis, we evaluated the effect of full spectrum and UVB light on DOM photodegradation in mountain lake inflows and outflows during snowmelt and baseflow conditions. Given that lake water retention increases UV exposure and previous UV exposure can decrease the capacity of DOM to photodegrade, we predicted that DOM photodegradation in lake inflows and outflows would be similar during spring
snowmelt but would be greater in lake inflows than in lake outflows during baseflow conditions. We then assessed how DOM photodegradation affects heterotrophic processing through the use of a field incubation and laboratory bioassay. We predicted that UV exposure would increase DOM quality in lake inflows given the ability of light exposure to degrade complex DOM, resulting in increased heterotrophic processing, while light exposure would have an opposite effect in lake outflows given the potential negative effects of UV on the bioavailability of algal-derived DOM.

Study Area

The Sawtooth Mountain Lake District (44°10’44” N, 114°55’34” W) forms the headwaters of the Upper Salmon and South Fork Payette Rivers and has many lakes in cirque basins at high elevation and behind moraine dams at lower elevations. Photodegradation experiments were conducted on four stream-lake systems (i.e., paired lake inflows and outflows) within the Sawtooth Mountain Lake District area: Alturas, Bull Trout, Pettit, and Stanley, with more intensive experiments at Bull Trout (Fig. 3.1, Table 3.1). These watersheds are designated or effectively wilderness areas with only limited recreational land use and low wet atmospheric nitrogen (N) deposition, ~1.0 kg ha\textsuperscript{-1} yr\textsuperscript{-1} (NADP 2001). The elevation of study sites ranges from 2000 to 2150 m, and the area is typically snow covered from November to May. The stream hydrographs are dominated by spring snowmelt. The Sawtooth Mountains are primarily granitic, and the dominant upland forest vegetation in this region is lodgepole pine (\textit{Pinus contorta}), while the riparian areas are dominated by sedges (\textit{Carex} sp.), willows (\textit{Salix} sp.) and grasses (Arp et al. 2006).
Methods

Photodegradation Experiments

To evaluate the effect of lakes and season on stream DOM photodegradation, we conducted UV breakdown experiments during 2008 spring snowmelt (June) and summer baseflow (August) from the four lake inflows and outflows described above. In order to minimize the effect of bacteria on DOM breakdown, water was filtered-sterilized with a 0.8/0.2-μm filter (AcroPak, Pall. Corp., Ann Arbor, MI, USA), pre-rinsed with 300 mL of sample water. Following filtration, 100 mL of the filtrate was placed into UV-transparent sterile Whirl-Pak (Nasco, Fort Atkinson, Wisconsin, USA) bags (3.75 x 7 cm) (Visser et al. 1999; Larson et al. 2007a). There were three replicate light and dark (aluminum foil covered bags) treatments for each lake position (i.e., inflow or outflow) and season.

To evaluate the importance of UVB on DOM photobreakdown, three additional replicates of both light and dark treatments from Bull Trout Lake inflow and outflow were placed in borosilicate biological oxygen demand (BOD) bottles. Borosilicate bottles do not allow for UVB transmission (Reche et al. 2000), which allowed us to evaluate the importance of UVB on DOM breakdown, by comparison with the full spectrum treatments above. UVB was measured hourly using a broadband UVB sensor (YMT, Interscience Technologies, Silver Spring, Maryland, USA). During both snowmelt and baseflow experiments, UVB levels peaked at the water surface around 14:00 h at 1.88 and 1.54 kJ m⁻², respectively.
Bags and BOD bottles were incubated just below the water surface (average of 1.7 and 2 cm depth, respectively) in a large inflatable pool, with running water to maintain a constant temperature (average 10.5°C), as well as to create a water current within the pool to keep bag contents mixed and to reduce self-shading. All experiments were conducted at the Stanley, ID field station and began at 09:00 h to maximize UV exposure. Samples from the snowmelt and baseflow experiments were collected after 52 and 56 h, respectively. Water samples in both experiments were exposed to sunlight for approximately 30 h. During the June snowmelt experiment, 3 replicate samples for each lake and location were also collected following 6 and 30 incubation h (approximately 6 and 20 h of sunlight exposure). At each sample collection, a 60 mL sub-sample was acidified with HCl to a pH <2 and stored in pre-ashed amber glass bottles.

Dissolved organic carbon (DOC) concentration was measured using wet persulfate oxidation (Menzel and Vacarro 1964). Loss in DOC concentration indicated photomineralization (i.e., the conversion of DOC to CO₂). SUVA<sub>254</sub> (specific ultraviolet absorbance) was evaluated at 254 nm and standardized by dividing by the respective DOC concentration (Weišhaar et al. 2003). SUVA<sub>254</sub> is an indicator of average UV absorbance and DOM aromaticity (Westerhoff et al. 1999). The loss of light-absorbing capacity, as measured with SUVA<sub>254</sub>, indicated photobleaching. Since there was no observed loss of DOC concentration during this experiment, photodegradation is simply a measure of photobleaching and was expressed as the % reduction in absorbance at 254 nm (%R) of samples exposed to light relative to dark controls.

One-way analysis of variance (ANOVA; JMP 7.0.1, SAS Institute, Cary, North Carolina, USA) was used to compare spatial (i.e., inflow and outflow) differences in %R
for each season independently (i.e., snowmelt and baseflow), as well as to evaluate seasonal changes (i.e., snowmelt vs. baseflow) in inflow and outflow %R. One-way ANOVA was also used to compare %R between full spectrum and no-UVB treatments in Bull Trout Lake inflow and outflow during snowmelt and baseflow conditions. During snowmelt, changes in mean photodegradation (%R) over time (6, 20, 30 h of sunlight exposure) was analyzed using a two-way full factorial ANOVA (position (lake inflow/outflow) was a categorical effect, while time was a continuous effect).

To evaluate the relationship between residence time and DOM photodegradation, we calculated lake area from digital hydrography layers (1:100,000) using ARC/INFO (Environmental Systems Research Institute, Inc., Redlands, California, USA). Lake area in the Sawtooth Mountains is highly correlated with lake volume measured bathymetrically. Lake volume was calculated using a lake area-volume regression developed from 12 lakes in the Sawtooth mountains with areas ranging from 0.04 to 6.15 km² following (Wurtsbaugh, unpublished data, $R^2=0.995, p<0.0001$):

$$\text{Log (Vol)} = -1.757 + 1.517 \text{Log (Area)}.$$

For baseflow conditions, assuming lake hydrologic steady state, maximum water residence time in each of the four lakes was calculated as:

$$\text{WRT} = \frac{V}{Q},$$

where WRT is water residence time within the lake, V is lake volume and Q is outflow discharge at the time of sample water collection (Table 3.1). Despite changing hydrologic state, retention times were estimated using the equation above for the June snowmelt experiment in order to illustrate the difference in lake residence times between experiments. During snowmelt runoff, lake volume increases. Thus, we calculated lake
volume during snowmelt as above, given a 12% increase in lake area, assuming an average water year (Arp et al. 2006). Outflow %R for both the snowmelt and baseflow experiments was regressed against WRT to evaluate the relationship between lake WRT and photodegradation.

**UV Effects on Microbial Processing**

**Field Experiment**

We hypothesized that together, UV exposure and presence of microbial communities would alter DOM characteristics and increase DOM bioavailability. To evaluate the effects of photodegradation, microbial processing and processing time on DOM characteristics, we conducted a two-month long field incubation of Bull Trout Lake inflow water, collected on 27 June 2007. Inflow water was used because that is the water being retained and acted upon in the lake. Treatments included 1) microbes present, prepared by filtering water through a pre-ashed (450°C for 2 h) 0.7-µm glass-fiber filter (Whatman GFF, Whatman International, Ltd., Maidstone, England); and 2) no microbes present, prepared by filter-sterilizing the water using a 0.2-µm nylon filter (Millipore, Bedford, Massachusetts, USA). Samples from both of the above treatments were exposed to natural sunlight (i.e., incubated in clear BOD bottles) or incubated in the dark as controls (i.e., foil-covered BOD bottles). Bottles containing water from each treatment were attached to a poly-vinyl chloride (PVC) rack 20 cm below the surface of Bull Trout Lake. Four replicates of each treatment were removed randomly after 12, 28 and 55 d, filtered with a 0.2-µm nylon filter (Millipore, Bedford, Massachusetts, USA),
and acidified to pH 2 using HPLC-grade HCl. Note that all nylon filters were pre-rinsed with double-deionized (DDI) water to minimize DOM leaching from the filter.

In order to evaluate changes in DOM quantity and quality (measured as aromaticity), DOC concentration and SUVA<sub>254</sub> were analyzed as above. To evaluate changes in the dissolved organic matter origin, fluorescence properties of three of the four replicates were measured using a multi-wavelength fluorescence spectrophotometer (Horiba Fluoromax, Carlsbad, California, USA). These data were used to calculate the fluorescence index (FI) as the ratio of emission intensities at 450 nm: 500 nm (both produced by excitation at 370 nm) following McKnight et al. (2001). Using this technique, terrestrial DOM from headwater streams and large rivers has values ranging from 1.4 to 1.5, while autochthonous DOM from lakes has values ranging from 1.6 to 1.9 (McKnight et al. 2001; Hood et al. 2003; Hood et al. 2005). Changes in DOM characteristics (SUVA<sub>254</sub> and FI) throughout the course of the experiment were analyzed using a general linear model incorporating light and microbial treatment as categorical explanatory factors, incubation days as a continuous explanatory factor, and all interactions among these three factors. SUVA<sub>254</sub> data were log transformed to better meet assumptions of normality and homogeneity of variance; assumptions of a linear relationship between log SUVA<sub>254</sub> and incubation days appeared adequate. No transformation was needed for FI data, as all assumptions appeared adequate. Alpha values were set at 0.10 due to the inherently high variability associated with bioassays.

Changes in DOC uptake over time were evaluated for light and dark treatments. %DOC loss was calculated on each sampling day using the no-microbe treatment as a control to account for losses due to photo-oxidation as:
%DOC Loss = (Mean[DOC]_{NM} – [DOC]_M)/ Mean[DOC]_{NM} x 100,

where NM is the no-microbe treatment and M is the microbe treatment. The effect of light and time on the %DOC loss was analyzed using a two-way full factorial model with light treatment and incubation days as categorical factors. Incubation days were used as a categorical factor because the relationship between mean %DOC loss and days was not linear.

**Laboratory Bioassay**

We hypothesized that during baseflow conditions photodegradation alone could increase DOM bioavailability and nutrient limitation of an inflow stream while having an opposite effect on a lake outflow stream. To evaluate the effects of photodegradation on carbon and nutrient uptake, we conducted a laboratory bioassay using lake inflow and outflow water that was exposed to full-spectrum sunlight for approximately 30 h, as well as dark controls, with half of the bioassay receiving nutrient amendments. Water was collected from Bull Trout Lake inflow and outflow on 1 August 2008, put on ice and returned to the field station, where it was filtered through pre-ashed (450°C for 2 h) Whatman GF/D filters (pore size = 2.7 µm, Whatman International, Ltd., Maidstone, England) to remove particulates from the water. Water was then filtered through a 0.2-µm nylon filter (Millipore, Bedford, Massachusetts, USA), pre-rinsed with 100 mL of DDI, to remove microbes. Inflow and outflow 0.2-µm filters with the collected bacteria were stored in DDI water to be used as inocula for the bioassay (Servais et al. 1987).

For both lake inflow and outflow filtrate, light and dark (i.e., foil covered) treatments were incubated in sterile polyethylene Whirl-Pak bags (19 x 30 cm) in the
pool, as above, for 52 h starting at 10:00 h. Following incubation, a 60 mL sample was collected from each water treatment and analyzed as above for DOC concentration and SUVA$_{254}$ in order to evaluate any changes in DOC quantity and quality due to sunlight exposure.

Upon returning to the laboratory, we set up a bioassay using a protocol similar to that presented by Servais et al. (1987). In brief, eight replicate 100 mL water samples, for each of the two locations and light treatments, were added to pre-ashed (450°C for 2 h) 125 mL Erlenmeyer flasks. Inflow and outflow microbes reserved from the filtration (above) were re-suspended in DDI water and added to the respective water source at a volume of 1% of the total volume. In order to evaluate the addition of DOC due to inoculum, inoculum was added to three replicate samples of DDI and the mean DOC concentration was subtracted from final DOC of the respective treatments at the end of the experiment. Four of the eight replicates were used as ambient-nutrient controls. Since biological immobilization in lakes is known to reduce inorganic nutrient concentration (Jansson et al. 1994; Brown et al. 2008), nutrients (+N (KNO$_3$, 0.2 mg N L$^{-1}$) +P (K$_2$PO$_4$, 0.03 mg P L$^{-1}$)) were added to the other four flasks to ensure that DOC consumption was not nutrient limited. Flasks were stored in the dark at 17°C and shaken for 26 d. At the end of the experiment, each flask was filtered with a pre-rinsed 0.2-µm nylon Millipore filter to remove microbes, acidified to a pH 2 and stored in amber glass bottles until analyzed for DOC, as above. DOC remaining at the end of the incubation period was deemed refractory (RDOC) and the difference between initial DOC and RDOC was considered to be biodegradable (BDOC) (Marmonier et al. 1995). BDOC is
presented as percent initial DOC (%BDOC) so as to standardize for initial DOC concentration.

We evaluated the utility of SUVA\textsubscript{254} as a quality indicator by regressing initial SUVA\textsubscript{254} values of the inflow and outflow streamwater against the %BDOC. We report %R for comparison between the field and laboratory experiment. We completed separate one-way ANOVAs for each lake position (i.e., inflow and outflow) to compare dark and light exposure effects on %BDOC in nutrient amended treatments only, in order to avoid differences in %BDOC due to nutrient limitation. Nutrient limitation was evaluated as the %BDOC response ratio and calculated as the log ratio of nutrient amended treatments divided by the mean of ambient controls, where the greater the ratio the greater the nutrient limitation (Tank and Dodds 2003). As above, we analyzed the effect of dark and light exposure on nutrient limitation for each lake position separately. Alpha values were set at 0.10 due to the inherently high variability associated with bioassays.

Results

Patterns of DOM Photodegradation

DOM photodegradation, measured as % reduction in absorbance at 254 nm (%R), which was used as an indicator of the loss of aromatic compounds, varied seasonally and with position relative to lakes. During spring snowmelt (June) the %R was similar between lake inflows and outflows (ANOVA, F\textsubscript{1,6}=0.21, p=0.67), averaging ca. 18% (Fig. 3.2). However, during August baseflow conditions, outflow %R was approximately half that of the inflow (ANOVA, F\textsubscript{1,6}=7.49, p=0.034). Inflow %R did not differ between spring runoff and baseflow conditions (ANOVA, F\textsubscript{1,6}=1.58, p=0.25). In contrast, outflow
%R differed seasonally, such that %R measured during spring snowmelt was approximately 1.5X higher than during summer baseflow (ANOVA, \( F_{1,6} = 7.58, p=0.033 \)). During summer baseflow, there was an inverse relationship \( (y=-2.6948x + 18.77, R^2=0.84, p=0.0014) \) between lake water residence time (Table 3.1) and outflow %R (Table 3.2).

DOM photodegradation during snowmelt varied with incubation time. During the snowmelt experiment, there was no significant interaction between position (i.e., inflow and outflow) and incubation time \( (F_{1,1}=0.012, p=0.91, \text{Fig. 3.3}) \), but there were significant main effects of both lake position and incubation time \( (F_{1,1}=6.69, p=0.015 \text{ and } F_{1,1}=90.6, p<.0001, \text{respectively}) \). %R was 8X greater in inflows than outflows after 6 h of sunlight exposure \( (\text{ANOVA}, F_{1,6}=7.79, p=0.032, \text{Fig. 3.3}) \). However, after 20 and 30 h of sunlight exposure there was no significant difference between inflows and outflows \( (\text{ANOVA} F_{1,6} = 3.4, p=0.11 \text{ and } F_{1,6}= 0.21, p=0.66, \text{respectively}) \).

The effect of UVB on DOM characteristics varied both spatially and temporally for Bull Trout Lake inflow and outflow. Differences between the full and no-UVB treatment ranged from -0.2 to 26.4% (Table 3.3). During snowmelt, the % reduction in UV absorbance (%R) for Bull Trout Lake inflow in the full spectrum treatment was 11.8% and was not significantly different than the no-UVB treatment \( (\text{ANOVA}, F_{1,4}=0.03, p=0.95) \). Conversely, during snowmelt, outflow %R was 1.5X greater in the full-spectrum treatment than the no-UVB treatment \( (\text{ANOVA}, F_{1,4}=21.1, p=0.01) \). During baseflow, %R of the no-UVB treatments was significantly lower than those of the full spectrum treatments for both inflow and outflow \( (\text{ANOVA}, F_{1,4}=204.1, p=<0.0001 \text{ and } F_{1,4}=16.3, p=0.016, \text{respectively}) \).
Effect of Photodegradation on Microbial Activity

Field Experiment

Exposure to light (PAR and UVA) increased DOM quality as indicated by a decline in SUVA$_{254}$, regardless of whether or not microbes were present (Fig. 3.4A; $F_{1,1}$=47.2, $p<0.0001$). After 55 d of incubation, SUVA$_{254}$ decreased in both light treatments from 0.019 to 0.011 (L mg$^{-1}$ C cm$^{-1}$) (Fig. 3.4A). There was a significant interaction between time and light treatment ($F_{1,1}$=4.0, $p=0.052$) and a significant effect of time alone ($F_{1,1}$=3.8, $p=0.058$) on SUVA$_{254}$ values, which were driven by a decrease in SUVA$_{254}$ following light exposure (Fig. 3.4A). There was no significant three-way interaction among light, microbial presence and time ($F_{1,1}$=0.04, $p=0.83$), no significant interaction between time and microbial presence ($F_{1,1}$=0.004, $p=0.95$) and no significant effect of microbial presence alone ($F_{1,1}$=0.33, $p=0.57$) on SUVA$_{254}$ values.

While changes in FI were not as dramatic as changes in SUVA$_{254}$, FI increased in the presence of light and microbial communities. There was a significant interaction between light and microbial treatment ($F_{1,1}$=4.0, $p=0.058$), which resulted from an increase in FI in the light/microbe treatment over the two-month experimental period (Fig. 3.4B). In that treatment, FI increased from 1.5 at the start of the experiment to 1.65 at the end (Fig. 3.4B). There were no significant interactions or main effects of light or microbes over time on FI (ANOVA, $F_{7,24}=1.6$, $p=0.19$).

In addition to DOC characteristics (i.e., SUVA$_{254}$ and FI) changing over time, we also found that DOC quantity significantly decreased over time in the light/microbe treatment (ranging from 14.6% loss after 12 d to 37% loss after 55-d incubation) relative
to no-microbe controls (ANOVA, $F_{5,15}=9.6, p=0.0003$; Table 3.4). In fact, dark treatments did not exhibit any DOC loss attributed to microbes. There was no significant interaction between incubation days and light treatment ($F_{2,2}=1.9, p=0.19$).

**Laboratory Bioassay**

Data from the laboratory bioassay support our hypothesis that photodegradation increases DOM bioavailability in lake inflows, but did not support our hypothesis that photodegradation decreases DOM bioavailability in lake outflows. Similar to the August Bull Trout Lake photodegradation field experiment (Table 3.3), for the laboratory bioassay we observed a decrease in the ability of lake inflow and outflow DOM to absorb light at 254 nm following UV exposure (Table 3.5), and the %R (% reduction in absorbance at 254 nm) was 33.3% and 16.7% in Bull Trout Lake inflow and outflow, respectively. Similar to the %R, inflow and outflow SUVA$_{254}$ values decreased by 42 and 15%, respectively, following light exposure (Table 3.5). %BDOC was negatively related to the quality metric SUVA$_{254}$ ($R^2=0.59$; Fig. 3.5), and lake inflow and outflow nutrient-amended %BDOC was 53.0 and 20.3% greater in photodegraded water relative to dark controls ($F_{1,6}=18.3, p=0.0052$ and $F_{1,6}=17.6, p=0.0057$, respectively; Table 3.5).

When we compared the %BDOC in ambient (non-nutrient amended) controls to the %BDOC in nutrient amended treatments, our bioassay results also showed that DOM utilization by native microbes is limited by inorganic nutrients. In dark controls, addition of nutrients increased the %BDOC response ratio in the outflow, but not the inflow (Table 3.5). In both inflow and outflow streamwater, nutrient addition significantly
increased the %BDOC response ratio by 8 and 11% following light exposure (ANOVA, $F_{1,6} = 7.6, p=0.03$ and $F_{1,6} = 4.0, p=0.09$, inflow and outflow, respectively, Table 3.5).

Discussion

Our results support the hypothesis that the presence of lakes in mountain surface water networks changes the chemical character and bioavailability of DOM because longer water residence times enhance photodegradation of DOM. First, we showed that DOM photodegradation varied both temporally and spatially. Seasonal differences in DOM photodegradation were explained by lake water residence time. Spatial differences resulted from lake presence within fluvial networks during baseflow, with DOM from lake outflows being more resistant to photodegradation than DOM from lake inflows. Second, during the field incubation photodegradation of lake inflow water resulted in changes in DOM chemical character as reduction in SUVA$_{254}$ and an increase in the fluorescence index (FI). Finally photodegradation of DOM increased its bioavailability to heterotrophic microbes as measured by a bioassay.

Patterns of DOM Photodegradation

Our results indicate that during spring snowmelt, inflow and outflow DOM photodegradation was similar. The similarities observed between inflows and outflows during snowmelt likely result because lakes in this region are incapable of storing the large inputs of water received during peak snowmelt runoff (Arp et al. 2006), therefore DOM characteristics should be similar between lake inflows and outflows (K. J.
Goodman unpubl.); our estimates of water residence time during snowmelt support this assertion.

Contrary to results from spring snowmelt, during August baseflow conditions when lake water residence time is longer, DOM from lake outflows was more resistant to UV than was the DOM from lake inflows. Seasonal changes in DOM photodegradation, as measured by photo-oxidation, have been observed in both humic (Lindell et al. 2000; Suhett et al. 2007) and non-humic, clearwater systems (Lindell et al. 2000; Amado et al. 2006), and the magnitude of photodegradation is thought to be related to DOM origin, humic content and previous light exposure (Lindell et al. 2000). Despite the fact that lake outflows in our study area have a higher DOC content, the DOM is less photodegradable than that of lake inflows during summer baseflow. Lindell et al. (2000) hypothesized that lake water residence time is likely an indirect factor controlling DOM photodegradation in low humic systems, since larger lakes have greater water residence times and therefore longer exposure to natural sunlight. Our results support this hypothesis, as we found an inverse relationship between lake water residence time and the ability of outflow stream DOM to photodegrade during baseflow conditions.

Although no DOC loss was observed during the short-term photodegradation experiments, photo-oxidation (i.e., the oxidation of DOC to CO₂) may still be occurring in the Sawtooth Mountain lakes. DOC loss measurements are less precise and therefore, harder to measure accurately than DIC production (which we did not measure). Lindell et al. (2000) measured DIC production in a low humic lake, despite no observed loss in DOC concentration. Additionally, we observed a decrease in streamwater absorbance
from all lake inflows and outflows following light exposure, which has been shown to be related to DIC production (Graneli et al. 1998).

High elevation aquatic systems are thought to be highly susceptible to the effects of UVB (Morris et al. 1995), which is the range of wavelengths considered to be the predominant cause of photodegradation (Kieber et al. 1990; Herndl et al. 1993). Therefore, we expected to observe large UVB effects in both Bull Trout Lake inflow and outflow streams. Our results showed that UVB had a large effect on Bull Trout Lake inflow and outflow during August baseflow and Bull Trout Lake outflow during spring snowmelt. However, we observed no effect of UVB on DOM photobreakdown in Bull Trout inflow during spring snowmelt. Lindell et al. (2000) found UVA to have a greater affect than UVB in both a humic (74%) and a non-humic (57%) lake, indicating that terrestrial, humic material found in aquatic systems is more susceptible to UVA than UVB. Therefore, during snowmelt, a time of high connectivity between streams and the surrounding terrestrial landscape (Boyer et al. 1997; Brooks et al. 1999), it is not surprising that we did not see an effect of UVB on inflow stream DOM photodegradation.

**Photodegradation Alters DOM Chemical Characteristics**

Results of the long-term field incubation indicate that photodegradation changes DOM quality as indicated by a decrease in SUVA$_{254}$ (i.e., aromaticity) (Westerhoff et al. 1999) and increasing aquatically derived DOM (McKnight et al. 2001). On the contrary, we observed no change in SUVA$_{254}$ in the dark/microbe treatment throughout the 55 d of incubation. Although bacterial activity has been shown to be an important pathway of
DOM degradation (Wiegner and Seitzinger 2001; Amado et al. 2006), heterotrophic microbial communities alone did not significantly alter the DOM characteristics measured in our study, suggesting that UV photodegradation of DOM is an important step in heterotrophic carbon processing in oligotrophic mountain systems. Amado et al. (2006) found that bacterial degradation was an important pathway for autochthonous carbon degradation, while photodegradation played a larger role in allochthonous DOM degradation. The sample water used for this experiment was collected from Bull Trout inflow in a forested location during late spring and may have been too recalcitrant (i.e., composed of complex allochthonous compounds) for heterotrophs to degrade (Tranvik 1998) in the absence of photodegradation (Moran and Zepp 1997; Bertilsson and Tranvik 1998).

Light exposure increased carbon uptake by heterotrophic bacteria in the field experiment, as determined by increased carbon loss in the microbe treatment relative to the non-microbe treatment. In addition to DOM photodegradation in the light/microbe treatment, autochthonous production may have played a role in creating high quality DOM (Kaplan and Newbold 2003). Hence, the increase in BDOC we observed may be a result of the tight coupling of algae and bacteria in nutrient-poor stream systems (Rier and Stevenson 2002; Scott et al. 2008), as well as an increase in the DOM lability following photodegradation (Moran and Zepp 1997; Bertilsson and Tranvik 1998). Consequently, the observed increase in FI (i.e., and increase in aquatically derived source material) in the light/microbe treatment may be a result of an increase in both heterotrophic and autotrophic DOM production and processing (McKnight et al. 2001; Hood et al. 2005).
Photodegradation Increases DOM Bioavailability

The laboratory DOC bioassay further illustrates that DOM photodegradation increases heterotrophic processing. Our results indicate that exposure to full spectrum sunlight decreased the inflow and outflow DOM aromaticity (as measured by SUVA\textsubscript{254}) and significantly increased both inflow and outflow %BDOC in nutrient amended treatments.

Surprisingly, we observed no difference between inflow and outflow streamwater %BDOC that was not exposed to sunlight. This result may be due to several factors. SUVA\textsubscript{254} values were higher in Bull Trout outflow than inflow, indicating more aromatic DOM in the outflow (Weishaar et al. 2003). The increase in DOM aromaticity may due to macrophyte DOM inputs from Bull Trout Lake, which occur during late summer (Carpenter 1980; K. J. Goodman, unpubl.). DOM bioavailability is influenced by inorganic nutrient availability and temperature (del Giorgio and Davis 2003). We added nutrients in order to reduce nutrient limitation and our experiment was run at 17°C. This temperature is similar to the mean temperature of Bull Trout Lake outflow, but approximately 10°C warmer than Bull Trout Lake inflow (Marcarelli and Wurtsbaugh 2006); thus incubation temperature may have increased inflow microbial activity (Webster and Benfield 1986). However, given the long term duration of this study, we assume that the remaining DOC is refractory (Marmonier et al. 1995), therefore, an increase in activity should have no effect on the final proportion of refractory DOC.

Both the %R and the %BDOC for the laboratory experiment were 2 and 1.4 times greater, respectively, in Bull Trout Lake inflow than the lake outflow following light
exposure. Thus, a greater change in aromaticity resulted in a greater %BDOC. The greater % change in aromaticity of inflow DOM is likely a result of the terrestrial nature of headwater stream DOM (Vannote et al. 1980), as complex terrestrial compounds are more photodegradable than simple compounds (Moran and Covert 2003), resulting in higher quality carbon for heterotrophic uptake (Wetzel et al. 1995; Moran and Zepp 1997; Tranvik and Bertilsson 2001). In addition to photoproduction of labile DOM, DOM photodegradation can also provide a source of bioavailable N in N-limited systems by releasing NH$_4^+$, amino acids (Bushaw et al. 1996; Vahatalo and Zepp 2005) or NO$_3^-$ (Wiegner and Seitzinger 2001). Inorganic nutrient production has been shown to stimulate microbial DOC uptake (Smith and Benner 2005) and may have aided to the observed increase in %BDOC following light exposure.

We predicted that lake outflow DOM bioavailability would decrease following UV exposure, as UV exposure of labile DOM has been shown to have a negative effect on bacterial productivity in a few marine (Benner and Biddanda 1998; Obernosterer et al. 1999; Obernosterer et al. 2001) and freshwater (Tranvik and Bertilsson 2001) studies. However, we observed an increase in %BDOC of outflow streamwater following light exposure. This observed increase in bioavailability is likely due to the fact that these are extremely oligotrophic waters with mean epilimnetic chlorophyll $a$ values <1 µg L$^{-1}$ (Budy et al. 1995), as well as the abundance of macrophytes in Bull Trout Lake (D. Epstein pers comm.). Regardless of DOM origin, in oligotrophic systems (both humic and clearwater) a positive relationship had been found between UV irradiated DOM and bacterial growth (Tranvik and Bertilsson 2001). Amado et al. (2006) also found UV to have no negative effect on bacterial uptake of already labile DOM in a clear-water
Amazonian stream. We could find no other evidence in the literature showing that photodegradation changes DOM bioavailability in oligotrophic streams.

Heterotrophic nutrient limitation, as measured as a response relative to the control (Tank and Dodds 2003), differed spatially between inflow and outflow streams at Bull Trout. In the absence of light, the lake outflow expressed nutrient limitation, while the lake inflow did not. This result is not surprising since in general, lakes are known to be sinks for inorganic nutrients (Jansson et al. 1994) and lakes in this region are no exception (Brown et al. 2008).

Light exposure increased %BDOC and nutrient limitation in both the lake inflow and outflow. Interestingly, unlike dark controls, lake inflow water expressed nutrient limitation following light exposure, indicating that an increase in DOC lability following light exposure created a nutrient limitation. Rier and Stevenson (2002) and Olapade and Leff (2006) observed bacteria in oligotrophic streams to be both limited by organic carbon quality and inorganic nutrients. Our results support their findings that heterotrophic microbes in oligotrophic mountain streams may be limited by both nutrient availability and bioavailable DOC and further illustrates that increasing DOC bioavailability may exacerbate nutrient limitation in nutrient-poor aquatic ecosystems.

Conclusions

To our knowledge, no previous studies have addressed how lakes alter the immediate downstream chemical properties of DOM and affect biological DOM processing. The presence of lakes in fluvial networks can alter DOM characteristics and decrease stream DOM resistance to photodegradation, and these changes are strongly
related to DOM source, sunlight exposure and water residence time. Since photodegradation can increase DOM bioavailability, lakes within fluvial networks may lead to seasonal variability in heterotrophic processing as water residence times and UV exposure vary. Water residence time and clarity (i.e., light penetration) in subalpine stream-lake systems are important for organic matter degradation and processing in these systems, providing biologically available DOM to lake outflows and potentially increasing both carbon and nutrient uptake.

References


Table 3.1. Physical characteristics of four study lakes and their associated watersheds in the Sawtooth Mountain Lake District, central Idaho, USA during 2008. Q is discharge at the time of water collection for snowmelt and baseflow 2008 experiments. Water residence time (WRT) is calculated as lake volume/Q. Snowmelt WRT was estimated assuming a 12% increase in lake area.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Watershed Area (km²)*</th>
<th>Forest Cover (%)*</th>
<th>Lake Area (km²)</th>
<th>Volume (km³)</th>
<th>Snowmelt Outlet Q (m³ s⁻¹)</th>
<th>Snowmelt Outlet WRT (yrs)</th>
<th>Baseflow Outlet Q (m³ s⁻¹)</th>
<th>Baseflow Outlet WRT (yrs)</th>
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<td>3.34</td>
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<td>0.014</td>
<td>3.53</td>
<td>0.15</td>
<td>0.71</td>
<td>0.63</td>
</tr>
</tbody>
</table>

* data from Brown et al. (2008)
Table 3.2. Summary of dissolved organic matter characteristics from four lake inflows and outflows during snowmelt (June) and baseflow (August) 2008. DOC is dissolved organic carbon concentration (mg L\(^{-1}\)), A is absorbance at 254 nm, %R is reduction in absorbance as percent of dark control after 30 h of sunlight incubation. Data are presented as mean ± SE.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Location</th>
<th>Snowmelt DOC (mg C L(^{-1}))</th>
<th>Snowmelt A (cm(^{-1}))</th>
<th>Snowmelt %R</th>
<th>Baseflow DOC (mg C L(^{-1}))</th>
<th>Baseflow A (cm(^{-1}))</th>
<th>Baseflow %R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alturas</td>
<td>Inflow</td>
<td>1.27</td>
<td>0.039</td>
<td>20.0 ±1.7</td>
<td>0.75</td>
<td>0.017</td>
<td>27.0 ±0.0</td>
</tr>
<tr>
<td>Alturas</td>
<td>Outflow</td>
<td>1.21</td>
<td>0.034</td>
<td>17.4 ±1.1</td>
<td>1.27</td>
<td>0.023</td>
<td>12.3 ±0.0</td>
</tr>
<tr>
<td>Bull Trout</td>
<td>Inflow</td>
<td>1.12</td>
<td>0.034</td>
<td>11.8 ±2.1</td>
<td>0.64</td>
<td>0.007</td>
<td>35.7 ±0.0</td>
</tr>
<tr>
<td>Bull Trout</td>
<td>Outflow</td>
<td>1.78</td>
<td>0.059</td>
<td>18.9 ±0.0</td>
<td>1.45</td>
<td>0.024</td>
<td>17.5 ±1.6</td>
</tr>
<tr>
<td>Pettit</td>
<td>Inflow</td>
<td>1.18</td>
<td>0.033</td>
<td>28.0 ±1.1</td>
<td>0.66</td>
<td>0.014</td>
<td>33.3 ±3.3</td>
</tr>
<tr>
<td>Pettit</td>
<td>Outflow</td>
<td>1.56</td>
<td>0.024</td>
<td>18.9 ±1.9</td>
<td>1.45</td>
<td>0.019</td>
<td>7.6 ±2.9</td>
</tr>
<tr>
<td>Stanley</td>
<td>Inflow</td>
<td>0.92</td>
<td>0.025</td>
<td>20.0 ±1.4</td>
<td>0.47</td>
<td>0.008</td>
<td>13.6 ±4.5</td>
</tr>
<tr>
<td>Stanley</td>
<td>Outflow</td>
<td>1.50</td>
<td>0.048</td>
<td>18.6 ±1.2</td>
<td>1.14</td>
<td>0.022</td>
<td>13.6 ±0.0</td>
</tr>
</tbody>
</table>
Table 3.3. Effects of full-spectrum sunlight and no-UVB sunlight on DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) after 30 h exposure to radiation. DOM source waters were collected from the inflow and outflow of Bull Trout Lake, central Idaho, USA during snowmelt (June) and baseflow (August). Data are means ±SE of three samples; significant differences (ANOVA df =1,4  p<0.02) between radiation treatments are indicated by *.

<table>
<thead>
<tr>
<th></th>
<th>Snowmelt</th>
<th>Baseflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full</td>
<td>No UVB</td>
</tr>
<tr>
<td>Inflow</td>
<td>11.8 ±2.1</td>
<td>12.0 ±2.0</td>
</tr>
<tr>
<td>Outflow</td>
<td>18.9 ±0</td>
<td>13.1 ±1.4*</td>
</tr>
</tbody>
</table>
Table 3.4. Effect of microbes and light exposure on dissolved organic carbon (DOC) loss during 55-d incubation of inflow water in Bull Trout Lake. DOC loss due to microbes was calculated as the percent difference between sterilized (no-microbe) and microbe treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Days</th>
<th>12</th>
<th>28</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light</td>
<td>12</td>
<td>14.6 ±2.5</td>
<td>29.4 ±6.3</td>
<td>37.0 ±5.5</td>
</tr>
<tr>
<td>Dark</td>
<td>-1.2 ±8.7</td>
<td>-1.2 ±3.6</td>
<td>-2.0 ±6.7</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.5. DOM quantity (as dissolved organic carbon, DOC), Absorbance (A) at 254 nm, quality as specific ultra violet absorbance at 254 nm (SUVA$_{254}$), and bioavailability (%BDOC) under ambient nutrients and nutrient-amended conditions. DOM quality and quantity are reported as initial conditions (±0.038 mg C L$^{-1}$ analytical error), and bioavailability is reported as mean ±SE of four replicate bioassays. %BDOC nutrient response is calculated as the log$_{10}$ (+ nutrient %BDOC/ mean control %BDOC).

<table>
<thead>
<tr>
<th>Position</th>
<th>UV Treatment</th>
<th>Initial DOC (mg C L$^{-1}$)</th>
<th>A (cm$^{-1}$)</th>
<th>SUVA$_{254}$ (L mg$^{-1}$ C cm$^{-1}$)</th>
<th>Ambient %BDOC</th>
<th>+Nutrient %BDOC</th>
<th>Nutrient Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow</td>
<td>Dark</td>
<td>0.513</td>
<td>0.006</td>
<td>0.012</td>
<td>48.25 ± 3.1</td>
<td>41.91 ± 4.7</td>
<td>-0.07 ± 0.05</td>
</tr>
<tr>
<td>Inflow</td>
<td>Light</td>
<td>0.576</td>
<td>0.004</td>
<td>0.007</td>
<td>53.76 ± 2.9</td>
<td>64.11 ± 2.1</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>Outflow</td>
<td>Dark</td>
<td>1.185</td>
<td>0.020</td>
<td>0.020</td>
<td>31.58 ± 1.8</td>
<td>37.61 ± 1.6</td>
<td>0.07 ± 0.02</td>
</tr>
<tr>
<td>Outflow</td>
<td>Light</td>
<td>1.210</td>
<td>0.017</td>
<td>0.017</td>
<td>34.64 ± 1.5</td>
<td>45.23 ± 0.8</td>
<td>0.11 ± 0.01</td>
</tr>
</tbody>
</table>
Figure 3.1. Map of study area in the Sawtooth Mountain Lake District (44° 89’ 10” N, 114° 56’ W), central Idaho, USA. Samples for DOM characterization were collected above and below four study lakes: Stanley (A), Bull Trout (B, as inset 30 miles NW of Stanley Lake), Pettit (C), and Alturas (D).
Figure 3.2. Seasonal variation in DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) after 30 h exposure to sunlight. Individual bars are means ± 1 SE of samples collected from four lake inflows and outflows of the Sawtooth Mountain Lake District, central Idaho, USA. Capital letters represent a position effect; lower case letters represent a time effect. Bars with different letters are significantly different (ANOVA, df=1,6, p<0.04).
Figure 3.3. DOM photodegradation (measured as % reduction in absorbance at 254 nm, %R) as a function of sunlight exposure time for samples collected from four lake inflows and outflows during snowmelt. Individual bars are mean ± 1SE. Mean %R was significantly higher for inflow samples at 6 h incubation (ANOVA, df =1,6, p=0.032).
Figure 3.4. Temporal changes in A) SUVA at 254 nm and B) Fluorescence Index (FI) during a 55-d incubation of Bull Trout inflow stream water in Bull Trout Lake throughout the summer of 2007. A FI of ~1.7 is associated with aquatically derived DOM and an FI of ~1.5 is associated with terrestrially derived DOM (McKnight et al. 2001). Data are means ±1E for four SUVA and three FI samples.
Figure 3.5. Relationship between DOC-Specific Ultraviolet Absorbance at 254 nm (SUVA$_{254}$) and % preincubation bioavailable DOC (%BDOC) for light treated (white symbols) and dark control (black symbols) streamwater from Bull Trout Lake inflow (diamonds) and outflow (squares).
CHAPTER 4
PREDICTING THE EFFECTS OF ENVIRONMENTAL CHANGE ON AN OLIGOTROPHIC SUBALPINE LAKE: BULL TROUT LAKE, BOISE NATIONAL FOREST, IDAHO\textsuperscript{1,2}

Abstract

Environmental changes, resulting from increases in global air temperatures, changes in atmospheric circulations and weather patterns, and increases in atmospheric nitrogen (N) deposition are affecting even the most remote and protected areas, including the high-elevation mountain ecosystems of the Intermountain West. Little is known about how these sensitive ecosystems will respond to future environmental changes. We used LAKE2K, a one-dimensional, stratified lake model, to predict the effects of increases in air temperature, advances in the snowmelt hydrograph timing, declines in snowmelt flows and increases in N deposition on the hydrology and biogeochemistry of a subalpine lake (Bull Trout Lake) in the Sawtooth Mountains, central Idaho. Given that lakes can store water and nutrients, we hypothesized that lakes may act as buffers to environmental change. Our model results indicated that the magnitude and timing of snowmelt runoff will have the greatest effect on water and nutrient exports from this subalpine lake. Furthermore, changes in the duration of baseflow (i.e., longer lake water residence times) altered lake biogeochemistry and resulted in an increase of inorganic N exports from mountain lakes. In phosphorus (P) limited lakes, increases in lake inorganic N concentrations and exports are likely to occur with increases in temperatures and lake

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\textsuperscript{2} Coauthored by KJ Goodman, DE Epstein, and BT Neilson.
water residence times. Increases in atmospheric N deposition will further enhance inorganic N export if P limits autotrophic production.

Introduction

Even the most remote and protected areas are being affected by changes occurring at a global scale, such as global climate change, altered weather patterns, and increased atmospheric deposition (Galloway et al. 2004; IPCC 2007). Alpine and subalpine aquatic ecosystems may be among the most sensitive to changes in climate and nutrient loading due to the inherent characteristics of the surrounding landscapes (e.g., high proportion of barren land, rapid hydrologic flushing rates and limited vegetation and soil development) (Baron et al. 1991; Baron et al. 2009). Environmental changes (i.e., alterations in hydrologic patterns and nutrient availability, as well as air temperature) may also have pronounced effects on the hydrology and biogeochemistry of the aquatic systems within these sensitive high-elevation ecosystems (Williams et al. 1996a). However, few studies have addressed how high-elevation aquatic systems will respond to future changes, and even fewer studies have evaluated how an interaction of these environmental changes may magnify these individual physical and chemical influences.

While many areas of the Intermountain West are not directly affected by human activities, they may be indirectly affected by large-scale environmental changes occurring on regional and global scales. Global climate change predictions indicate a mean temperature increase of 1 to 2°C in these mountain areas over the next 100 years (IPCC 2007). Elevated winter and spring temperature and altered atmospheric circulations may decrease snowpack by 10 to 30% in the Intermountain West (Jin et al. 2006), which may
alter terrestrial nutrient cycling under winter snowpack (Monson et al. 2006) and advance the timing of spring runoff (Hamlet et al. 2007; Stewart et al. 2004). Changes in the timing and magnitude of snowmelt runoff, as well as in the mass of nutrients associated with this runoff, will likely affect nutrient exports during high flows and biogeochemical cycling during the clear-water phase (i.e., low flows) (Droscher et al. 2009). Thus, increases in air temperature may have significant indirect effects on water and nutrient dynamics in these sensitive aquatic systems.

In addition to changes in climate, human activities (i.e., fossil fuel burning, agricultural fertilizers, urbanization) across the globe have increased the rate of reactive nitrogen (N) supplied to the atmosphere 2-fold (Vitousek 1994), resulting in terrestrial N saturation in many regions (Aber et al. 1998). As a consequence of N saturation in terrestrial systems, terrestrial N export to aquatic systems has increased (Aber et al. 1998), which affects nutrient and organic matter pool sizes and process rates (Clair et al. 1999; Grimm et al. 2003; Manabe et al. 2004).

Although the Intermountain West receives lower rates of N deposition than many other regions of the United States (NADP 2001), high-elevation mountain systems may be particularly vulnerable to increases in N deposition. In fact, the Colorado Front Range may already be exhibiting signs of N saturation (Williams et al. 1996b; Williams and Tonnessen 2000). The Colorado Front Range receives 4 to 6 kg N ha\(^{-1}\) yr\(^{-1}\) wet plus dry atmospheric deposition, which is greater than any other area of the Intermountain West (Burns 2004). Increased N deposition in the Front Range has been linked to altered terrestrial foliage stoichiometry (Rueth and Baron 2002; Williams et al. 1996b), shifts in plant species composition and decreases in species richness (Bowman et al. 1993). In
addition to alterations across the terrestrial landscape, this increase in N deposition has been linked to increased N concentrations in high-elevation lakes (Baron et al. 2000) and shifts in lake biological community biomass and composition (Baron et al. 2000; Wolfe et al. 2001).

The response of the Front Range ecosystem to N deposition has received considerable attention. However, less research has been done in other high-elevation areas of the Intermountain West, which are predicted to be impacted by N deposition in the future (Burns 2004). Increases in N deposition may have a considerable effect on these high elevation ecosystems, as terrestrial systems in alpine and subalpine systems have a low capacity to attenuate nutrients due to the high proportion of barren land and shallow soil (Little et al. 2008). Additionally, the short growing season typical of these ecoregions limits the potential for N uptake, therefore leaving N stocks within soils (Edwards et al. 2007). Increased N deposition may result in increased N concentrations in runoff and groundwater (Campbell et al. 2000; Stottlemyer 1997), and thus, increased N delivery to aquatic ecosystems.

Concerns regarding the effect of increased N supply on water quality has lead to a greater focus on the importance of headwater streams (Mulholland et al. 2000; Peterson et al. 2001), as well as the hyporheic zone (Valett et al. 1996), in processing and retaining N and thereby decreasing N export downstream. Lakes may also serve to retain N within stream-lake systems and decrease N export, yet have received less attention (but see Kling et al. 2000; Saunders and Kalff 2001). In many mountain landscapes, aquatic networks are comprised of complex linkages between streams and lakes (Meybeck 1995). Since lakes have the capacity to store water and nutrients (Kaste et al. 2003), mountain
lakes may be key integrators of environmental changes occurring across the watershed and may act to dampen the impact of these changes to downstream ecosystems through material storage and processing (Goodman et al. in review; Ito et al. 2007; Kaste et al. 2003; Kling et al. 2000).

Here we present a case study for Bull Trout Lake (BTL), Boise National Forest, Idaho. We combine water quality monitoring data with a modeling framework to address how a changing environment may alter the hydrology and biogeochemistry of an oligotrophic mountain lake. The objectives of this research were 1) to populate and calibrate a water quality model for a subalpine lake and 2) to evaluate how high-elevation lakes may respond to increases in air temperature, decreases in the magnitude of snowmelt flows, advances in snowmelt, and/or increases in atmospheric N deposition. We focused on epilimnetic temperatures, Chlorophyll a (Chl a), dissolved organic carbon (DOC), total N and phosphorus (TN and TP) concentrations, as well as fluxes of water and nutrients (e.g., TN and TP, DOC, organic N, and inorganic N (NH$_4^+$ and NO$_3^-$) and P (PO$_4^{3-}$)) out of the lake. We limited our evaluation to the epilimnion, since in these subalpine systems the majority of water is routed through the epilimnion between times of lake turnover, and the lake outflow is fed by the epilimnion. Thus, epilimnetic water quality (i.e., chemistry) combined with outflow discharge will be the best predictor of nutrient fluxes out of BTL.
Study Site

Bull Trout Lake is located in the Boise National Forest, just northwest of the Sawtooth National Recreation Area, central Idaho (44° 17’ 58” N, 115° 15’ 16” W), and forms the headwaters of the South Fork Payette River. Bull Trout Lake is a 0.29 km$^2$ moraine-dammed lake at 2118 m elevation, which drains a 10.3 km$^2$ glaciated watershed. Mean lake depth is 4.3 m with a maximum depth of 15 m. Mean secchi depth during baseflow is 6.5 m. Lake water residence time ranges from 7 to 180 days, from peak spring snowmelt to summer baseflow, respectively (Goodman et al. in review). Bull Trout Lake is a dimictic lake, and in 2008, the lake was completely mixed by late May and again in early October.

Bull Trout Lake watershed uplands are comprised of Cretaceous granodiorite from the Idaho Batholith, while the valley bottom consists of till, alluvium and colluvium from the Pleistocene and Holocene (Kiilsgaard et al. 2003). Directly upstream of BTL inlet is a 15 ha, sand-gravel delta consisting of fine-grained sediment deposits (Kiilsgaard et al. 2003). Bull Trout Lake watershed is 99.9% vegetated; uplands of this subalpine watershed are dominated by lodgepole pine (Pinus contorta), and riparian areas are dominated by willows (Salix sp.), sedges (Carex sp.) and grasses (Arp et al. 2006).

Bull Trout Lake inflow is a low-gradient (0.003 to 0.007 m m$^{-1}$) second-order, gravel-bed stream (Arp et al. 2006). Bull Trout Lake outflow, is a wide (approximately 12.7 m), slow-moving stream (Arp et al. 2006). The stream hydrographs are dominated by spring snowmelt, and the area is typically snow covered from mid-November to late-May or early-June.
Bull Trout Lake watershed is relatively pristine with only limited recreational land use and low wet atmospheric N deposition, ~1.0 kg ha\(^{-1}\) yr\(^{-1}\) (NADP 2001). Bull Trout Lake watershed has low nutrient concentrations and primary production is co-limited by N and P availability (Wurtsbaugh et al. 1997).

Methods

Data Collection

Hydrologic and Meteorologic Data

We measured stream discharge (Q) weekly, using a flow meter and top-setting wading rod (Flo-mate 2000, Marsh-McBirney Inc., Frederick MD) and stream stage was measured hourly using capacitance rods (Tru-Track, Inc., Christchurch, New Zealand) from April 2007 through October 2008 for both the BTL inflow and outflow. Inflow and outflow gauging stations were located approximately 56 and 556 stream meters upstream and downstream of BTL, respectively. We developed stream stage-discharge relationships and used these curves to estimate continuous stream discharge.

Daily rain and snow precipitation data was obtained from the Banner Summit SNOTEL site, which is located at an elevation of 2140 m and a distance of less than 2 km from BTL. Daily mean wind data was obtained from the USFS Ranger Station in Stanley, ID, approximately 20 km SE of BTL.

Lake bathymetry was generated using hypsographic data collected by Arp (from 2002 to 2004). A series of transects were made across BTL where depth and location were concurrently measured with a hand-held echosounder and a GPS (Arp et al. 2006).
Additional GPS and total station points were taken along the lake margin to delineate the 0-depth isopleth. A 1-m digital elevation model (Hardy et al. 2001) was developed, and subsequent depth isopleths at 1 m intervals were generated with Surfer (Golden Software, Golden, CO). The area within each isopleth was integrated to produce the hypsographic curve (Arp et al. 2006).

Sample Collection and Chemical Analysis

We collected streamwater samples at BTL inflow and outflow gauging stations every 2 to 3 days during the ascending and descending limbs of the 2008 snowmelt hydrograph peak and weekly throughout summer baseflow. We use a subset of this data to populate and calibrate the model for the time period between spring and fall lake turnover (1 June to 1 October, respectively), hereafter referred to as the summer stratification period. We filtered replicate stream-water samples through ashed 0.7-µm glass-fiber filters (Whatman GFF, Maidstone, UK), for DOC, dissolved organic nitrogen (DON), NO\textsubscript{3}-N, NH\textsubscript{4}-N, and PO\textsubscript{4}-P analysis. Filtered stream water samples for DOC concentration were acidified with HCl to a pH <2 and stored in the dark until analyzed, while filtered stream-water samples for the other solutes were frozen until analyzed.

Additionally, we collected unfiltered water samples for the analysis of TN and TP, which were measured colorimetrically on an Astoria autoanalyzer (Astoria Pacific International, Portland OR) after persulfate oxidation following Valderrama (1981). We measured DOC concentrations on a Shimadzu TOC analyzer (OI Corporation model 700, College Station TX) using wet persulfate oxidation (Menzel and Vacarro 1964). All other dissolved nutrient analysis was measured colorimetrically on an Astora
autoanalyzer. DON was calculated as total dissolved N (Valderrama 1981) minus dissolved inorganic N (NO$_3^-$ and NH$_4^+$). We measured TDN, as for TN, above. We measured NO$_3^-$-N by colorimetric analysis via cadmium reduction on an automated analyzer (Astoria Pacific International, Portland, OR), and NH$_4^+$-N concentrations by colorimetric analysis via phenolhypochlorite (Solorazo 1969). TDP was measured by potassium persulfate digestion followed by an ascorbic acid molybdenum reaction for soluble reactive phosphorus (SRP, Murphy and Riley 1962).

Weekly to biweekly throughout the growing season, we measured BTL temperature, dissolved oxygen (DO), transparency (i.e., secchi depth), and Chl $a$. Temperature and DO were measured at 0.5, 1, 3, 5, 8, 12, and 14 m depth (YSI Model 85, Yellow Springs, OH). Secchi transparency was measured using a 25 cm secchi disk. Chlorophyll $a$ was measured by filtering 50 mL of lake water collected at 0.5 and 3 m depth, onto a 0.7-µm pore, 25-mm diameter Glass Fiber Filter (Whatman GFF, Maidstone, UK), and incubating filters in 95% ethanol overnight in a dark environment. We measured chlorophyll concentration on a Turner 10-AU Fluorometer (Tuner Designs, Sunnyvale, CA) following Welschmeyer (1994).

We collected particulate organic carbon (POC) by filtering a known volume of stream (both lake inflow and outflow) and lake (3 m depth) water through a pre-combusted GFF filter until the filter was clogged. The filter was then dried at 60°C for 48 hours and analyzed at UC Davis for elemental carbon (C) content using a PDZ Europa ANCA-GSL elemental analyzer (Sercon Ltd., Cheshire, UK).
Model Calibration

Model Assumptions

To develop a water quality model for BTL, field data and appropriate literature values for certain kinetic constants and coefficients (Table 4.1) were used to populate and calibrate LAKE2K (Chapra and Martin 2004). The model incorporates physical, hydrologic and biogeochemical processes to simulate seasonal patterns within stratified lakes (epi-, meta- and hypolimnion). LAKE2K model outputs include temperature, light extinction, as well as concentrations of inorganic and organic nutrients, dissolved oxygen (DO), phytoplankton, and zooplankton. In the model, organic N includes particulate and dissolved organic N and inorganic phosphorus is assumed to be in the form of phosphate ($PO_4^{3-}$).

The BTL simulation and calibration period spanned from 1 June 2008, through 1 October 2008, during the summer stratification period. We calibrated the model to BTL outflow water chemistry data, assuming the outflow was representative of epilimnion water during the simulation period. When available, we additionally used lake data (i.e., temperature, DO and particulate organic carbon (POC)) as input parameters for the epilimnion, metalimnion and hypolimnion.

Within the model, the lake outflow exited the lake via the epilimnion as specified by the mean daily outflow discharge time-series data. The inflow discharge was set equal to the measured outflow discharge, therefore assuming a constant lake volume. This was necessary because during the portion of the high flows modeled, the BTL inflow loses water to the subsurface in the topographically unconfined, sand-gravel delta directly
upstream of BTL (Hall et al. 2009). During May and June of 2008 (i.e., spring snowmelt), we could not account for approximately 20% of the inflow discharge. It was found that at flows of 0.50 m$^3$ s$^{-1}$, high interaction between the surface and subsurface result in turnover times of approximately 30 minutes (C. Arp, unpublished data). Thus, during high flows, rapid turnover times imply that the temperature and quality of the water entering the lake via subsurface flowpaths are likely similar to those measured in the lake inflow stream.

**Adjustments of the LAKE2K Model and Model Parameters**

In the original LAKE2K code, the inflow is assumed to enter into the lake layer that is most similar in density based on the temperature of the water. Thus, a cold hypolimnion would receive water from a cold inflow (i.e., the plunging inflow phenomenon). However, based on tracer studies in this area, these lakes do not exhibit a plunging of the inflow to the hypolimnion. Instead, the lake inflow water enters into the intersection between the lower epilimnion and the upper metalimnion (W. Wurtsbaugh, personal communication). Thus, despite differences in density and temperature, the model code was modified to split the inflow water into the epilimnion and metalimnion, at 65 and 35% of the inflow volume, respectively. No inflow water was routed to the hypolimnion.

During a manual sensitivity analysis, we found that the BTL model was relatively insensitive to changes in many of the model parameters. However, we found 12 sensitive parameters: hydrolysis and settling rates of organic carbon, nitrogen and phosphorus, dissolved organic carbon oxidation rate, nitrification and denitrification rates, maximum
phytoplankton growth rate, phytoplankton nitrogen and phosphorus half saturation constants (Table 4.1; Figure 4.1).

From mid-July through the rest of the summer, BTL outflow had higher TN concentrations than did the inflow, which was a result of elevated DON concentrations in the lake outflow relative to the inflow. Given the inherent oligotrophic nature of subalpine lakes in the region, phytoplankton growth rates are low (Budy et al. 1995), and the model, which only includes phytoplankton primary production was unable to replicate this significant increase in DON. The LAKE2K model does not account for benthic processes that can influence lake biogeochemistry, such as benthic algae (including N fixers) and macrophyte primary production. This is important because NH$_4^+$ inputs via benthic N fixation have been found to be at least 2% of the TN load in BTL (Marcarelli and Wurtsbaugh 2009). To account for this benthic N fixation, we incorporated this daily lake-scaled N fixation rate as an additional NH$_4^+$ input to the lake via the inflow nutrient load.

Bull Trout Lake contains dense submerged macrophytes between 1 and 9 m depths (i.e the epilimnion and metalimnion) that may total up to 30 tons (dry weight) of biomass during parts of the summer (D. Epstein, unpublished data). Submerged macrophytes are capable of mobilizing nutrients from the sediments directly via root uptake and can be a source of nutrients to the water column (Barko et al. 1991). Primary macrophytes in Bull Trout Lake include Potamogeton praelongus, Elodea canadensis, and Chara spp., and mortality for these macrophytes is known to occur from mid-July to late-September (Carpenter 1980; Janse et al. 1998).
To account for dissolved organic matter inputs to the lake from macrophytes, we further adjusted the DOC and DON inputs to the lake via the inflow nutrient fluxes. We assumed ~6% of the macrophyte OM is converted to DOM through mortality and excretion; slightly less than the 10% observed by Rich and Wetzel (1978). We also assumed DOC is 45% of DOM (Craft et al. 1991). Given a molar C:N ratio of these macrophytes of 10:1 (D. Epstein, unpublished data), which is similar to C:N ratios of epiphytes and macrophytes in other studies (Alber and Valiela 1994; Wolfer and Straile 2004), we calculated the DOC inputs to be 0.6 mg C L$^{-1}$ and DON to be 0.069 mg N L$^{-1}$. These additional inputs were 3.3% of the total inflow DOC load and 16.7% of the total inflow DON load for the modeled time period. Hereafter, we refer to the calibrated model with included N fixation and macrophyte influences as the current conditions or “Base Case” model.

Model Scenarios

We evaluated environmental change effects on BTL biogeochemistry based on 6 different model scenarios. To evaluate how increases in air temperature (warming scenario) would increase lake temperature and alter lake biogeochemistry, we increased mean daily air temperature by 2°C over the entire simulation period. To simulate changes in water inputs to the lake, a potential result of decreased snowpack (snowpack decline scenario), we decreased inflow and outflow discharge during high flows, 25 April – 31 July, by 20%. To simulate earlier snowmelt (hydrograph advance scenario), we advanced the hydrograph and the associated nutrient concentrations so as to occur 7 days earlier. We then evaluated how a change in all of the previously described scenarios
(combination scenario) would alter BTL biogeochemistry. To simulate increases in N loading to lakes as a result of increased N deposition (~ 4 kg ha\(^{-1}\) yr\(^{-1}\)) across the BTL watershed (N deposition scenario), we increased NO\(_3^-\) and NH\(_4^+\) by 46 µg L\(^{-1}\) during high flows and 25 µg L\(^{-1}\) during low flows, consistent with increases observed in the Colorado Rocky Mountains (Baron et al. 2009; Williams et al. 1996b). Finally we evaluate how the interaction (interaction scenario) of changes due to weather patterns (i.e., the combination scenario) with increased N deposition would alter the biogeochemistry of BTL.

Results

In 2008, the ascending limb of the snowmelt hydrograph began on 15 May; therefore, our simulation, which begins on 1 June does not capture the ascending limb (Fig. 4.2A). However, the simulation does capture the majority of the high flow, spring-melt time period when the majority of nutrients are flushed into BTL (Table 4.2). Bull Trout Lake outflow stream temperature was greater than the lake inflow, increased rapidly following spring turnover, and remained elevated throughout most of the summer (Fig. 4.2B). In general, BTL outflow had lower inorganic nutrient concentrations and higher organic nutrient concentrations than the inflow stream (NO\(_3^-\)-N concentrations shown; Fig. 4.2C), as lakes convert inorganic nutrients to organic nutrients via autotrophic and heterotrophic production.
**Base Case Scenario**

The calibrated model for 2008 produced physical, biological (i.e., Chl \(a\)) and chemical (both inorganic and organic) seasonal trends similar to empirical data (Temperature, Chl \(a\), TN and TP concentrations shown, Figure 4.3A-D, respectively). However, the model under predicted TN and TP in late June and early July (Fig 4.3C and D), which is likely associated with the inability of the model to capture the decline in Chl \(a\) in late June and early July (Fig 4.3B). Furthermore, the model did not accurately capture the magnitude of the late summer Chl \(a\) peak (Fig 4.3B). This inability to capture the Chl \(a\) spring decline and late summer peak is potentially due to modeling only one class of phytoplankton throughout the spring and summer. Additionally, during both early spring and early fall the model fails to capture an increase in PO\(_4^{3-}\) concentration, thus under predicts inorganic P by 0.7 to 1.5 µg L\(^{-1}\), and consequently TP (Fig. 4.3D). This inability to capture peak PO\(_4^{3-}\) concentrations is potentially due to minimal mixing and resuspension of nutrients under stratified conditions.

**Warming Scenario**

A 2°C increase in air temperature resulted in a 1.5°C increase in BTL epilimnion temperature during the majority of the summer stratification period (Fig. 4.4A), and had a minimal effect on TN and TP concentrations (Fig 4.4C and D, respectively; Base Case curve same as warming scenario curve) and export (Table 4.2). However, higher water temperatures and subsequently greater rates of temperature-dependent organic matter hydrolysis resulted in a decline of organic N flux by 3%, and an increase in NH\(_4^+\) and NO\(_3^-\) flux by 19 and 8.5%, respectively (Table 4.2). DOC export declined slightly in
both high and low flow periods, but given the magnitude of DOC flux, this decline was <3%. Additionally, this increase in organic matter hydrolysis rates resulted in increased PO$_4^{3-}$ flux by 13% during low flows, which corresponded to a 0.1 to 0.2 µg L$^{-1}$ increase in concentration. Despite an increase in temperature and inorganic nutrient concentrations, Chl $\alpha$ values were similar to the Base Case results during high flows and were 0.1 µg L$^{-1}$ lower from mid-July to mid-September (Fig. 4.4B). This decline in Chl $\alpha$ concentration may be a result of elevated phytoplankton mortality associated with higher water temperatures (Table 4.1).

**Snowpack Decline Scenario**

A decrease in snowpack of 20%, evaluated by decreasing snowmelt flows to the lake by 20%, decreased discharge during high and low flows, by 22 and 2%, respectively. Decreased water export resulted in decreased export of all nutrients of interest during high flows (Table 4.2) and small decreases (<5%) in the export of TN, DOC and Organic N during baseflow.

A decrease in the amount of water routed through the lake resulted in longer water residence times and a more rapid increase in epilimnion temperature following spring turnover (Fig. 4.4A). However, during low flows (i.e., August and September) the temperatures were similar to the Base Case. Longer water residence time caused extended physical retention of nutrients resulting in higher total nutrient concentrations from mid-June through mid-July (Fig. 4.4C and D) and subsequently higher Chl $\alpha$ concentrations (approximately 0.15 µg L$^{-1}$).
Hydrograph Advance Scenario

Advancing the hydrograph by 7 days resulted in a physical shift in the spring water pulse and consequently, an earlier recession of the hydrograph to baseflow. Similar to the decreased snowpack, advancing the hydrograph resulted in a more rapid increase in epilimnetic temperature. Following spring turnover, the decrease in TN and TP concentrations occurred approximately 7 days earlier (Fig. 4.4C and D, respectively), suggesting that during this time of year advection processes dominate nutrient dynamics. An advance in the hydrograph resulted in a decrease of nutrient inputs in mid-June, and a subsequent decline in peak June Chl a concentration by 0.2 µg L⁻¹ (Fig. 4.4B). However, Chl a concentrations were 0.1 to 0.15 µg L⁻¹ higher from July to September, possibly a result of longer nutrient retention and higher TN concentrations (Fig. 4.4C).

Advancing spring snowmelt flows resulted in a 20% decrease in water exported from the lake during high flows and a 7% decrease in water export during low flows (Table 4.2). Accordingly, this scenario resulted in a decrease in the export of all nutrients of interest during high flows (Table 4.2), and lower summer flows were associated with decreased DOC, TP and PO₄³⁻ exports (9, 6, and 7%, respectively). Despite higher TN concentrations, advancing the hydrograph did not result in any large changes in TN exports during low flows. However, NH₄⁺ and NO₃⁻ export increased by 19% and 38% (Table 4.2) suggesting an increase in organic matter hydrolysis during longer water residence times.
**Combination Scenario**

The combination scenario resulted in a faster increase in epilimnion temperatures than all other models as a result of decreased snowmelt and advanced hydrograph. Furthermore, the increased air temperature resulted in water temperatures that remained elevated throughout the season (Fig. 4.4A). Chlorophyll $a$ concentrations were similar to the Base Case, with only small variations in July and August (Fig. 4.4B), indicating a contrasting influence of hydrology and temperature on primary production. TN and TP concentrations were similar to the hydrograph advance scenario (Fig. 4.4C and D, respectively), indicating that advection is the primary control of total nutrient dynamics in this lake during the spring.

Advancing spring snowmelt and decreasing the magnitude of snowmelt flows by 20% resulted in a 23 and 2% decrease in water exported from the lake during high and low flows, respectively (Table 4.2). Nutrient export during high flows was similar to the hydrograph advance scenario. Conversely, during low flows inorganic nutrient (particularly $\text{NH}_4^+$ and $\text{NO}_3^-$) export was greater than in any of the physical change scenarios alone, indicating that the combination of increased physical retention, increased temperature (i.e., increased hydrolysis), and P limitation act synergistically to magnify inorganic nitrogen export.

**Increased N Deposition Scenario**

Increased inorganic N inputs to the lake increased TN concentrations by 70 to 80 $\mu$g L$^{-1}$ (Fig. 4.5B) and increased TN, $\text{NH}_4^+$ and $\text{NO}_3^-$ exports from BTL across the total modeled period by 77, 564, and 1485%, respectively (Table 4.2). Increasing inorganic N
inputs did not alter TP concentrations (Fig. 4.5B; Base Case and N deposition scenario curves are the same) or TP export. However, we observed a decrease in PO$_4$-3 exports in the spring by 4%, which was likely driven by an increase in autotrophic production (i.e., Chl a increased from 0.5 to 2.0 mg L$^{-1}$) from mid-June to mid-July (Fig. 4.5A). Increasing inorganic N inputs to the lake did not alter Chl a concentrations during early spring or late summer, indicating that N is not the primary limiting factor on phytoplankton growth during those times. Given minimal changes in autotrophic production, we did not observe any significant increases in DOC or organic N concentrations or export of these constituents across the spring and summer (Table 4.2).

**Interaction of Physical and Chemical Change Scenario**

Increasing inorganic N inputs in combination with physical changes (i.e., increased temperature, decreased snowmelt flows and an advanced hydrograph) resulted in relatively large (approximately 15%) increases in Chl a, TN, and TP concentrations (Fig. 4.5A-C, respectively). Increases in TN and TP concentration were driven by increases in organic N and P concentrations (Table 4.2). These changes did not occur until early July, indicating that hydrologic transport still dominates nutrient dynamics during peak spring snowmelt, while nutrient availability combined with increased water residence time and temperature can result in increased biological retention during lower flows. TN, NH$_4^+$, and NO$_3^-$ exports from June through October were lower than in the N deposition only scenario, indicating that longer water residence times and higher temperatures can increase the retention of inorganic N and reduce inorganic N exports from the lake.
Discussion

Environmental changes due to anthropogenic activities (i.e., changes in land-use, atmospheric deposition, etc.) have already been observed to affect hydrological and biogeochemical cycles in even the most remote and protected ecosystems (Baron et al. 2009; Elser et al. 2009; Williams et al. 1996a). While lakes are known to alter physical and chemical constituents of their inflow streams (Kling et al. 2000), less is known about how environmental change may enhance these alterations.

Modeling is one of the most practical approaches to predict how future changes in climate and atmospheric deposition will interact to affect high-elevation ecosystems. Few studies have addressed how shallow lakes will respond to climate change, and those that have, have focused on eutrophic or restored, non-stratified lakes (Mooij et al. 2007). With the use of a one-dimensional lake model, we tested how environmental changes might alter the aquatic biogeochemistry of a small oligotrophic, stratified lake within a subalpine watershed.

During the calibration of the model to BTL, we observed that macrophytes are a large contributor to water column dissolved organic matter concentrations during summer months, and indicate the need to better understand the influence of macrophytes on lake biogeochemistry. Additionally, changes in temperature and precipitation patterns, causing a modification of the magnitude and timing of snowmelt flows and increases in water temperatures will likely result in decreased export of water, organic nutrients and TP, with increased inorganic N (both $\text{NH}_4^+$ and $\text{NO}_3^-$) exports. Increases in N deposition will further amplify inorganic N exports from P-limited lakes. However, if a decline in
the magnitude of snowmelt or an advance in snowmelt occurs in combination with an increase in N deposition, lakes may buffer increases in N deposition and decrease N export from the lake by creating more favorable conditions for phytoplankton growth when N is limiting (i.e., during spring snowmelt) and increasing N retention.

**Model Limitations**

Our model assumes that the volume of the metalimnion and hypolimnion is constant, and in typical applications only the volume of the epilimnion fluctuates with lake levels. By setting the inflow equal to the outflow, we also assume a constant volume of the epilimnion, with only minor changes due to precipitation and evaporation. During low flows, the epilimnion volume in BTL is fairly constant; therefore our representation is reasonable. However, during peak snowmelt flows, our model does not capture changes in the lake volume. In small, mountain lakes the water residence time during snowmelt is often very short (i.e., days) (Baron et al. 1991), and hydrologic transport, rather than biogeochemical processing, may dominate nutrient dynamics (Hauer et al. 1997). Therefore, keeping the epilimnion constant throughout the model period should have little influence on outputs.

Bull Trout Lake was completely mixed on 1 October 2008, however only the epilimnion and metalimnion were mixed by this date in the Base Case calibration. The increase in inorganic P observed in BTL after mid-August, which was not captured in the model, is likely a result of the model’s failure to capture complete lake turnover. Thus, a lack of benthic resuspension of inorganic P likely contributed to the discrepancy between modeled and predicted inorganic P and TP from mid-August to 1 October.
Our model represents only one group of phytoplankton with fixed stoichiometry. Despite similarities in the measured and predicted temperature and chemical parameters, the LAKE2K model does not capture the early spring Chl $a$ decline, and consequently underpredicts TN and TP concentrations in late June and early July, as well as the late summer Chl $a$ peak. This discrepancy may be due in part to the lack of multiple phytoplankton classes represented within the model. Multiple classes of phytoplankton with different stoichiometry (Arrigo 2005) likely exist in the BTL pelagic zone, and the inclusion of these classes could improve the Chl $a$ predictions (Fragoso et al. 2009). Regardless, both measured and predicted Chl $a$ values are low ($<1.5 \, \mu g \, L^{-1}$), typical of oligotrophic aquatic systems in this region (Budy et al. 1995), and seasonal trends are similar between modeled and predicted data despite the inability to capture the magnitude of those changes. Thus, the results from the model scenarios will still provide insight into the effects of a changing environment on the dynamics of one class of phytoplankton.

Production within the LAKE2K model framework is restricted to the pelagic zone and does not incorporate benthic processes such as N fixation and macrophyte growth. We attempted to address this limitation through the addition of nutrient inputs to the lake via the inflow at the appropriate times and concentrations based on previous research and literature values. While this fix allows us to simulate the effects of N fixation and macrophytes on lake biogeochemistry, we are not representing the actual processes, which may increase with increases in water temperature (Marcarelli and Wurtsbaugh 2006) or decrease with increases in inorganic N inputs (Vitousek et al. 2002). Furthermore, environmental change could alter macrophyte production or community
structure (Hauer et al. 1997), thus altering nutrient dynamics within the lake littoral and pelagic zones. Unfortunately, our model would not be sensitive to such changes. Given the extensive interactions between the benthos and the pelagic zones in many lakes (Vadeboncoeur et al. 2002), the effects of climate change on benthic processes and benthic-pelagic coupling merit further study.

Since this is a receiving lake model, we are not taking into account the changes in terrestrial biogeochemical cycling; such as altered microbial activity in soils during snow-covered periods due to changes in the depth and duration of snowpack (Monson et al. 2006). Instead, we are estimating the possible effect of this phenomenon through the interaction of potential change scenarios. For example, a decline in the depth and the duration of snowmelt could decrease terrestrial microbial activity in the winter (Monson et al. 2006), and given the short water residence times (i.e., days) of mountain lakes during peak flows (Baron et al. 1991), could increase inorganic nutrient inputs to and export from the lake during snowmelt (Edwards et al. 2007).

If N deposition increases terrestrial N saturation, as is currently occurring in the Colorado Front Range (Burns 2004; Williams et al. 1996b), then inorganic N inputs to aquatic systems may increase as much as ten-fold (Williams et al. 1996a). Additionally, increased N deposition in these sensitive, high-elevation ecosystems may alter terrestrial and aquatic community structure (Bowman and Steltzer 1998; Morris and Lewis 1988; Williams et al. 1996b), which may lead to even greater alterations in lake biogeochemical cycling. A shift in terrestrial community structure is outside the scope of this model.
Changes Resulting from Altered Physical Conditions

By comparing the results of individual and combined model scenarios, we can better evaluate the dominant drivers of lake biogeochemistry and nutrient export. We evaluated the effects of changes in 3 physical variables (i.e., temperature, snowpack quantity and snowmelt timing), as well as the combination of all three. Our results indicate that advection dominates lake nutrient dynamics during spring snowmelt, a time when large quantities of water and nutrients are moving through mountain systems. Small mountain lakes are unable to physically retain these large pulses of water (Arp et al. 2006), and subsequently, retention and transformation during this time is minimal (Goodman et al. manuscript in preparation).

In alpine and subalpine environments, spring snowmelt represents the dominant source of nutrient inputs to aquatic systems, and therefore nutrients become limiting as the growing season progresses (Spaulding 1992; K. Goodman unpublished data). However, short residence times and high flushing rates may reduce the ability of phytoplankton to use the large quantity of nutrients entering the lakes during snowmelt (Cloern et al. 1985; Dickman 1969). Thus, changes in the magnitude and timing of snowmelt flows could have significant effects on lake biogeochemical cycling. Our results suggest that a reduction of hydrologic transport and subsequent increase in water residence times during high flows, as seen in the decreased snowpack scenario (during peak flows) and the hydrograph advance scenario (during the descending limb of the snowmelt hydrograph), can increase biological uptake of nutrients, thus increasing nutrient storage within the lake and reducing nutrient export.
Increasing water residence times in mountain lakes will likely lead to altered biogeochemical process by an increased clear water phase (Droscher et al. 2009), increased microbial processing and production time, as well as increased photodegradation (Goodman et al. manuscript in preparation). For example, despite lower flows into and from the lake in the combination scenario, we observed an increase in inorganic N export during low flows, which was likely due to the combination of higher temperatures (i.e., greater mineralization), longer water residence times and P limitation. These results indicate that while changes in the magnitude of flow is a good predictor of changes in nutrient export from lakes, physical changes occurring during low flows can play an important role in the form (i.e., inorganic or organic) of nutrients exported.

**Changes Resulting from Increased Nitrogen Availability**

Increased phytoplankton production following N additions has been observed in a low-N shallow, mountain lake (Nydicke et al. 2004), and suggests that nutrient limited lakes may act to buffer the predicted changes in high-elevation catchment N availability through in-lake retention. In our N deposition model, phytoplankton production increased following increased N inputs from mid-June to mid-July, which suggests some N limitation following the spring snowmelt pulse. However, the 4-fold increase in N-inputs did not result in an equal increase in Chl a concentrations and indicates that phytoplankton production was limited by a resource other than N. Primary production in lakes of this region are often co-limited by both N and P (Wurtsbaugh et al. 1997), and an increase in the predominance of P limitation throughout the summer has been observed.
on heterotrophic (K. Goodman unpublished data) and autotrophic (Marcarelli and Wurtsbaugh 2006; Spaulding 1992) processes in this region. Thus, in these oligotrophic systems N retention may be inversely related to N availability in the summer, as phytoplankton N requirements are met and phosphorous availability begins to limit growth (Elser et al. 2009; Levine et al. 1986).

If P is the dominant nutrient limiting primary production in these oligotrophic lakes, then the presence of lakes within the watershed will do little to buffer increases in N export associated with increases in N deposition. Atmospheric P deposition is rarely measured, yet atmospheric transport and deposition of soils and dust may be significant in the western United States (Neff et al. 2008). A shift toward N limitation of primary production with an increase in P deposition has been observed in high-elevation lakes in the Sierra Nevada regions of California (Sickman et al. 2003) and Spain (Morales-Baquero et al. 2006). These results indicate that dry P deposition may alleviate P limitation and increase primary production, ultimately increasing uptake of inorganic nutrients, in these oligotrophic mountain watersheds. However, an increase in nutrient availability due to N and P deposition may lead to eutrophication in systems, such as those in the Rocky Mountains, which do not have large food webs with higher trophic levels to provide top-down controls on phytoplankton biomass (McKnight et al. 1991).

We observed a small increase (~ 0.2 µg L\(^{-1}\)) in Chl \(a\) concentrations with the interaction of physical changes and increased N deposition following peak snowmelt flows. These results further suggest that hydrologic transport is the primary control on lake biogeochemistry in subalpine lakes during high flows. However, increased water
residence times, as well as increased nutrient availability, can support additional autotrophic production, and thus increased nutrient retention, in the lake.

Conclusion

We present a model for a shallow, stratified, oligotrophic mountain lake and evaluate scenarios to predict how a changing environment will alter its biogeochemistry. High-elevation aquatic ecosystems depend on spring snowmelt for the delivery of nutrients, and changes to the magnitude and timing of spring-runoff may alter lake nutrient dynamics. Our results indicate that the hydrologic regime is the primary control on nutrient dynamics during high flows, thus the magnitude and timing of snowmelt is an important regulator of mountain lake nutrient dynamics. Additionally, the hydrologic regime can indirectly influence nutrient dynamics by adjusting the length of baseflow when biogeochemical processes influence nutrient dynamics. Given P limitation, this lengthened baseflow period could result in increased export of inorganic N (30 to 50%), and this result would be amplified (>100%) if snowmelt flows advance or decrease in combination with increases in N deposition in the region. This may lead to downstream eutrophication if P is less limiting due to changes in land-use or if P deposition increases and N begins to limit autotrophic production.

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Table 4.1. Calibration parameter values for the Bull Trout Lake model. Highlighted values indicate parameters that were adjusted to calibrate the Bull Trout Lake model. Low and high values are the parameter ranges suggested by the EPA (Bowie et al. 1985).

<table>
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Table 4.2. Summary table of water and nutrient flux from Bull Trout Lake outflow, Boise National Forest, central Idaho for different model scenarios. Total represents 1 June to 1 October, high flow represents 1 June to 31 July, and low flow represents 1 August to 1 October. In the warming scenario, air temperature was increased by 2°C. In the snowpack decline scenario, inputs to the lake were decreased by 20% during high flows. In the hydrograph advance scenario, the snowmelt hydrograph and associated nutrient concentrations were advanced by seven days. The combination scenario is a combination of the Warming, Snowpack Decline and Hydrograph Advance model scenarios. The N deposition scenario increases inorganic inputs to the lake 4-fold, while the interaction scenario is the interaction of the physical combination scenarios and the N deposition increase scenario.

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<th>Model Scenario</th>
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<th>Discharge ($\times 10^9$ L)</th>
<th>TN (kg)</th>
<th>TP (kg)</th>
<th>DOC (kg)</th>
<th>Org N (kg)</th>
<th>NH$_4$ (kg)</th>
<th>NO$_3$ (kg)</th>
<th>PO$_4$ (kg)</th>
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<td>277.8</td>
<td>15.5</td>
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<td>12.8*</td>
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</tbody>
</table>

* indicates a positive % change relative to the Base Case.
† indicates a negative % change relative to the Base Case.
*3 to 15%, **15 to 30%, ***30 to 50%, ****>50% change relative to the original model.
Figure 4.1. Schematic of the kinetics and interactions from LAKE2K that were the focus of the Bull Trout Lake model calibration. Parameter values are defined in Table 4.1. DO is dissolved oxygen, POC is particulate organic carbon, DOC is dissolved organic carbon and SOD is sediment oxygen demand.
Figure 4.2. Measured data for A) Bull Trout Lake outflow discharge during 2008. The arrow indicates start of modeled time period on 1 June, B) Bull Trout Lake inflow and outflow mean daily temperature, and C) Bull Trout Lake inflow and outflow NO$_3$-N concentrations.
Figure 4.3. Epilimnetic A) Temperature, B) Chlorophyll a, C) TN and D) TP measured (points) and predicted (line) from the Base Case model for Bull Trout Lake, Boise National Forest, Idaho.
Figure 4.4. Epilimnetic A) Temperature, B) Chlorophyll $a$, C) TN and D) TP results from different model scenarios for the Base Case Bull Trout Lake model (gray dashed), increase in air temperature by 2°C (gray solid), a 20% decline in snowpack (black dotted) advance in hydrograph by seven days (black dashed) and a combination of increased air temperature, advanced hydrograph and decrease in snowpack (black solid).
Figure 4.5. Epilimnetic A) Chlorophyll $a$, B) TN and C) TP results for different model scenarios from the Base Case Bull Trout Lake model (gray dashed), increase in N deposition (black dotted), combination of physical changes (gray solid) and an interaction of the physical combination and N deposition increase (black solid).
CHAPTER 5
SUMMARY AND CONCLUSIONS

This research sought to evaluate how lakes within stream networks can alter the quantity and quality of dissolved organic matter (DOM) in oligotrophic stream networks (Figure 5.1). To my knowledge, this is the first study that attempts to address how lakes alter DOM concentrations and characteristics in mountain streams. Additionally, I used a modeling approach in combination with field data to predict how environmental changes (e.g., global climate change, altered weather patterns, and increased atmospheric deposition) may alter the hydrochemistry of oligotrophic stream-lake networks in the Intermountain West.

Analysis of DOM temporal patterns in seven-paired lake inflows and outflows illustrated the potential for lakes to alter DOM dynamics in oligotrophic mountain streams (Chapter 2). For example, the magnitude of change in dissolved organic carbon (DOC) concentration over the course of a growing season was almost two times greater in lake inflows than outflows. The magnitude of change in DOC concentration from spring to fall in lake outflows was strongly related to lake area, which indicates that the extent to which lakes can buffer (i.e., decrease the magnitude of temporal variability in outflow stream) DOC concentrations is related to water residence times. Despite relatively constant DOC concentrations during baseflow, our results indicate that inflow stream DOM characteristics (i.e., specific ultraviolet absorbance ($\text{SUVA}_{254}$), DOC: Dissolved Organic Nitrogen (DON) ratio and $\delta^{13}\text{C}_{\text{DOC}}$) do not remain constant, which is likely related to a shift in DOM source pools. However, the presence of lakes can
decrease the magnitude of this temporal variability in outflow stream DOM characteristics.

Furthermore, lakes can alter DOM export, measured as DOC flux, from watersheds (Chapter 2). Temporal patterns of DOC concentrations in high-elevation watersheds are typified by DOC flushing from the surrounding terrestrial systems, which depletes terrestrially-derived subsidies to the stream. Mountain lakes can dampen this flushing response by acting as a carbon sink during spring snowmelt and a DOC source to downstream locations later in the season. This DOC source may provide a carbon source to downstream locations when terrestrial supplies of DOC are low, potentially providing temporal stability of DOM and nutrient dynamics to downstream ecosystems.

Increases in DOC concentration in outflow streams during baseflow may be a result of storage during snowmelt, autotrophic production within the lake, or a combination of both. Snowmelt DOC storage in lakes occurs on a relatively short time period, as indicated by the 5 day average time lag in the DOC center of mass export in lake outflows relative to lake inflows. Thus, the observed increases in outflow DOC concentrations relative to the respective inflow concentrations during baseflow are likely due to autotrophic production within the lake, which releases DOM throughout the summer and fall. This hypothesis is supported by the stable DOM characteristics in lake outflows following snowmelt flushing.

Chapter 3 evaluates the relationship between lake water residence time, lake inflow and outflow DOM photodegradation, and the implication for heterotrophic processing in streams. Outflow DOM was twice as resistant to photodegradation during summer baseflow as was lake inflow DOM. Outflow DOM resistance to
Photodegradation was inversely related to water residence time. Photodegradation of DOM increased its bioavailability by 1.6 and 1.2 times in one study lake inflow and outflow, respectively. This increase in bioavailable DOM increased nutrient limitation in inflows and outflows, and indicates that these oligotrophic mountains systems are co-limited by bioavailable DOC and inorganic nutrients.

Alpine and subalpine lakes receive a large amount of light and are often nutrient limited during summer baseflows. Thus, photodegradation has the potential to exert a strong influence on DOM characteristics in high-elevation aquatic systems. These results suggest that the presence of lakes within fluvial networks may act to increase bioavailable DOC to downstream locations, potentially increasing both carbon and nutrient uptake and retention.

Finally, I evaluated how the hydrology and biogeochemistry of a high-elevation mountain lake may be altered by changes in air temperature, magnitude and timing of snowmelt, and N inputs (Chapter 4). Organic matter dynamics, microbial processes and nutrient retention in oligotrophic mountain systems are strongly influenced by hydrology and nutrient availability, and primary production is often co-limited by N and phosphorus (P). Thus, changes in climate and weather patterns, in addition to increases in nitrogen (N) deposition, may alter organic matter pools and process rates.

Our results indicate that changes in the magnitude and timing of snowmelt will likely have the largest effect on lake biogeochemistry in oligotrophic mountain systems by altering water and nutrient exports. Furthermore, changes in the duration of baseflow (e.g., longer lake water residence times) can alter lake biogeochemistry and will likely result in an increase of inorganic N export from mountain lakes. In P-limited lakes, as
well as N and P co-limited lakes, increases in lake inorganic N concentrations and
eXports are likely to occur with increased temperatures and lake water residence times.
Increases in atmospheric N deposition will further enhance inorganic N export in P-
limited high-elevation lakes, which can negatively affect water quality downstream.

Studies of carbon cycling in freshwater often consider lakes and streams as
separate entities without taking into consideration their hydrologic linkages. Thus, we
know little about how streams and lakes interact within fluvial networks. This
dissertation provides a means to evaluate how streams and lakes interact in mountain
landscapes and furthers our knowledge of the coupling between hydrologic and
biogeochemical cycling.

Lakes present a unique landscape feature that can alter watershed DOM dynamics
through biotic and abiotic transformations. For example, lakes may act as a DOM sink
through physical water retention and sediment burial, photodegradation, and
heterotrophic uptake. Conversely, lakes can act as a DOM source through primary
production. These changes in DOM can alter both the quantity and quality of DOM in
downstream locations and has potential to alter downstream ecosystem function.

These results indicate that lakes are an important regulator of DOC concentrations
and export in mountain watersheds and are applicable across many aquatic ecosystems
where water and nutrients may be retained (e.g., beaver ponds, small ponds, larger lakes
and reservoirs). In snowmelt-driven high-elevation aquatic systems, lakes add temporal
stability to DOC dynamics in downstream locations and may increase downstream uptake
of both carbon and nutrients. The extent to which lakes can buffer DOM temporal
dynamics and alter DOM characteristics is strongly influenced by water residence time.
Future changes in the hydrologic inputs to mountain fluvial networks, resulting from changes in weather patterns, may have profound effects on aquatic organic and inorganic nutrient dynamics. The largest changes will likely result from altered water residence times within lakes, which can increase nutrient retention by altering direct (physical) and indirect (biological) processes.
Figure 5.1. Conceptual diagram of lake influence on mountain stream DOC variability, quantity and quality. DOC variability is the magnitude of variability in DOC concentration over time.

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12-February-2010

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Appendix A.2 Co-author release for chapter 3.

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EDUCATION

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Cumulative GPA: 3.85/4.0
December, 2003

B.S. in Biology, Cum Laude
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Overall GPA – 3.475/4.0
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PROFESSIONAL EXPERIENCE

Research Fellow, Utah State University, Stream-Lake Interactions
Jun. 2006 – Present
- Design and conduct field and laboratory research on stream dissolved organic matter (DOM; quantity and quality) dynamics in relation to watershed complexity and stream-lake interactions, including DOM export, heterotrophic processing and UV breakdown
- Collaborate on a watershed-scale $^{15}$N isotopic tracer study to evaluate nutrient and hydrologic retention and track fate of nitrogen in stream-lake systems; data collection included stream chemistry, biomass compartment (microbe, algae, plant and invertebrate) sampling, metabolism, decomposition, and discharge
- Sediment nitrification assays
- Organize and oversee both field and laboratory sampling and processing
- Mentor and develop projects with undergraduate students investigating 1) Changes in nutrient concentrations along a river continua and 2) Photodegradation effects on DOM bioavailability of lake inflow and outflow water
- Calibrate a lake model to predict impacts of environmental change on stream-lake systems

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- Instruct General Biology Labs
**Research Assistant**, Aquatic Biogeochemistry  
Aug. 2004 - Aug 2005  
- Field and laboratory technician  
- Planned and conducted research studying nitrogen dynamics in stream hyporheic zones in collaboration with LINX II western US studies, using a $^{15}$N isotopic tracer

**Research Technician**, Department of Water Quality, State of Utah  
Sept. - Oct. 2004  
- Conducted abiotic and biotic sampling of reference streams around the state of Utah to facilitate development of a statewide biomonitoring program

**Research Consultant**, Northeastern Forestry University, Shangzhi, China.  
July 2004  
- Lectured and trained students and professors in both field and laboratory protocols involving biological monitoring including both biotic and abiotic sampling in the Maoershan Experiment Forest Farm, northeastern China.

**Research Technician, Aquatic Ecology**, University of NC-Greensboro  
Jan. - June 2004  
- Planned several research projects focusing on urban impacts on streams, including nutrient dynamics, benthic macroinvertebrate field sampling, and study site selection  
- Executed weekly sampling of urban streams for use in restoration studies  
- Managed use and maintenance of YSI and Hydrolab sampling  
- Conducted Nutrient “Hotspot” study including Chironomidae deformity identification, Ceriodaphnia chronic and acute toxicity tests and nutrient analysis  
- Prepared manuscripts for publication and wrote progress reports

**Teaching Assistant**, University of NC-Greensboro  
- Instruct General Biology Labs for biology majors and non-majors

**Graduate Research Assistant, Aquatic Ecology**, University of NC-Greensboro  
May 2002 - Aug 2003  
Committee Chair: Dr. Anne Hershey  
**Effects of timber harvest on benthic macroinvertebrates and trophic dynamics**  
- Designed and conducted thesis research on benthic macroinvertebrates community structure and function in headwater streams in response to 3 different forest covers  
- Examined aquatic food webs using natural abundance stable isotopes  
- Compared land use effects on in-stream organic matter decomposition  
- Colonized periphyton and conducted Chl $a$ analysis  
- Completed EPA’s Rapid Bioassessment Protocol and the North Carolina Biotic Index (NCBI) field sampling and macroinvertebrate identification  
- Conducted nutrient limitation and nutrient uptake experiments  
- Completed extensive literature review

**Undergraduate Research Assistant**, Virginia Tech  
May 2000 - Aug. 2001  
- Assisted with field, greenhouse and lab research in plant ecology and physiology  
- Managed planting, harvesting, maintenance, data collection and data entry of greenhouse experiments and field experiments at Savannah River Site, S.C. and Coweeta LTER
PUBLICATIONS


PRESENTATIONS AT PROFESSIONAL MEETINGS


*LABORATORY AND FIELD SKILLS*

Analytical Instruments: Fluorometer, Spectrophotometer, C:H:N Element Analyzer, Mass Spectrometry, Gas Chromatograph, Astoria Auto Analyzer, Dionex Ion Chromatograph
Stable isotope use, collection, preparation and analysis
Multivariate statistics, Statistical Software: SAS, JMP IN, SPSS, Resampling Stats
Other Software: Parafac, PowerPoint, Excel, Word, ArcView, ArcMap, Ecosim
Modeling Software: OTIS, LAKE2K, HEC-HMS
Use and maintenance of YSI and Hydrolab water samplers
DOM chemistry and characterization
Trained in freshwater biomonitoring, use of benthic metrics and fish collection
Proficient with compound and dissecting microscopes

*SHORT COURSES AND WORKSHOPS*

OTIS Modeling Workshop, Ron Runkel - NABS, Grand Rapids, MI – May 2009
Mentoring Workshop – Utah State Univ., Logan, UT - February 2008
DOM Characterization Workshop – McKnight Lab, Univ. of Colorado, Boulder – May 2007
Stable Isotope Ecology Short Course – Ehleringer Lab, Univ. or Utah, SLC – June 2006
HONORS AND AWARDS

James A. and Patty MacMahon Scholarship:
- $500 for 2008
North American Benthological Society Presidential Endowment Award:
- $600 for 2007
USU Ecology Center Research Support Award:
Inland Northwest Research Alliance (INRA) Subsurface Science Graduate Fellowship:
- $25,000 for 2006-2008
Guilford County Wildlife Scholarship: Fall 2003
USU School of Graduate Studies Honor Roll: Fall 2005
Biological Honor Society: Phi Sigma
Virginia Tech Scholars Scholarship: August 1997-May 2001

ORGANIZATIONS AND ACTIVITIES

North American Benthological Society: 2001-present
American Geophysical Union: 2007-present
USU Water Fellow: 2007-present
Journal Reviews:
- Journal of the North American Benthological Society
- Hydrobiologia