Winter 2012

Spatial and temporal variation in degradation of dissolved organic carbon on the main stem of the Lamprey River

Lucy Miller Parham
University of New Hampshire, Durham

SPATIAL AND TEMPORAL VARIATION IN DEGRADATION OF DISSOLVED ORGANIC CARBON ON THE MAIN STEM OF THE LAMPREY RIVER

BY

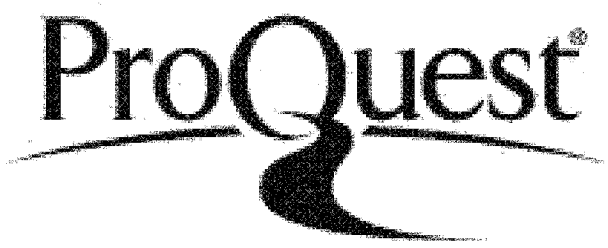
LUCY MILLER PARHAM
B.S. Natural Resources, Sewanee: The University of the South, 2005

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Master of Science
In
Natural Resources

December, 2012



ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

This thesis has been examined and approved.

Thesis Director, Dr. William H. McDowell
Professor of Environmental Sciences

Dr. Serita D. Frey
Professor of Environmental Sciences

Dr. Wilfred Wollheim
Assistant Professor of Environmental Sciences and
Earth, Oceans, and Space

11/29/2012
Date

ACKNOWLEDGMENTS

I would first like to thank my committee members, Serita Frey and Wil Wollheim for their insight and discussion of my work, particularly during the formation of my project. A special thanks goes to my advisor, Bill McDowell, for not only providing assistance with my thesis project, but also for instructing me in how to be a good scientist. I also want to thank him for taking me to Siberia and opening up the door for studying an entirely different and exciting ecosystem.

To the McD lab for keeping it fun, especially Jody Potter and Adam Baumann for their invaluable lab wisdom and patience. A thank you to Michelle Daley for assistance with GIS and modeling and Ania Kobylinski for her help in the field.

Lastly, I want to thank my fantastic grad school friends who made this experience bearable and kept me going through the low times and my family for all of their encouragement and support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

SPATIAL AND TEMPORAL VARIATION IN DEGRADATION OF DISSOLVED ORGANIC CARBON ON THE MAIN STEM OF THE LAMPREY RIVER

By

Lucy Miller Parham

University of New Hampshire, December 2012
Thesis Advisor: Dr. William H. McDowell

Degradation of dissolved organic carbon by microbial and photolytic processes was examined along the main stem of the Lamprey River Watershed located in southeastern New Hampshire. Eight sites were chosen and sampled biweekly throughout the seasonal hydrograph. Lab incubations were employed to assess microbial degradation of dissolved organic carbon (DOC) where one set of samples was exposed to natural sunlight for a day to assess photolytic degradation. Mean biodegradable dissolved organic carbon (BDOC) throughout the study period was 5.8% with no significant variation observed between sites. Temporal variation was found to be a much stronger driver of DOC composition with summer showing the highest degradation of 8.6% and winter the lowest. Initial DOC concentration was found to be the only significant positive predictor of BDOC on both an annual and seasonal scale. Photolysis had no significant effect on DOC degradation or availability of DOC to the microbial pool. Findings suggest that temporal variation is a significant driver of DOC composition via DOC sources that change throughout the season.

CHAPTER I

INTRODUCTION

Understanding the role of dissolved organic matter (DOM) in elemental cycling has become increasingly important given the dramatic nature of anthropogenically induced change occurring in both the carbon (C) and nitrogen (N) cycles. For most aquatic systems, dissolved organic matter is the major form of organic matter and its role in the global carbon cycle, specifically, the various ways in which it is transported and processed, continues to be rigorously addressed. Current models of the global C cycle are generated with increasing detail given to the vast number of intricate processes involved although the role of inland aquatic environments continues to be excluded from these models and has yet to be adequately delineated in its contribution to overall cycling (Cole et al. 2007).

When inland aquatic systems are included in global models, it is usually only for the transport of C through the riverine pipe even though a number of transformations and losses occur en route from land to sea (Cole et al. 2007). Riverine networks are a critical linkage among the various components of a landscape. Each year streams and rivers of the world transport, transform, or store nearly 2 Pg of terrestrial organic carbon, 0.25 Pg of which consists solely of dissolved organic carbon (DOC) (Battin et al. 2008). While the amount of DOC transported to the oceans via rivers is sufficient to account for turnover of the

marine DOC pool, surprisingly, terrestrial-derived DOM comprises only approximately 2.5% of the total DOM in the ocean (Opshal and Benner, 1997). Furthermore, the accepted notion of the composition of riverine organic matter as highly degraded, humic rich, and nitrogen poor would lead one to believe that its fate through marine respiration would be unlikely, yet only a small fraction is preserved in marine sediment (Hedges et al. 1997). Recent evidence indicates that the fate of dissolved organic matter does not lie in the ocean but rather in fueling heterotrophy in riverine systems (Cole et al. 2001; Raymond and Bauer, 2000;; Richey et al. 2002). Current global estimates of CO_2 emissions from inland waters are 1.2-1.4 Pg CO_2-C yr^{-1} (Tranvik et al. 2009; Aufdenkampe et al. 2011). While work is under way to refine these global estimates, the extent and nature of DOM processing through respiration in rivers has yet to be clearly defined through space and time, especially when considering the "refractory" nature of the DOM having already been processed in soils as well as the shorter residence times experienced in riverine systems.

DOM in riverine systems serves several functions from influencing contaminant transport (Morris and Hargreaves, 1997), affecting light regime, altering stream pH (McKnight et al. 1985), and acting as a source of nutrients for bacteria (Findlay and Sinsabaugh, 2003). Perhaps one of its more significant services is as a microbial energy source (Raymond and Bauer, 2000), fueling heterotrophy in large river systems. While the fate of most terrestrial primary production is to be respired in terrestrial environments, 0.5 Gt C per year escapes respiration and is exported to aquatic systems, thus making DOC an

important pathway for C loss from terrestrial systems (Meybeck, 1993). Once in stream, three primary pathways become available for DOC; export from the watershed with documented flux rates ranging from 1 to 140 kg C ha^{-1} yr^{-1} (Aitkenhead and McDowell, 2000) and mean annual DOC concentrations ranging from 0.1 to 36.6 mgC/L (Mulholland, 1997), storage in riverine sediments, and/or utilization by riverine bacteria in the form of uptake to build microbial biomass or complete mineralization. Utilization by bacteria is affected by both the composition of the DOC as well as extrinsic factors such as temperature, nutrient availability, trophic community structure, and composition of bacterial assemblages (del Giorgio and Davis, 2003). While extrinsic factors can be controlled for in lab experimentation, the complexity of DOC composition has made direct measurements of microbial utilization difficult.

Primary sources of DOC to aquatic systems can include both natural and anthropogenic sources with the land use of a catchment determining the proportion of contribution. Natural sources include leaching from leaf decomposition, throughfall, root exudates, decomposition of older soil organic matter (SOM), algal and macrophyte production, and abiotic leaching of SOM (Findlay and Sinsabaugh, 2003). Anthropogenic sources include effluent from wastewater treatment plants, fertilizers, and runoff (Seitzinger et al. 2002, Wiegner et al. 2006). These various sources result in a complex chemical composition that can be described as a continuum of organic matter pools with successively decreasing decomposition constants resulting in turnover times from hours to days, weeks, months, and years (Sondergaard and Middelboe,

1995). More recently, studies on microbial degradation have classified the DOC pool into two primary fractions characterized by a labile and semi-labile component where the labile component cycles rapidly and serves a large portion of the energy demands of heterotrophic bacteria, while the semi-labile DOC pool degrades more slowly providing a degree of metabolic stability for the downstream system (Qualls and Haines, 1992; Kaplan et al. 2008). Through an extensive analysis of several studies, Sondergaard and Middleboe (1995) found that for rivers, the average percentage of biodegradable dissolved organic carbon (BDOC) (defined as the amount utilized in 7 days or less) is approximately 19% of the total DOC pool. A second, more recent meta-analysis of 45 rivers by del Giorgio and Davis (2003) found that approximately 6% of the DOC pool degraded in 5 days and 12% degraded over 20 days. Lastly, a synthesis by Wiegner et al. (2006) found that riverine DOC biodegradation ranges from (0 to 72%) and averages around twenty-five percent.

Exposure to sunlight can also contribute to DOC transformation in streams resulting in a large range of photoproducts. Photoproducts that signify direct mineralization of carbon include inorganic compounds such as carbon monoxide or carbon dioxide (Graneli et al. 1996; Miller and Zepp, 1995) while other products may be organic molecules that are still a part of the DOC pool but with altered lability (Wetzel et al. 1995). The past twenty years of research in the photolysis field has revealed the generally accepted notion that recent algal-derived DOM is rendered less labile by sun exposure (Obernosterer et al. 1999; Tranvik et al. 2001) whereas humic-rich DOM of plant origin becomes more

bioavailable (Amon et al. 1996; Tranvik et al. 2001; Moran and Covert, 2003). Other studies have shown no effect of sun on availability (Wiegner and Seitzinger, 2001). Whether or not the movement of DOM to the microbial food web via photochemical processes is a significant ecological process in riverine systems is still under investigation and appears to differ on an individual ecosystem basis.

The purpose of this study was to gain a better understanding of C dynamics in the main stem of the Lamprey River through quantifying dissolved organic C degradation as a result of microbial processing and photolysis. While BDOC has frequently been quantified for streams and rivers throughout temperate watersheds, it has yet to be quantified with high spatial and temporal resolution. High resolution becomes important for evaluating if a single sample constitutes an accurate representation of BDOC through space and time and also allows assessment of the importance of DOC utilization as a pathway for organic matter transformation. Rivers are highly dynamic systems exposed to great heterogeneity both in-stream and throughout the watershed, manifested as changing river morphology and variation in both point and nonpoint sources of carbon. These factors are highly susceptible to anthropogenic influence and have the potential to cause changes in DOC composition suggesting significant variation in BDOC throughout the main stem. Furthermore, given how stream characteristics and processes change throughout the seasons, significant temporal variation in BDOC may also occur. Lastly, because the Lamprey River watershed is primarily forested, and therefore consisting of humic-rich, terrestrial

DOC, we also hypothesized that light exposure would alter DOC composition making it more available to the microbial community.

The watershed in which this study was conducted is projected to undergo rapid population growth in the coming years, therefore understanding the role that DOC currently plays in this ecosystem is imperative for predicting how that role may change with land use alteration. Specifically, my objectives were:

Objective 1: To determine variability in BDOC for eight sites distributed from headwaters to lower portions of the main stem of the Lamprey River throughout the seasonal hydrograph and relate to other in-stream characteristics.

Objective 2: To determine the effect of light exposure on DOC degradation and the availability of DOC to microbial degradation.

Objective 3: To identify the relative contribution of C from the riparian zone of the main stem of the Lamprey River and describe the implications for downstream transport.

CHAPTER II

METHODS

Site Description:

The Lamprey River Watershed is located in southeastern New Hampshire and encompasses nearly 479 km^2 of area with an elevation range of around 20 to 350 meters. The Lamprey is a sixth order stream that courses approximately 50 miles from its headwaters in Northwood, NH through several towns until it reaches its outlet in the Great Bay estuary. Although primarily forested (68% of the land area), the watershed is becoming increasingly urbanized with a projected population increase from 50 people/km^2 to 80 people/km^2 by 2020 (Lamprey River Hydrologic Observatory (LRHO)).

Throughout its 50 mile journey, the Lamprey travels primarily through mixed deciduous and coniferous forest with dominant species being red maple (*Acer rubrum*), sugar maple (*Acer saccharin*), red oak (*Quercus rubrum*), American beech (*Fagus grandifolia*), eastern white pine (*Pinus strobus*) and eastern hemlock (*Tsuga canadensis*). During the sampling period (June 2011-May 2012), average monthly air temperatures ranged from -2.3 °C (January 2012) to 22.1 °C (July 2011) with a mean temperature of 10 °C (National Climatic Data Center (NCDC) for Durham, NH). Total monthly rainfall ranged from 23.5 mm (July 2011) to 192.6 mm (October 2011) with a monthly mean of 94.7 mm and a total rainfall of 1136 mm (NCDC for Durham, NH). During the past ten

years, average annual discharge has ranged from 3.9m^3/s to 16.1m^3/s with a ten year mean of 10.1m^3/s (USGS station number 01073500).

Eight sites were sampled for this study, all of which were located along the main stem of the river beginning at river kilometer (rkm) 07 and extending to rkm 73. Relative location and name of the main stem sites are shown in Figure 1. Cumulative watershed characteristics such as basin area, land use, and population density can be seen in Table 1. Discharge was continuously monitored at both rkm 27(USGS station number 01073319) and rkm 73 (USGS station number 01073500). Throughout this 46 kilometer stretch, discharge increased by about 66% during the study period where average discharge was 8m^3/s with highest flows occurring in November (15.97 m^3/s) and December (16.91 m^3/s) and lowest in July (1.29 m^3/s) and August (2.57 m^3/s) (USGS station number 01073500) (Appendix A).

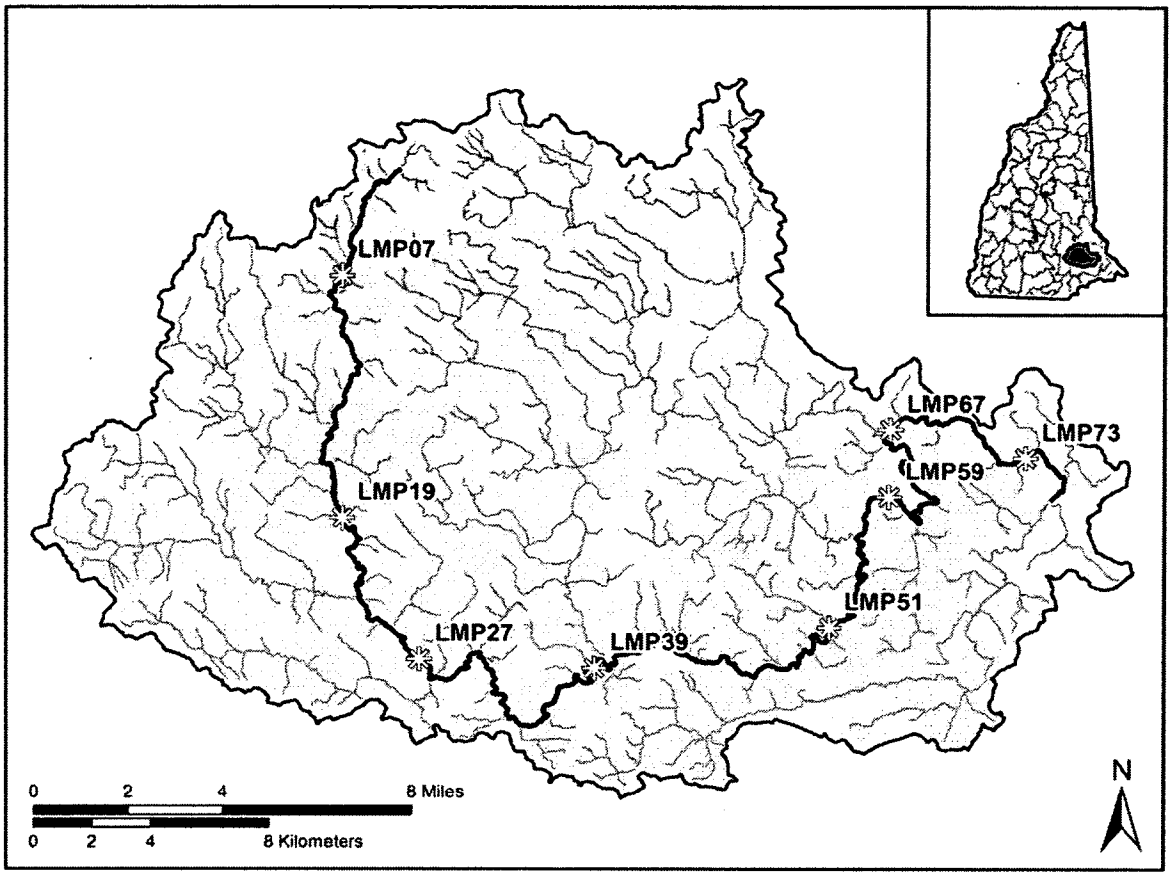


Figure 1. Map of the Lamprey River watershed with locations of the eight main stem sampling sites designated with white asterisks.

Table 1. Watershed characteristics for the Lamprey River Watershed and sub-basins (as classified by NH GRANIT, statewide GIS warehouse).

Site	Watershed Area (km^2)	Agriculture (%)	Forested (%)	Urban (%)	Wetlands (%)	Population Density (people/ km^2)
LMP07	14.7	1.2	87.2	0.4	6.7	19.9
LMP19	80.5	3.0	78.0	2.6	6.8	30.6
LMP27	144.7	2.3	75.6	3.0	7.5	40.7
LMP39	197.6	2.1	70.5	4.6	8.6	60.7
LMP51	251.4	2.5	69.3	4.6	8.8	63.7
LMP59	396.0	2.9	69.6	4.0	10.3	52.9
LMP67	468.6	2.9	69.6	4.0	10.3	52.9
LMP73	478.8	3.0	69.5	4.1	10.2	53.4

Sample Collection:

Water samples were collected on a biweekly basis from June 2011 through May 2012 at eight sites along the main stem of the Lamprey River. Samples were collected in 500 ml acid washed HDPL bottles and transported in a cooler to the lab where they were vacuum filtered through a pre-combusted glass fiber filter (Whatman GF/F; nominal pore size 0.7µm) and then through a 0.2 µm filter (Supor-200 membrane filter) and frozen until incubation setup. Filters were changed frequently to minimize cell lysis and clogging of the filter due to high POM load.

DOC biodegradation:

Incubation methodology was similar to previous studies (McDowell et al., 2006; Wiegner et al., 2006; Kaushal and Lewis, 2005) in that riverine DOM biodegradation was assessed by adding freshwater native bacteria to sterile filtered water with added nutrients and then monitoring loss in concentration at a standardized temperature over a predetermined incubation time. This approach allowed for assessment of the inherent lability of DOC at different sites throughout the year by minimizing site-specific conditions and reflecting differences in chemical composition.

On the day of the incubation setup, samples were thawed and a 50ml subsample was taken for initial analysis. Four hundred milliliters of volume from each site was transferred to a 500 ml flask. Inorganic nutrients were added in the form of $NaNO_3$ and K_2HPO_4 to raise the concentration of nitrate by 150 ug/L and

the concentration of phosphate by 20 ug/L. Each flask was amended with 4 ml of inoculum at a 1:100 ratio of inoculum to water with an estimated 10^5 cells/ml. A second 50 ml subsample was taken and frozen for analysis. The remaining 350 ml of sample was divided evenly into three standard glass BOD bottles, each of which contained half of a Whatman GF/F filter to act as a substrate for bacterial growth. Bottles were covered with aluminum foil and placed in the dark in an incubator at 20 °C for 7 days. An incubation time of 7 days was chosen as it is long enough to clearly characterize the labile DOC pool (McDowell et al., 2006). Bottles were shaken every day throughout the incubation period. At the end of seven days, samples were filtered again (Whatman GF/F, nominal pore size 0.7µm; Supor-200 membrane filter, pore size 0.22 µm) and frozen until analysis. To ensure the viability of the inoculum, a glucose solution was used for all incubations where on average, 90% of the carbon was degraded by the end of the incubation period. In addition, a control of deionized water (DI) with added nutrients and inoculum was used to assess evolution of carbon from the inoculum throughout the incubation. All glassware used in this experiment was acid washed and combusted.

On two sampling dates (10/12/2011; 05/08/2012), the incubation period was extended to 10 days and 30 ml subsamples for four of the eight sites (LMP07, LMP27, LMP51, LMP73) were taken on Day 2, 4, and 7 to capture the time sequence of degradation.

Biodegradability of DOC includes two microbial processes: 1) microbial uptake (the breakdown of original compounds which are then used for the

biosynthesis of microbial cell materials) and 2) mineralization to obtain energy and inorganic nutrients (Marschner and Kalbitz, 2003). In this portion of the study, process (1) and (2) were quantified using loss in concentration over seven days. The amount of DOC consumed during the incubation was calculated from initial and final concentrations in each flask. Total biodegradation of labile DOC is expressed as a percentage of DOC utilized (amount DOC consumed/amount DOC initially present x 100) (Seitzinger et al., 2002; Wiegner et al., 2004).

Inoculation:

In order to create a standardized inoculum that could be used throughout the twelve month period, 2 liters of river sediment, riparian soil, and water was collected from each of the eight sites during the spring of 2011. The mixture was stored at 4°C for the duration of the experiment. At the start of each incubation, a 100 ml sample of water, sediment, and soil was removed from the two liter container and stored overnight in the dark at 20°C. The day of the incubation, the 100 ml sample was shaken and then centrifuged at 3,000 rpm for 2 minutes to remove particulate matter and protists and filtered (Whatman GF/F; nominal pore size 0.7µm) (Seitzinger et al., 2002; Petrone et al., 2009).

Photolysis:

To determine the effect of sunlight on the composition of DOC, samples were taken from two sites (LMP07, LMP73) in July, filtered in the lab (Whatman GF/F; nominal pore size 0.7µm; Supor-200 membrane filter 0.2 µm) and stored over night at 4°C until exposure the following day. Samples were exposed to natural sunlight for one day (8am-6pm) in quartz flasks. For each site (and a control), there were two treatments. Half of the sample water was incubated in triplicate in quartz flasks while the other half was incubated in triplicate in BOD bottles wrapped in foil. The control consisted of DI water only. All samples were kept in a shallow water bath where temperature was maintained using ice. Average solar radiation for the ten hour period was 530.7 W/m^2 (NCDC for Durham, NH). At the end of exposure, 50 ml samples were taken and the remaining water from each similar site and treatment were combined and run through a standard incubation setup.

Riverine DOC Modeling:

Creating a partial mass balance model for estimating the contribution of carbon from the main stem riparian zone required several steps. The first step was to calculate the amount of carbon being produced in the landscape where both concentration and discharge data was available. For eight Lamprey tributaries, DOC concentration was measured monthly by the McDowell lab throughout the study period (June 2011-May 2012) and multiplied by total runoff to estimate DOC flux (kg/ha/yr). For the upper main stem sites (which were treated as tributaries), DOC flux (kg/ha/yr) was calculated using discharge-weighted concentration and total runoff which was then multiplied by watershed area to acquire a total cumulative flux (kg/yr) for each site. Total runoff for each sub-watershed was estimated from discharge measured at LMP27 (USGS station number 01073319) and LMP 73 (USGS station number 01073500). From these total cumulative fluxes, incremental fluxes were determined by subtracting the upstream flux from the downstream flux and any known tributary flux for that particular site. The resulting total flux was then divided by the area of the watershed to get area-weighted DOC flux (kg/ha/yr). All of these sites are designated as measured tributaries in Figure 2.

Secondly, a model was developed with which to predict DOC production in the landscape where discharge and concentration data was unavailable. In the Lamprey River Watershed, % wetlands has been found to be the best predictor of area-weighted DOC flux, therefore % wetland and DOC flux data was gathered where DOC concentration was available from both main stem sites and

tributary sites in order to estimate DOC flux from the unmeasured tributaries and riparian corridor (Fig. 2).

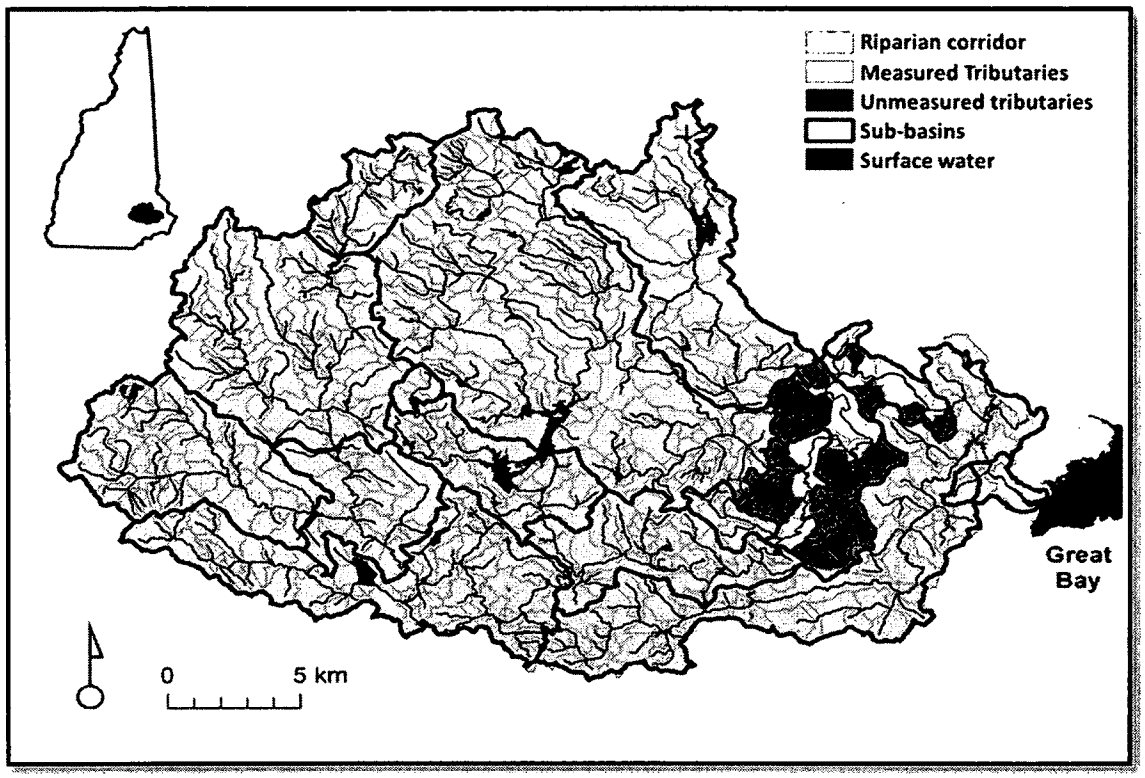


Figure 2. Location of the riparian corridor and both measured and unmeasured tributaries used in understanding carbon flux.

In order to minimize the amount of area from which we were predicting flux, we chose to examine only a portion of the lower main stem riparian corridor (LMP59-LMP73), treating the main stem above LMP59 as a tributary. This also allowed the use of those upper main stem sites (LMP07-LMP51) to be included as points in the model. Area-weighted fluxes were plotted against % wetlands for fourteen sites producing a model that could be used to estimate DOC contribution from both the unmeasured tributaries and the riparian corridor.

In ArcGIS 10.0, area and % wetlands was determined for the unmeasured tributaries and riparian corridor from LMP59-LMP73. Area-weighted fluxes were produced from the model and multiplied by total area to get total flux (kg/yr). Contribution from the riparian corridor was calculated as follows:

Riparian DOC (kg C/yr) = DOC @ LMP73 – DOC @ Measured tributaries - DOC @ Unmeasured tributaries

We then ran the % wetlands from our riparian corridor to estimate DOC flux from that area in order to further differentiate between possible in-stream production and wetland input. Lastly, using the 7 day incubation time and an estimated residence time of 3.5 days from the study reach to Great Bay, a degradation rate was determined and applied to the riparian DOC value to quantify the amount of carbon being transported downstream.

Analytical Measurements:

All water chemistry analyses were conducted at the Water Resources Research Center (WRRC) laboratory at the University of New Hampshire. Dissolved organic carbon (detection limit 0.1 mg C/L) and total dissolved nitrogen (detection limit 0.07 mg N/L) were measured using a Shimadzu TOC-5000 (Shimadzu Corp, Kyoto, Japan) coupled with TNM-1 Nitrogen Detector. Ammonium (detection limit 5 ug/L) was analyzed using a SmartChem 200 discreet automated colorimetric analyzer (Westco Scientific Instruments). Nitrate (detection limit 3 ug N/L) was

analyzed through ion chromatography using an Anions/Cations Dionex ICS-1000 with AS40 Autosampler. Dissolved organic nitrogen was calculated from filtered subsamples as TDN–(NH_4^++NO_3^-). Nitrite was assumed to be negligible. Specific ultraviolet absorbance (SUVA) was measured at 254 nm and normalized to DOC concentration.

Statistical Analyses:

Analysis of Variance (ANOVA) was used to compare solute means across sites and months and analyze the effects of Site and Month on BDOC with a significance threshold of $P < 0.05$. Tukey's HSD was conducted for post-hoc comparison of means. Linear regression was used to determine significant relationships between BDOC and initial DOC concentration, flow, initial DOC:DON ratio, and SUVA. Variables were tested for normality and log transformed in cases where kurtosis occurred. Statistics were performed in JMP Pro 10.

Two USGS gages exist on the main stem of the Lamprey River at site LMP27 and site LMP73. From these two gages, discharge was estimated for the other six sites. For each sampling date, discharge at main stem sites LMP07 and LMP19 was estimated using area-weighted discharge from site LMP27 (USGS station number 01073319) where discharge at sites LMP39, LMP51, LMP59, and LMP67 was estimated using area-weighted discharge from site LMP73 (USGS station number 01073500).

CHAPTER III

RESULTS

River Water Composition:

Stream solutes did not vary greatly between the eight sites with the exception of nitrate which had a range of 0.03 to 0.16 mg/L with the highest value occurring at LMP51 (Table 2). The DOC:DON ratio ranged from 27 to 31 with the highest value occurring at LMP07 and LMP19 (Table 2). Dissolved organic nitrogen showed a similar trend to DOC with increasing concentration from LMP07 to LMP73. DON and DOC were significantly and positively correlated (R^2=0.61, $P < 0.0001$). No significant relationship existed between mean annual DOC and flow (Appendix C-1) or SUVA and flow (Appendix D-2) for the study period. DOC concentration and SUVA were not significantly correlated (Appendix D-1).

Table 2. Chemical composition of the eight main stem sites with mean annual concentrations (± SE) for seven parameters.

Site	TDN (mg/L)	NO_3 (mg/L)	NH_4 (ug/L)	DON (mg/L)	PO_4 (ug/L)	DOC: DON	SUVA
LMP07	0.21±0.02	0.03±0	17.72±2.65	0.17±0.02	3.03±0.67	31 ± 2	4.41
LMP19	0.27±0.01	0.08±0.01	15.28±1.57	0.18±0.02	6.56±1.47	31 ± 3	4.17
LMP27	0.27±0.01	0.07±0.01	14.3±2.42	0.19±0.02	5.43±0.99	29 ± 2	3.92
LMP39	0.32±0.02	0.11±0.01	13.65±1.84	0.19±0.02	4.91±0.95	29 ± 2	4.26
LMP51	0.38±0.02	0.16±0.02	19.77±3.93	0.2±0.01	5.27±0.69	27 ± 1	3.89
LMP59	0.33±0.01	0.11±0.01	17.04±1.96	0.2±0.01	5.97±1.16	29 ± 2	3.92
LMP67	0.32±0.02	0.1±0.02	18.99±2.42	0.2±0.01	7.68±1.46	30 ± 2	3.95
LMP73	0.34±0.01	0.12±0.01	18.81±1.49	0.2±0.01	6.18±0.89	28 ± 1	4.05

Mean concentration of DOC for the eight main stem sites ranged from 5.07 to 5.87 mg/L and was not significantly different among sites although there was a slight trend of increasing concentration from LMP07 to LMP73 (Fig. 3). This pattern is consistent with mean DOC concentrations represented in the 2000-2011 data (Appendix B-1) although the trend in increasing concentration is not significant for the study period where it was significant for the 2000-2011 data (Appendix B-2).

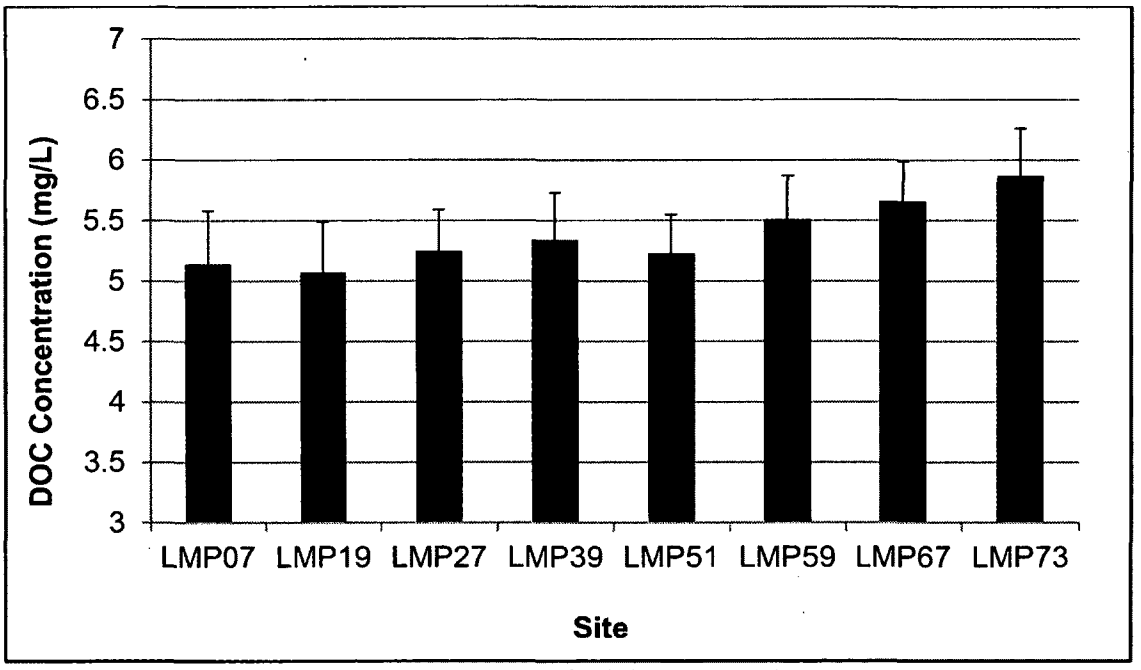


Figure 3. Mean DOC concentration (±SE) for the eight main stem sites throughout the entire sampling period.

There was greater temporal variation in mean DOC concentration with the fall months, particularly September and October, exhibiting significantly higher concentrations than the other nine months ($P < 0.0001$) (Fig. 4). Data from 2000-2011 also showed highest mean DOC concentration in the fall months (6.03 mg/L) although mean DOC concentration in the summer was nearly as high (5.84 mg/L) and was not significantly different from the fall (Appendix B-3).

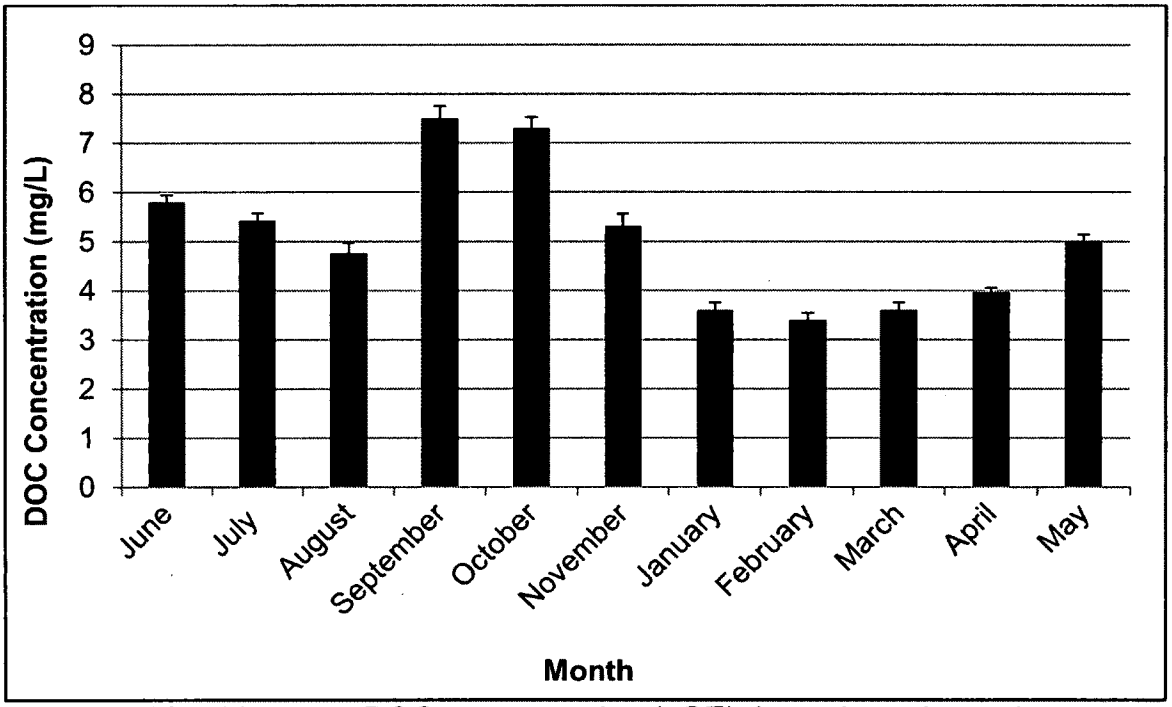


Figure 4. Monthly mean DOC concentration (±SE) throughout the entire sampling period.

One-way ANOVA revealed no significant difference in SUVA values by site but did show significant variation when compared by month (df = 10, F-ratio = 2.9496, $P < 0.0025$) with June exhibiting the highest mean value (4.64) and April the lowest (3.66) (Fig. 5). Mean SUVA value for all sites throughout the sampling period was 3.99.

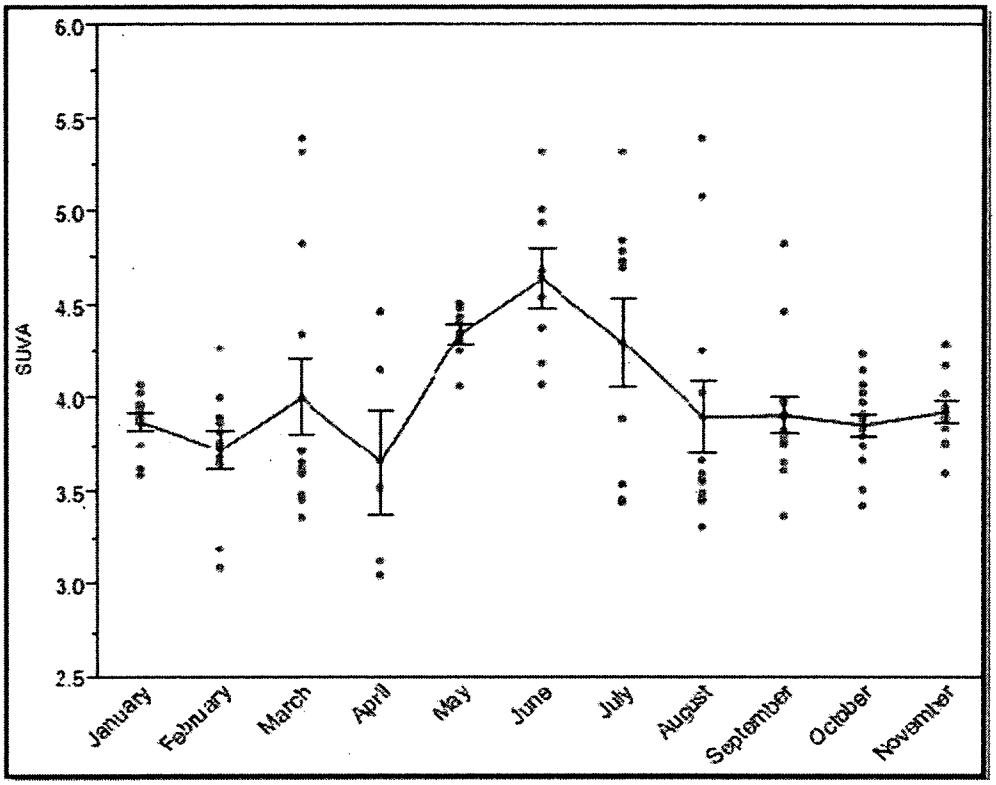


Figure 5. SUVA values across all sites by month for the study period. Solid line and bars represents the mean and standard error for each month. December was excluded due to lack of data.

DOC Biodegradation:

Mean BDOC for all sites on the main stem throughout the entire sampling period (n=366) was 5.8% (±1).

Spatial and Temporal Variation

When pooled over time, BDOC at each of the eight sites showed large variation with values ranging from 0% to upwards of 20% (Fig. 6). Because this large degree of variation occurred among all sites, mean values were similar. Mean BDOC for the eight sites ranged from 4% (LMP67) to 7% (LMP07) with no detectable trend from headwaters to mouth (Fig. 6). One-way ANOVA found that site location did not significantly affect BDOC. Coefficient of variation for replicates ranged from 0.4% to 16% with an average of 2.2%. In any case where variation was larger than 10%, the sample was not used.

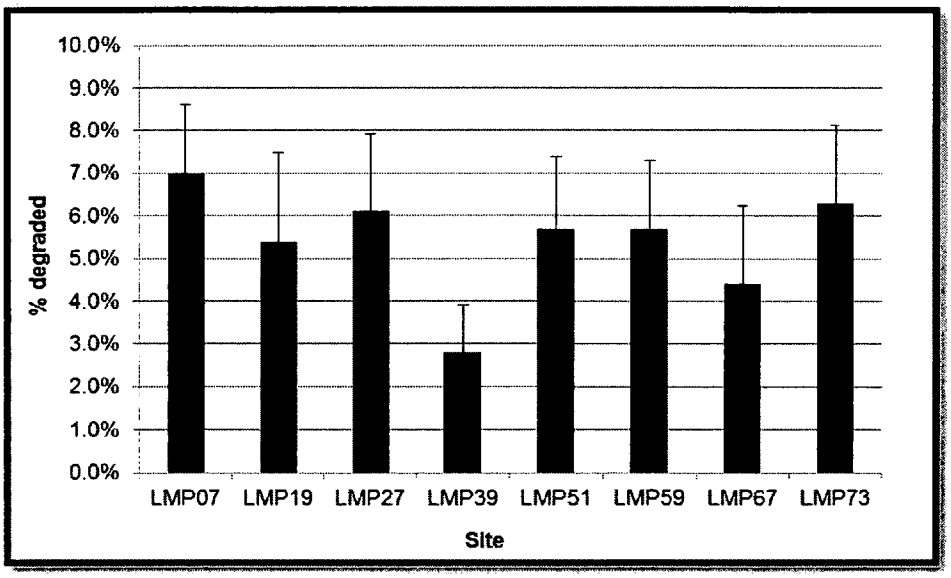


Figure 6. Mean BDOC for the eight main stem sites throughout the sampling period. Bars represent one SE from the mean.

When all sites were averaged by month, there were noticeable differences in mean values. BDOC ranged from 1% (November) to 13% (June) with June and July showing the highest values followed by October (Fig. 7). One-way ANOVA revealed that month significantly affected BDOC ($df = 10$, $F\text{-ratio} = 15.9755$, $P < 0.0001$). Post-hoc comparison analysis showed June with a significantly higher mean BDOC than most other sites ($P < 0.0001$).

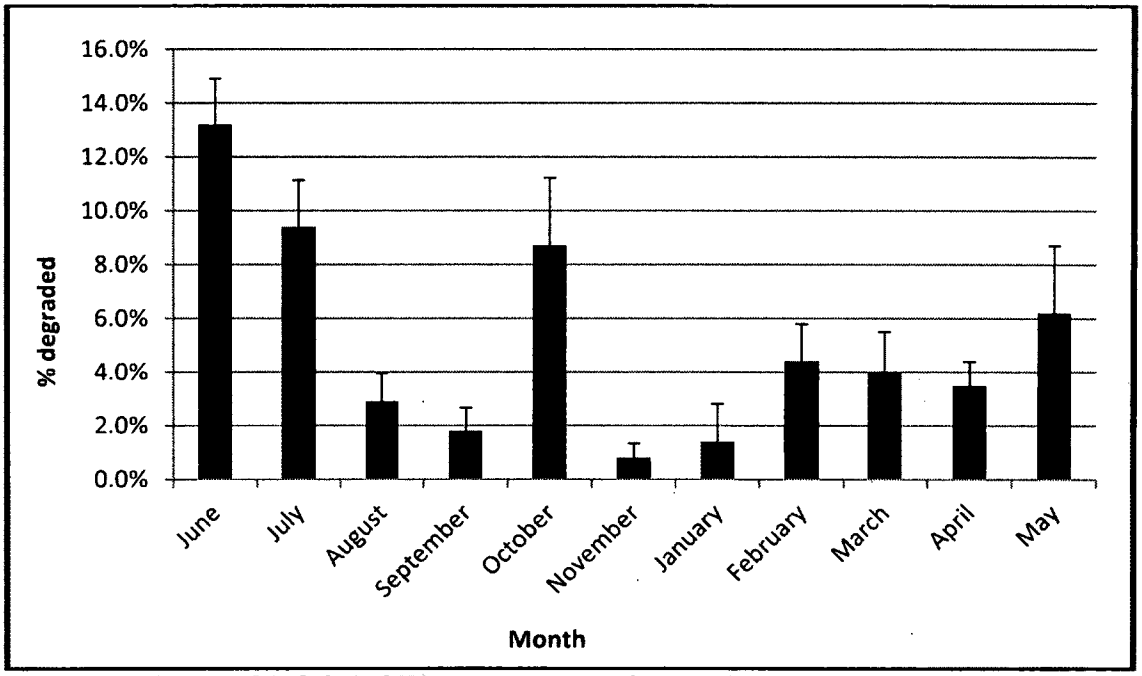


Figure 7. Mean BDOC (±SE) across sites for each month of the sampling period.

A seasonal analysis of BDOC also revealed significant differences (df = 3, F-ratio = 13.9472, $P < 0.0001$) with summer showing the highest BDOC of approximately 9% (Fig. 8).

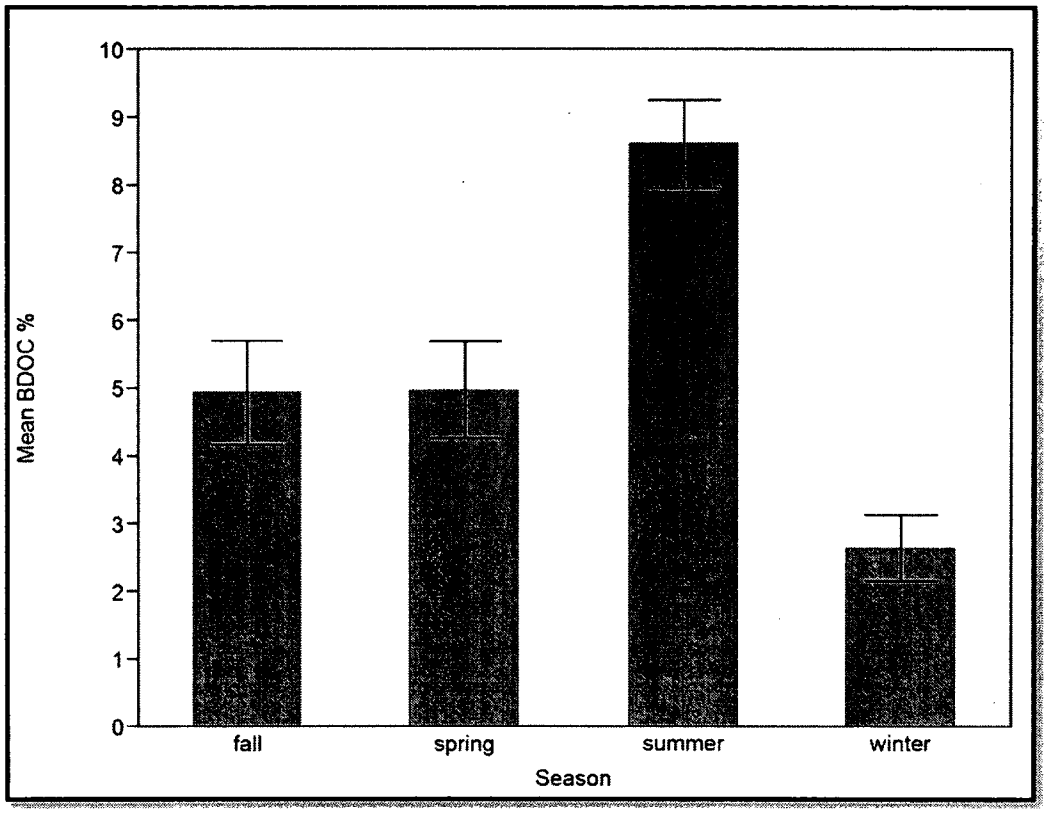


Figure 8. Mean BDOC (±SE) across sites by season throughout the entire study period.

Two-way ANOVA revealed a statistically significant interaction between Site and Season (df = 31, F-ratio = 3.0913, $P < 0.0067$) meaning that differences in BDOC among sites varied according to the season analyzed.

BDOC and in-stream characteristics

There was only a marginally significant relationship between initial DOC concentration and BDOC (R^2=0.03, P < 0.002) (Fig. 9). Exploration of relationships between BDOC and SUVA, DOC:DON ratio, and flow resulted in no significant findings (Appendix E). Land cover (wetland, forested, urban, and agriculture) was also not a successful predictor of BDOC.

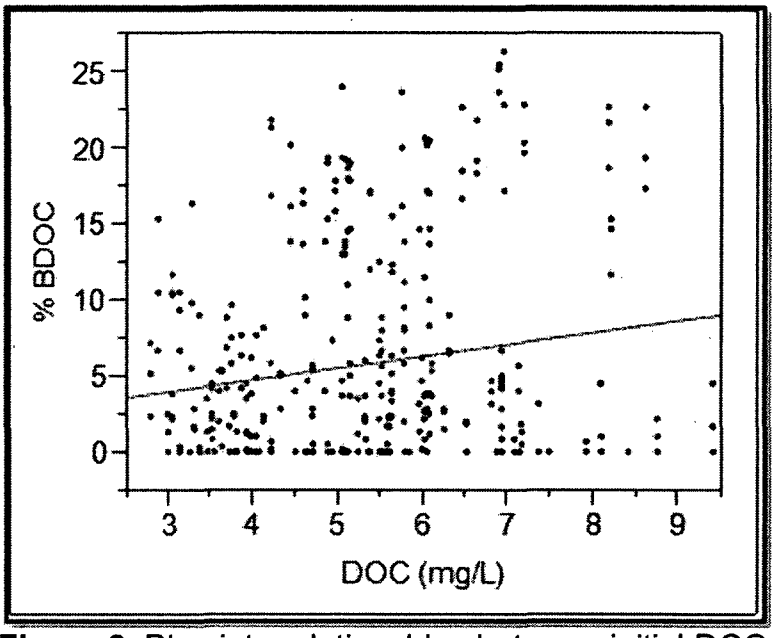


Figure 9. Bivariate relationships between initial DOC concentration and BDOC for all sites.

When the dataset was isolated by season and bivariate relationships between BDOC and other in-stream factors reassessed, the relationship between BDOC and initial DOC concentration was significant during the summer (R^2=0.26, P < 0.0001) and winter (R^2=0.15, P < 0.0009) (Fig. 10) but not for spring or fall.

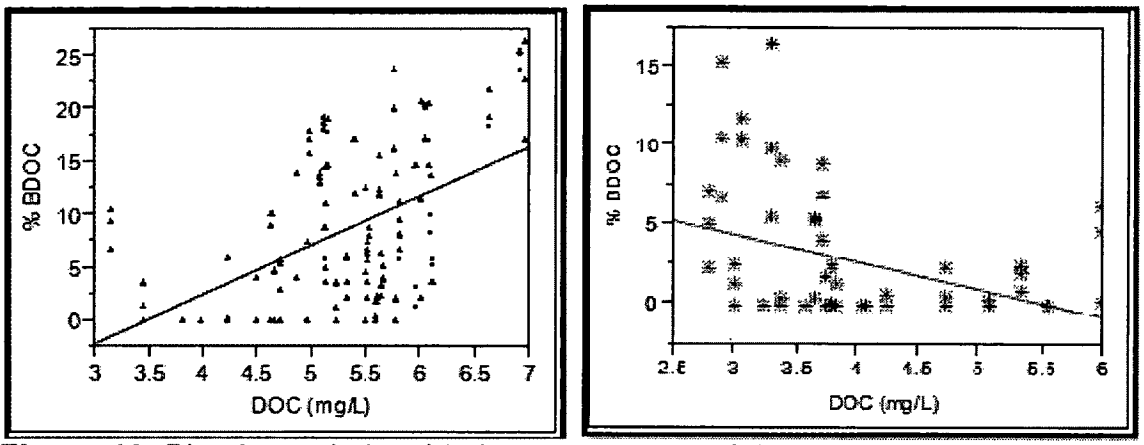


Figure 10. Bivariate relationship between initial DOC concentration and BDOC for the summer (▲) and winter (✱) months.

There was also a significant relationship between SUVA and BDOC in the spring (R^2 = 0.62, P < 0.0001) (Fig. 11).

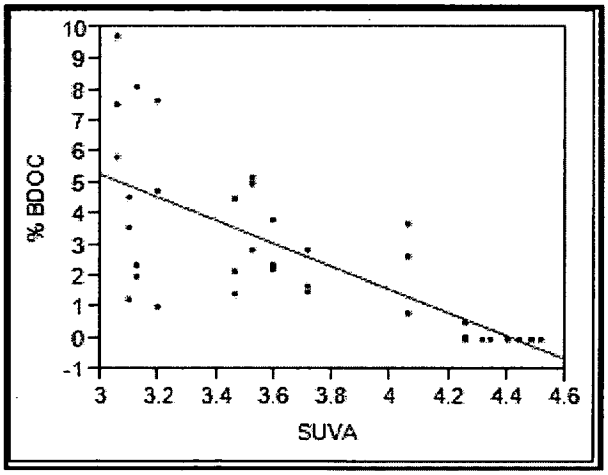


Figure 11. Bivariate relationship between SUVA and BDOC in the spring.

Seasonal spatial variation

On account of the significant interaction between site and month, spatial differences were furthered explored by season with the intent of teasing out the influence of biological processes. For BDOC, winter was the only month that showed a significant spatial trend of decreasing BDOC downstream ($R^2 = 0.12$, $P < 0.0036$) (Fig. 12). During the summer months when BDOC was highest, no relationship was found (Appendix F-1).

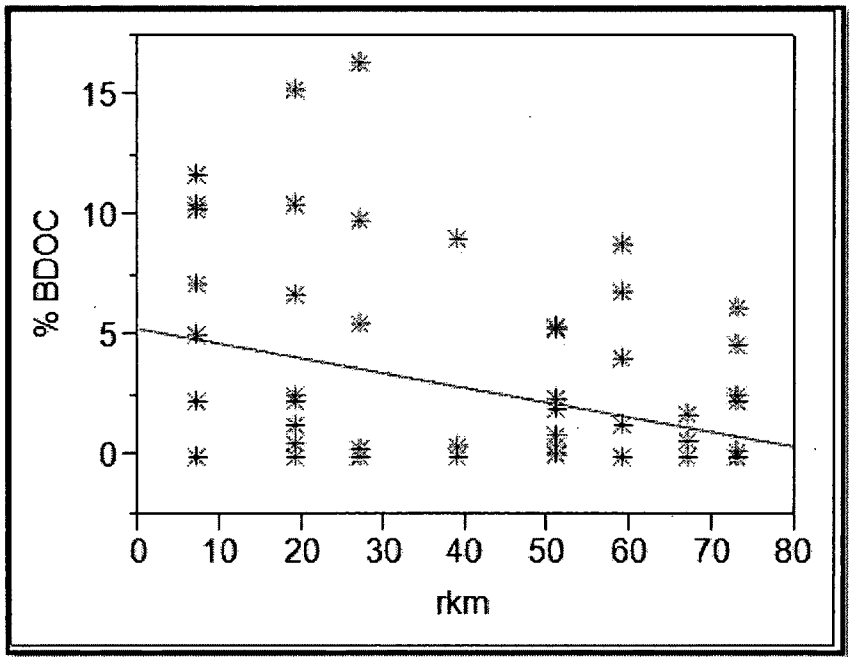


Figure 12. Relationship between rkm and BDOC during the winter months of the study period.

When analyzed by river kilometer (rkm) and season, DOC concentration showed a strong significant downstream increase during the winter (R^2=0.88, P < 0.0001) (Fig.13), but not during the other three seasons (Appendix F-2).

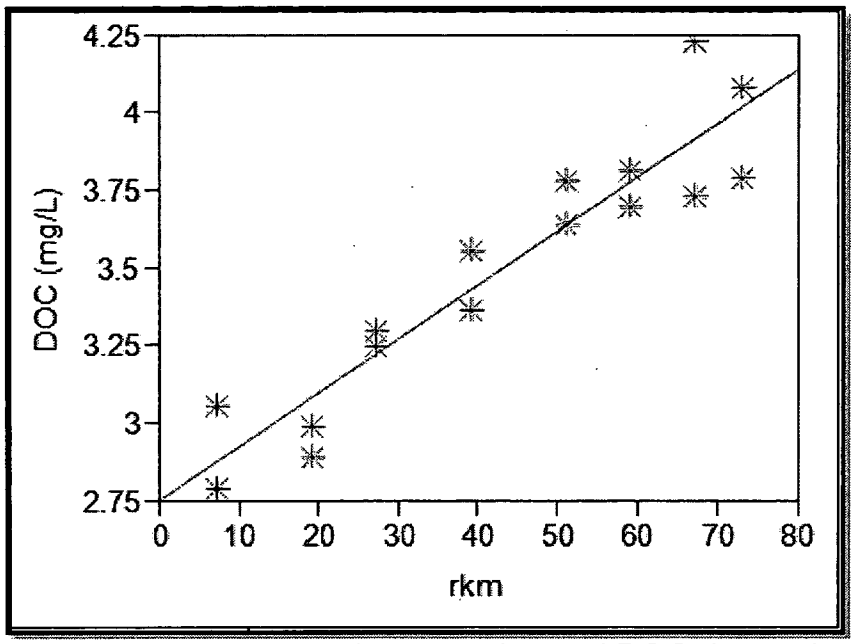


Figure 13. Relationship between rkm and DOC during the winter months of the study period.

When analyzed by rkm and season, SUVA showed a significantly negative relationship in the summer (R^2=0.31, P < 0.0001) and fall (R^2=0.19, P < 0.0001) (Fig. 14). No significant trend was detected during the spring or winter.

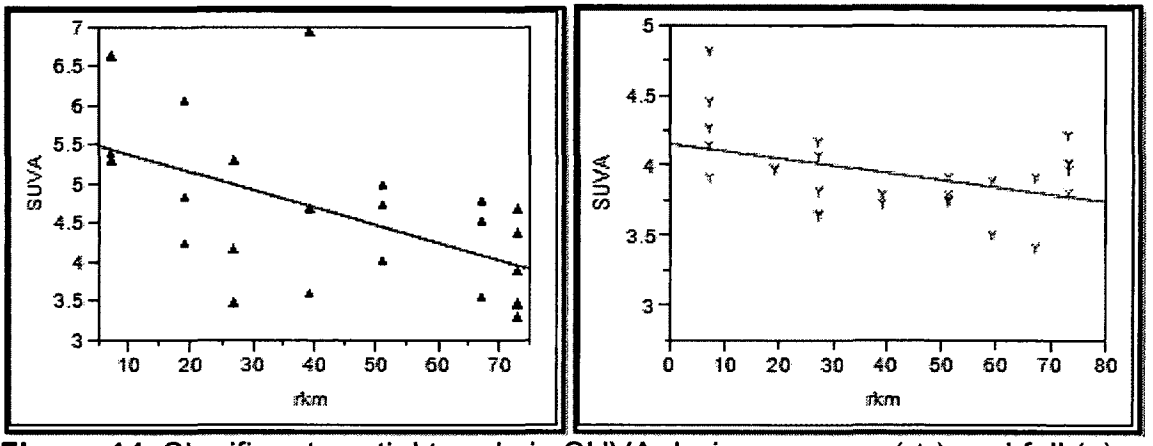


Figure 14. Significant spatial trends in SUVA during summer (▲) and fall (Y).

Time sequence of degradation

Sub-sampling of four sites on two selected dates in May and October showed a decrease in DOC concentration up until Day 7 for most sites at which point concentration increased (Fig. 15). Mean BDOC for all sites (n=8) reported at Day 7 was 19% compared to 7% at Day 10.

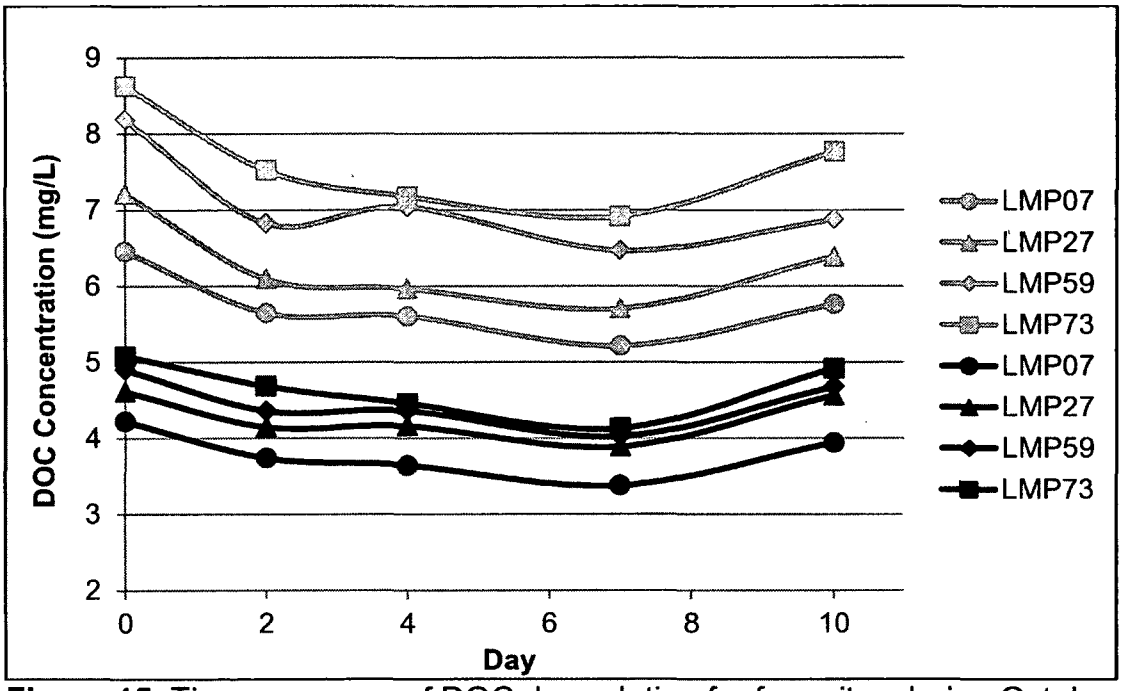


Figure 15. Time sequence of DOC degradation for four sites during October 2011 (grey line) and May 2012 (black line).

Photolysis:

Exposure to sunlight did not directly degrade DOC at either site (Table 3). Although the table reports small percentages of degradation, similar amounts of DOC loss occurred in both the light exposed flask and the dark control flask for both sites that were not significantly different. Furthermore, sun exposure had no significant effect on availability of DOC to the microbial community with only a 3.4% and 4.7% loss at LMP07 and LMP73 for the microbial light exposed treatment. At both sites, there was an increase in DOC concentration for the dark treatment bioassays resulting in negative degradation values.

Table 3. Percent degraded of DOC from photolysis and/or microbial degradation. Positive percentage indicates a loss in concentration where a negative value indicates an increase in concentration.

Site	Experiment	Treatment	Change in concentration
LMP07	photolysis	light	6.1 %
LMP07	photolysis	dark	5.3 %
LMP07	microbial	light	3.4 %
LMP07	microbial	dark	-6.7 %
LMP73	photolysis	light	5.3 %
LMP73	photolysis	dark	4.7 %
LMP73	microbial	light	4.7 %
LMP73	microbial	dark	-1.8 %

Riverine DOC Modeling:

The model created from our fourteen tributaries using % wetlands and DOC flux was significant (R^2=0.54, P < 0.003) (Fig. 16). Percent wetlands ranged from 1.6 to 16.4 and DOC flux ranged from 16.69 to 47.28.

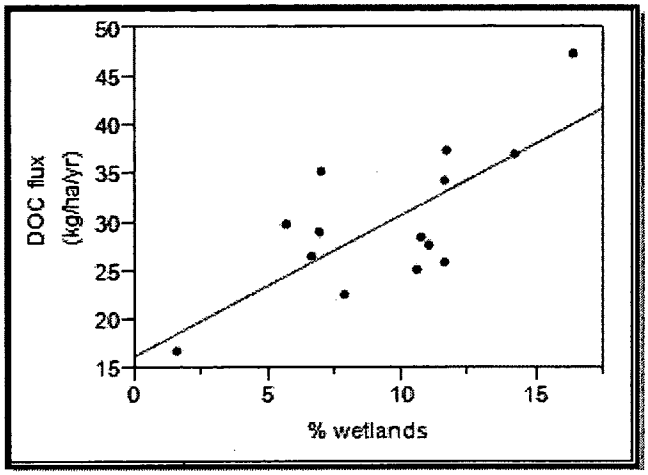


Figure 16. Predictive DOC flux model using percent wetlands (DOC flux (kg/ha/yr) = 16.303414 + 1.4569454*% wetlands).

Total flux calculated at LMP73 for the entire study period was 1,566,150 kg C/yr (Fig. 17) where total flux from the measured tributaries was 1,266,666 kg C/yr and modeled flux from the unmeasured tributaries was 103,637 kg C/yr. Percent contribution of C from both measured and unmeasured tributaries and the riparian corridor can be seen Figure 17. When taking model error into account by using slope and intercept at the upper and lower 95% bounds, flux from the unmeasured tributaries was 161,433 kg C/yr and 45,836 kg C/yr resulting in a percent contribution range from the riparian corridor of 9 to 16%.

The degradation rate calculated from incubation time and mean BDOC was 0.86% per day or approximately 3% for the 3.5 day residence time which resulted in a total loss of 5,680 kg C/yr.

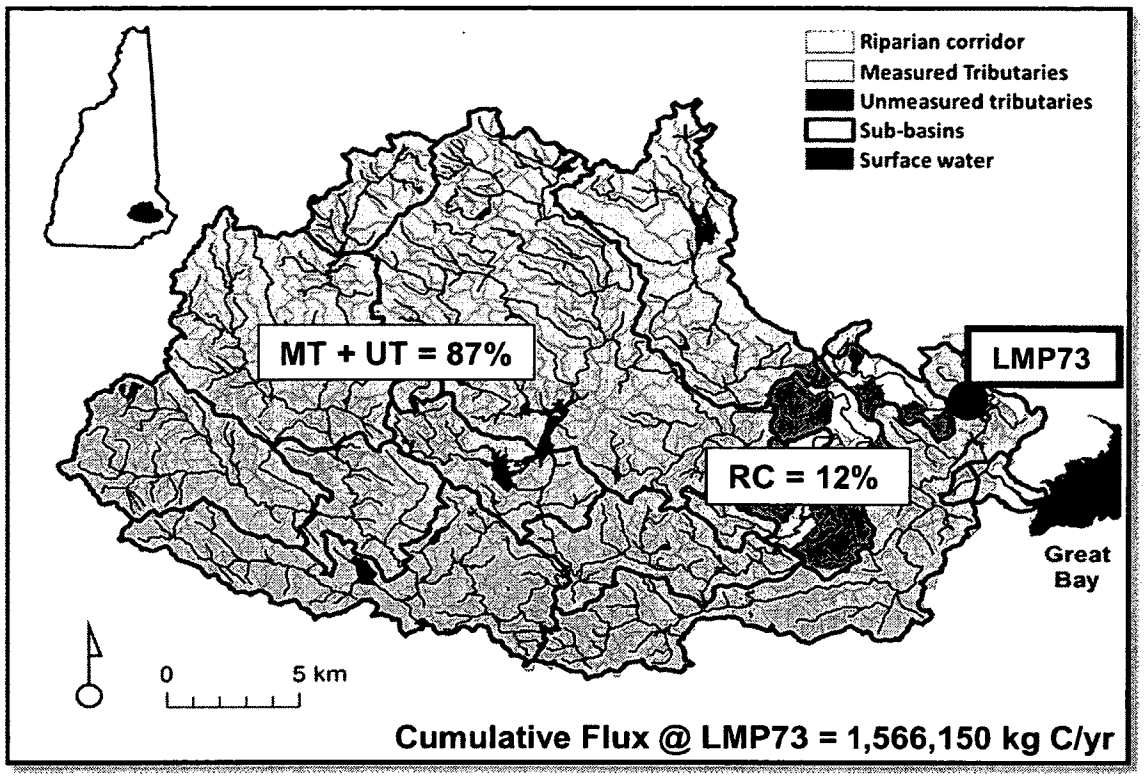


Figure 17. Map showing the percent DOC contribution from both the measured (MT) and unmeasured tributaries (UT) and the riparian corridor (RC).

Percent wetlands in the riparian corridor (12.7%) resulted in a flux of 48,263 kg C/yr. When that value was included as another parameter in our equation, the remaining C in-stream was 141,904 kg C/yr or 9% of total DOC being produced in the landscape. The fringing wetlands in the riparian corridor of the main stem were accounting for only 3% of the C input versus the 9% possibly being produced in-stream.

CHAPTER IV

DISCUSSION

High resolution samplings in the main stem of the Lamprey River revealed that neither microbial utilization nor photolysis were significant causes of DOC transformation on an annual scale. Furthermore, temporal variation in BDOC rather than spatial variation plays a much more important role when considering main stem C dynamics.

DOC Biodegradation:

The overall DOC loss of only 5.8% in the main stem suggests a chemical composition of DOC that renders it largely unavailable to the Lamprey River microbial community. Chemical composition of DOC is a product of both source and flow path. With respect to source, the Lamprey River Watershed is a primarily forested landscape (69%), resulting in riverine DOC that is mostly of terrestrial origin. Terrestrially derived stream DOC is humic and lignin-rich, consisting of high molecular weight compounds and hydrophilic acids, generally considered to be unavailable to bacteria (Qualls and Haines, 1992; Aitkenhead-Peterson et al. 2003). A heavily forested landscape also implies less input from anthropogenic sources such as waste water treatment plants and nonpoint sources which are largely considered to be more labile supplies of carbon (Petrone et al. 2009; Wiegner et al. 2004). The Lamprey Watershed currently has

only one small waste water treatment plant discharging into the main stem and while population growth is increasing, it is unclear to what extent DOC quality will be affected by nonpoint sources.

Algal and/or macrophyte production of DOC in-stream can also contribute to the DOC pool and has been found to be readily available to bacteria (Cole et al. 1982; Mann and Wetzel, 1996). In the Lamprey, the actual contribution of this source is unknown as a detailed organic matter budget has not been conducted, however in an analysis of organic matter budgets for 29 streams, Webster and Meyer (1997) found that in-stream primary production accounted for more than 40% of carbon input in eight of the streams and more than 80% in five streams (Bertilsson and Jones, 2003). These results were largely dependent on stream size, temperature, and light availability. As the Lamprey is a sixth order stream with temperatures reaching 24°C in the summer, one could suggest that in-stream production is a significant contributor to the DOC pool but only on a seasonal scale, particularly during the summer when light intensity and stream temperature are highest.

The flow path of water from terrestrial to aquatic systems also has the potential to affect DOC composition (Aitkenhead-Peterson et al. 2003; Findlay et al. 2001; Hood et al. 2006). As water infiltrates the soil, concentration and composition change due to adsorption of hydrophobic compounds in mineral soil (Kaiser and Zech, 1998; McDowell and Likens, 1988) and utilization of labile carbon by soil microbes (Qualls and Haines, 1992; Kalbitz et al. 2003). In cases where base-flow dominates stream water, DOC composition may be more

recalcitrant due to prior soil processing whereas with storm-flow, DOC concentration is higher on account of a flushing response from riparian area and catchment hill-slopes (Hood et al. 2006) and more labile due to shorter residence time in soils and lack of contact with the mineral horizon. For the Lamprey River Watershed, the abundance of wetlands confounds this model resulting in no significant relationship between flow and DOC concentration (D-2) or flow and BDOC (Appendix E-3) indicating that hydrologic transport was not as important as DOC source when understanding in-stream concentration and composition. This idea was further confirmed by the lack of influence flow exerted on SUVA values (Appendix C-4), a direct indicator of DOC composition. Mullholand (2003) suggested that wetland presence can cause surface flow paths to dominate even during times of high flow, thus eliminating any "flushing" effect and subsequent change in composition.

In addition to source and transport, there is also the possibility that DOC experienced prior processing in tributaries. The eight tributaries sampled by the McDowell lab throughout the study period showed a wide range in DOC concentration (0.9 to 10.4 mg/L), but more constrained SUVA values with an overall mean of 4.15 (±0.10). This 4.15 mean corresponds to an approximately 30% aromatic content according to the linear model developed by Weishaar et al. (2003) and is slightly higher than values reported in the main stem indicating an increasing difficulty in utilization. Without conducting bioassays for each tributary, it is difficult to draw any solid conclusion about the extent of in-stream processing that might have occurred.

Our mean DOC biodegradation value compares well to other studies of riverine DOC degradation. It's within the 0 to 72% range of riverine DOC biodegradation reported by Wiegner et al. (2006), and compares well to the del Giorgio and Davis (2003) review that reported only a 6% DOC loss over five days and the study by Wiegner et al. (2006) of BDOC from nine rivers in the eastern United States that found only 4% DOC consumed over six days. However; it is noticeably lower compared to the Sondergaard and Middleboe (1995) meta-analysis that documented an average of 19% degradation in riverine systems. This discrepancy can be attributed to factors related to incubation set up such as incubation time, temperature, nutrient availability, light availability, bacterial community composition, and DOM chemical composition (reviewed in del Giorgio and Davis (2003) and Marschner and Kalbitz (2003). Because all studies are constructed differently, making across the board comparisons is difficult, thus emphasizing the need for standardized incubation methodology (McDowell et al. 2006).

Spatial and Temporal Variation

It was originally proposed that the heterogeneity of both the watershed and the main stem would result in significant spatial differences in BDOC. That was not the case in the Lamprey for BDOC (Fig. 6) or any other indicators of DOC composition such as DOC concentration (Fig. 3), SUVA, and DOC:DON ratio (Table 2). These results speak to the ability of the river to assimilate heterogeneity of both in-stream and watershed processes that affect DOC

concentration and composition on an annual scale and suggest that source and flow path may be more similar at each site than previously hypothesized.

Longitudinal studies of DOC bioavailability in a single river continuum are scarce; however, Maranger et al. (2004) reported on bacterial production (BP) and bacterial respiration (BR) in a 250km stretch of the Hudson River and found that BP was higher in the northern reaches versus the lower whereas respiration showed no spatial pattern. Higher BP rates in the north were attributed to specific quantified DOC inputs such as sewage effluent and macrophyte leachate. Stable respiration rates were indicative of the concept that all bacterial cells respire, yet only some divide and increase biomass creating a difference in the two parameters. Lamprey bioassay methodology did not differentiate between BP and BR, therefore the absence of any spatial differences in BDOC may reflect the consistent respiration rates depending on the proportion of degradation that was mineralization versus uptake. More likely, land cover in the Lamprey Watershed and the physical characteristics of the main stem channel are not diverse enough to produce significant spatial differences in DOC composition.

Temporal variation exerted much more influence than spatial variation on BDOC and other in-stream characteristics. June and July showed the highest amount of BDOC when in-stream production of labile DOC from algae and macrophytes was greatest (Fig. 7). There was another pulse during October when leaf litter input became a part of the DOC pool providing more labile sources. DOC concentration was highest in the fall months (Fig. 4) on account of leaf litter input yet that was not reflected in the BDOC values as they were

highest in the summer (Fig. 8) highlighting the significance of autochthonous production for main stem carbon dynamics. The lack of relationship between both DOC concentration (Appendix C) and flow and BDOC (Appendix E-3) and flow verifies that this temporal variation was not driven by discharge. Surprisingly few studies have looked at seasonal effects on riverine DOC bioavailability. Wiegner and Seitzinger (2004) found that BDOC was higher in the spring and fall rather than summer in pristine and polluted wetlands which they attributed to soil freezing and thawing. Several other studies have concluded that DOC lability increases during spring flooding (Michaelson et al. 1998; Holmes et al. 2008), yet these studies were carried out in Arctic systems where DOC dynamics fundamentally differ due to the presence of permafrost. The Wiegner et al. (2006) study that reported on BDOC for nine rivers in the east found only 4% degradation during summer months where Petrone et al. (2009) found a range of 1-17% BDOC in ten rivers in southern Australia during summer base-flow compared to the 8% Lamprey BDOC. This range in BDOC again highlights the difficulty in making cross system comparisons when differences in incubation methodology and initial DOC composition exist.

Throughout the study period, SUVA values were highest during the summer months particularly June and July (Fig. 5) and within the range of reported values for other studies (Petrone et al. 2009; Wiegner et al. 2006). As SUVA is a surrogate measure of the aromatic content of DOC and thus, a proxy for humic content (Weishaar et al. 2003), high summer SUVA values are indicative of terrestrial-derived DOC that has already been processed in soils.

BDOC and in-stream characteristics

The lack of any strong significant relationships between BDOC and other in-stream characteristics on an annual scale is evidence that these parameters vary throughout the seasonal hydrograph. The relationship between initial DOC concentration and BDOC was only marginally significant indicating that higher concentrations do not necessarily mean greater lability. Evidence of this in the Lamprey is seen by observing seasonal trends in DOC concentration and BDOC specifically during fall and summer. The fall is when DOC concentrations are highest and although there is a pulse in BDOC, it is not nearly as high as in the summer. When the relationship is revisited on a seasonal basis, initial DOC concentration and BDOC are not correlated in the fall but in the summer when a labile source of carbon is being produced in-stream causing the relationship to become much stronger (Fig. 10). A commonly accepted paradigm in river ecology is that a larger DOC pool implies a larger source of energy for microbes (Sondergaard and Middleboe, 1995), yet that is not necessarily the case depending on variation in DOC source as seen in the Lamprey and also in the del Giorgio and Davis review that found no significant relationship between initial DOC concentration and BDOC in their meta-analysis of 45 rivers. The relationship between decreasing BDOC and increasing DOC concentration in the winter (Fig. 10) is not as easily explained. It could be that the labile portion of the DOC pool stays relatively constant through changes in DOC concentration (due to the absence of in-stream production/utilization) so that any increase in concentration is mostly refractory compounds.

The relationship between BDOC and SUVA has yet to be reconciled in the scientific community with studies reporting both the existence and absence of relationships. Fellman et al. (2009) described a non-significant relationship between BDOC and SUVA in a forested upland stream which was attributed to complex and various interactions between abiotic and biotic removal and differences in soil hydrologic flow paths. Petrone et al. (2009) also found higher BDOC values in riverine samples with higher SUVA values than reported for the Lamprey although the time scale for degradation was longer. Contrastingly, Kalbitz et al. (2003) showed a significant negative correlation between BDOC and SUVA in soils. For the Lamprey, the lack of relationship between SUVA and BDOC on an annual scale indicates that the aromatic content of the DOC pool is not driving utilization and that different factors may be driving variability in the two. While a relatively strong relationship between BDOC and SUVA exists in the spring, the relatively low BDOC values make it difficult to draw a solid conclusion. It would be helpful if future research in BDOC incorporated both pre-incubation SUVA and post-incubation SUVA to further delineate the relationship between these two DOC quality parameters in order to determine what components of the DOC pool are being utilized during incubation. Ultimately, these results suggest that for the Lamprey system, SUVA is not a good indicator of BDOC and other factors should be explored such as fluorescence which has been proven to be a useful predictor (Fellman et al. 2008).

Because flow does not appear to be a driver of either DOC quality or quantity, these seasonal changes in relationships can be mostly explained by a

shifting DOC source, specifically through in-stream production during the summer and leaf litter input in the fall. Furthermore, the lack of relationship between BDOC and flow and SUVA and flow indicates that flow paths are not changing to an extent that affects DOC composition during high flow events which could partly be explained by the presence of wetlands. However; it should be noted that this was a relatively low flow year with highest flows occurring in November and December, two months that are under represented by the sampling regime. Higher flow years could produce a different scenario.

Seasonal spatial variation

Exploration of spatial variation by season for several parameter led to further insight on DOC quality and quantity dynamics in the main stem. When analyzed by rkm and season, BDOC showed a significant decreasing downstream trend during the winter only (Fig. 12). Assuming that in-stream biological processes are greatly reduced during the winter, this relationship indicates a change in DOC composition independent of autochthonous production. More surprisingly, was the lack of relationship during the summer when autochthonous production was highest and the lower reaches of the river did not show higher values indicating that in-stream production is consistent along the river continuum. A detailed analysis on primary production and macrophyte coverage across sites is needed to confirm this finding.

DOC showed a strong significant increase in concentration downstream during the winter only, illustrating the lack of biological processes occurring

during those months. In the winter, temperature limits in-stream processing allowing DOC concentration to increase downstream. Relationships between DOC and rkm during other seasons showed much more scatter in the downstream direction (Appendix F-2). While variation in DOC concentration can be caused by several factors, such as microbial utilization, hydrologic regime, and morphological change (Vannote et al. 1980), the trend in DOC concentration in the winter clearly identifies the importance of biological processes in this system during warmer months. A similar finding was reported by Sabater et al. (1993) in the Ogeechee River where intermediate and high molecular weight DOC showed a more linear longitudinal pattern than labile compounds.

Longitudinal trends in SUVA became much more apparent when examined by season. Summer and fall showed significant decreasing longitudinal trends meaning aromatic content became reduced downstream which could be a product of changing DOC source through in-stream production and leaf fall. SUVA may also be at the cusp of reflecting a population signal evidenced by the significantly negative relationship between SUVA and % urban land cover. As high spatial and temporal resolution SUVA for a single system has not been reported on thus far in the literature, drawing conclusions about these patterns is difficult.

Time sequence of degradation

The time sequence of DOC degradation (Fig. 15) illustrates the importance of incubation time in assessing degradation and also provides insight into kinetics of

the decay process. Sites within each month showed a comparable linear decline until day 7 confirming the similar composition of DOC along the main stem. October saw a slightly higher BDOC than May, the majority of which occurred by Day 2 indicating a readily usable DOC most likely a product of leaf fall. Concentration in all sites increased by Day 10 probably due to lysis of bacterial cell walls as carbon evolution was also observed in the control flasks at this time. Average BDOC for the eight sites at Day 7 was almost double the BDOC documented at Day 10 due to carbon production from the inoculum.

Photolysis:

Photolytic removal of DOC in aquatic environments has been reported to range from 0 to 50% under exposure to natural sunlight and up to 60% under artificial light exposure (Wiegner and Seitzinger, 2001). This large spread in values reflects the differences in exposure methodology as well as the inherent complexity in DOC composition and how it reacts to sunlight. In the Lamprey, sun exposure did not appear to directly degrade DOC nor did it alter the composition of DOC molecules in terms of making them more labile to the microbial community (Table 3). Small amounts of degradation did occur in the light exposed flasks but a similar amount also degraded in the dark treatment leading to the conclusion that no sun-induced degradation actually occurred.

Other studies conducting natural sun exposures have reported varying results on DOC degradation. Wiegner (2001) reported no photolytic degradation of DOC in runoff from either agricultural or anthropogenic sources whereas Amon and Benner (1995) found that over 15% of DOC in the Amazon was photochemically reactive. It has also been reported that initial DOC composition is responsible for the extent to which the DOC degrades where humic-rich organic matter is more available to photolysis than algal-derived DOC (Amado et al. 2005). Given that the Lamprey samples were taken during the summer when algal-derived DOC was presumably the highest, it may be that the composition was resistant to change although the fact that microbial degradation did not occur in the dark treatment bioassay (Table 3) hampers this theory. If the DOC was algal-derived, microbial degradation would be expected to have occurred.

Additionally, Tranvik et al. (2001) found that photolysis had no effect on DOC degradation and it also altered the composition of the DOC pool in such a way to make it less available to the microbial community. The study concluded that DOC compounds from algae which contain no lignin and are less aromatic can be converted to compounds of lower lability through photochemical condensation reactions that render the pool less prone to degradation. Furthermore, humic-rich terrestrial DOC becomes more available due to the breakdown of high molecular weight compounds (Moran and Zepp, 1997).

Isotopic tracers have shown that summer base-flow in the Lamprey is sourced from a very shallow groundwater reservoir resulting from surrounding surface water bodies and wetlands (Frades, 2008) indicating that water is consistently exposed to the sun in this system with no effect on the DOC pool. However, further studies are required to understand if that result changes on a seasonal basis as DOC composition changes.

Riverine DOC Modeling:

The DOC modeling exercise provided a better understanding of carbon sources within the landscape by identifying a 12% contribution of DOC from the riparian corridor in the lower reaches of the river (Fig. 17). Due to proximity to the main stem of the river, carbon sourced from this riparian corridor is most likely less processed than carbon being input from the farther reaches of the landscape and therefore much more susceptible to degradation. Coupled with the relatively short travel distance from this corridor to the Great Bay outlet, additional riverine processing is unlikely, suggesting an input of labile carbon to the Great Bay. Further utilization of the model provided a distinction between C being input from fringing wetlands in the riparian corridor versus C being produced in-stream. A 9% contribution from in-stream is relatively large compared to the 3% loss that C in this reach experiences en route to the bay. Therefore, when considering C dynamics in the main stem, production is bigger relative to loss indicating that C from the Lamprey is a potentially significant usable source of energy in the bay.

Delineating carbon processing in the estuary is a recommended avenue for future research not only for understanding the cycling and export of carbon, but also for shedding light on dissolved organic nitrogen (DON) dynamics. Nitrogen impairment is currently the most pressing environmental concern for the Great Bay and as DON has been shown to be the dominant form of nitrogen leaving the Lamprey River Watershed, it's utilization in the bay is of interest. Studies have shown estuarine DON bioavailability to be 23% from forested landscapes and as high as 59% from urban/suburban landscapes (Seitzinger et

al. 2002). As the Lamprey is becoming increasingly urbanized, DON bioavailability will probably increase further compounding nitrogen impairment.

Using DOC consumption as a proxy for DON requires some initial experimentation to determine their synchronicity as they have been shown to be utilized at dramatically different rates in riverine systems with DON degradation being much higher (Petrone et al. 2009, Wiegner et al. 2006). Preliminary investigation into Lamprey DOC degradation in the estuary was conducted by inoculating Lamprey DOC in late spring with estuarine bacteria. Over a ten day incubation period, no degradation occurred although that could change with longer incubation times.

CHAPTER V

CONCLUSION

The 5.8% annual mean DOC loss in the main stem of the Lamprey is a measure of the *potential* for DOC to be utilized under optimal conditions. This study took a biological approach to assessing DOC quality through lab bioassays and therefore does not reflect *in situ* degradation rates which most likely vary both spatially and temporally on immeasurably small scales. It also does not take into account the possibility of hyporheic processing which has been shown to be an efficient utilization location of DOC, more so than lab incubations (Sobczak et al. 2002).

This study does however begin to create a picture of C cycling in the Lamprey River by identifying the importance of temporal variation in DOC composition more as a result of seasonal changes in biotic demand rather than hydrologic flowpath. Of course, this temporal variation is representative of only one year and may vary under different hydrologic regimes especially considering that the study period was a relatively low flow year that did not experience significant snow melt. This study also illustrated the relative unavailability of DOC to the Lamprey microbial community which could have implications for the Great Bay depending on extent of DOC processing in the estuary.

Because the Lamprey River Watershed has one of the fastest growing populations in the country, it is inevitable that both DOC quantity and quality will

be impacted. Evidence of this effect is already being seen through the significant negative relationships between urban land cover and SUVA values. DOC utilization has been shown to be greater in urban catchments (Petrone et al. 2009) and as a result, could potentially change the metabolism of the river by becoming more labile. Future research should focus on identifying chemical markers of BDOC and understanding how intensifying urbanization will affect DOC composition in the Lamprey River.

REFERENCES

Aitkenhead, J.A. and W.H. McDowell. 2000. Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochemical Cycles 14: 127-138.

Aitkenhead-Peterson, J.A., McDowell, W.H., and J.C. Neff. 2003. In: Aquatic Ecosystems: Interactivity of Dissolved Organic Matter (eds Findlay, S. E. G. & Sinsabaugh, R. L.) (Academic Press, Massachusetts).

Amado, A.M., Farjalla, V.F., Esteves, F.A., Bozelli, R.L., Roland, F., and A. Enrich-Prast. 2006. Complementary pathways of dissolved organic carbon removal pathways in clear-water Amazonian ecosystems: photochemical degradation and bacterial uptake. FEMS Microbial Ecology 56: 8-17.

Amon, R.M.W. and R. Benner. 1996. Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River System. Geochemica et Cosmochimica Acta 60: 1783-1792.

Aufdenkampe, A.K., Mayorga, E., Raymond, P.A., Melack, J.M., Doney, S.C., Alin, S.R., Aalto, R.E., and K. Yoo. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Frontiers in Ecology and the Environ 9: 53-60.

Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, J.D., and Sabater, F. 2008. Biophysical controls on organic carbon fluxes in fluvial networks. Nature 1: 95-100.

Bertilsson, S. and J.B Jones Jr. 2003. Supply of dissolved organic matter to aquatic ecosystems: autochthonous sources. In: Aquatic Ecosystems, Interactivity of Dissolved Organic Matter. (eds Findlay and Sinsabaugh) (Academic Press).

Caraco, N. and Cole, J. 2004. When terrestrial organic matter is sent down the river: the importance of allochthonous carbon inputs to the metabolism of lakes and rivers. In: Food Webs at the Landscape Level (eds Polis, G.A., Power, M.E., and Huxel, G.R.) (University of Chicago Press).

Cole, J.J., G.E. Likens, and D.L. Strayer. 1982. Photosynthetically produced dissolved organic carbon: An important carbon source for planktonic bacteria. Limnology and Oceanography 27: 1080-1090.

Cole J.J. and Caraco NF. 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Marine and Freshwater Resources 52: 101–10.

Cole, J. J., Praire, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middleburg, J.J., and Melack, J. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems 10: 172–185.

del Giorgio, P.A. and J. Davis. 2003. Patterns in dissolved organic matter lability and consumption across aquatic ecosystems. In: Aquatic Ecosystems, Interactivity of Dissolved Organic Matter (eds Findlay and Sinsabaugh) (Academic Press).

Fellman, J.B., D'Amore, D.V., Hood, E. and R.D. Boone. 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry DOI 10.1007/s10533-008-9203-x.

Fellman, J.B., Hood, E., D'Amore, D.V., Edwards, R.T., and D. White. 2009. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. Biogeochemistry 95: 277-293.

Findlay, S.E.G., Quinn, J.M., Hickey, C.W., Burrell, G., and M. Downes. 2001. Effects of land use and riparian flowpath on delivery of dissolved organic carbon to streams. Limnology and Oceanography 46: 345-355.

Findlay, S.E.G. and R.L. Sinsabaugh. 2003. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press.

Frades, M.C. 2008. Hydrologic analysis of the headwaters Lamprey River Watershed using water isotopes. M.S. Thesis. University of New Hampshire.

Graneli, W., Lindell, M., and L. Tranvik. 1996. Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content. Limnology and Oceanography 41: 698-706.

Hedges, J. I., Keil, R. G., Benner, R., Kvenvolden, K., and Curiale, J. 1997. What happens to terrestrial organic matter in the ocean. Organic Geochemistry 27: 195–212.

Hood, E., Gooseff, M.N., and S.L. Johnson. 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. Journal of Geophysical Research 111.

Kaiser, K. and W. Zech. 1998. Rates of dissolved organic matter release and sorption in forest soils. Soil Science 163: 714-725.

Kalbitz, K., Schmerwitz, J., Schwesig, D., and Matzner, E., 2003b.Biodegradation of soil-derived dissolved organic matter as related to its properties. Geoderma 113: 273–291.

Kaplan L.A. and J.D. Newbold. 2003. The Role of Monomers in Stream Ecosystem Metabolism. In: Aquatic Ecosystems: Interactivity of Dissolved Organic Matter (eds Findlay, S. E. G. & Sinsabaugh, R. L.) (Academic Press, Massachusetts).

Kaplan, L.A., Wiegner, T.N., Newbold, J.D., Ostrom, P.H., and H. Gandhi. 2008. Untangling the complex issue of dissolved organic carbon uptake: a stable isotope approach. Freshwater Biology 53: 855-864.

Kaushal, S.S. and W.M. Lewis. 2005. Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. Biogeochemistry 74: 303-321.

Lamprey River Hydrologic Observatory. UNH Water Resource Research Center. http://www.wrrc.unh.edu/lrho/index.htm.

Leff, L.G. and J.L. Meyer. 1991. Biological availability of dissolved organic carbon along the Ogeechee River. Limnology and Oceanography 36: 315-323.

Maranger, R. J., Pace, M. L., del Giorgio, P. A., Caraco, N. F. & Cole, J. J. 2005. Longitudinal spatial patterns of bacterial production and respiration in a large River-Estuary: Implications for ecosystem carbon consumption. Ecosystems 8: 318–330.

Marschner, B., and Kalbitz, K., 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. Geoderma 113: 211–235.

Mann, C.J. and R.G. Wetzel. 1996. Loading and utilization of dissolved organic carbon from emergent macrophytes. Aquatic Botany 53: 61-72.

McDowell, W.H. and G.E. Likens. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecological Monographs 58: 177-195.

McDowell, W.H., Zsolnay, A., Aitkenhead-Peterson, J.A., Gregorich, E.G., Jones, D.L., Jodemann, D., Kalbitz, K., Marschner, B., and Schwesig, D. 2006. A comparison of methods to determine the biodegradable dissolved organic carbon from different terrestrial sources. Soil Biology & Biochemistry 38: 1933-1942.

McKnight, D.M., Thurman, E.M., Wershaw, R.L., and H.Hemond. 1985. Biogeochemistry of aquatic humic substances in Thoreau's Bog, Concord, Massachusetts. Ecology 66: 1339-1352.

Meybeck, M. 1993. Riverine transport of atmospheric carbon: Sources, global typology and budget. Water, Air, and Soil Pollution 70: 443-463.

Michaelson, G.J., C.L. Ping, G.W. Kling, and J.E. Hobbie. 1998. Character and bioactivity of dissolved organic matter at thaw and in the spring runoff waters of the arctic tundra north slope, Alaska. Journal of Geophysical Research 103: 939-946.

Miller, W.L. and R.G. Zepp. 1995. Photochemical production of dissolved organic carbon from terrestrial organic matter: significance to the oceanic organic carbon cycle. Geophysical Research Letters 22: 417-420.

Moran, M.A. and J.S. Covert. 2003. Photochemically mediated linkages between dissolved organic matter and bacterioplankton. In: Aquatic Ecosystems, Interactivity of Dissolved Organic Matter (eds Findlay and Sinsabaugh) (Academic Press).

Morris, D.P. and B.R. Hargreaves. 1997. The role of photochemical degradation of dissolved organic carbon in regulating the UV transparency of 3 lakes on Pocono Plateau. Limnology and Oceanography 42: 239-249.

Mulholland, P.J. 1997. Dissolved organic matter concentration and flux in streams. Journal of North American Benthological Society 16: 122-131.

Mulholland, P.J. 2003. Large-scale patterns in dissolved organic carbon concentration, flux, and sources. In: Aquatic Ecosystems, Interactivity of Dissolved Organic Matter (eds Findlay and Sinsabaugh) (Academic Press).

National Climatic Data Center, UNH Thompson Farm, NH (ftp://ftp.ncdc.noaa.gov/) accessed on 7/22/2012.

Obernosterer, I., Reitner, B. and G.J. Herndl. 1999. Contrasting effects of solar radiation on dissolved organic matter and its bioavailability to marine bacterioplankton. Limnology and Oceanography 44: 1645-1654.

Opsahl, S., and Benner, R. 1997. Distribution and cycling of terrigenous dissolved organic matter in the ocean. Nature 386: 480–482.

Petrone, K.C., Richards, J.S., and P.F. Grierson. 2009. Bioavailability and composition of dissolved organic carbon and nitrogen in a near coastal catchment of south-western Australia. Biogeochemistry 92: 27-40.

Qualls, R.G. and B.L. Haines. 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Science 56: 578-586.

Raymond P.A., and Bauer J.E. 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology 22:1–12.

Richey, J. E., Melack, J. M., Aufdenkampe, A. K., Ballester, V. M. & Hess, L. L. 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. Nature 416: 617–620.

Sabater, F., Meyer, J.L, and R.T. Edwards. 1993. Longitudinal patterns of dissolved organic carbon concentration and suspended bacterial density along a blackwater river. Biogeochemistry 21: 73-93.

Seitzinger, S.P., Sanders, R.W., and R. Styles. 2002. Bioavailability of DON from natural and anthropogenic sources to estuarine plankton. Limnology and Oceanography 47: 353-366.

Sondergaard, M. and Middelboe, M. 1995. A cross-system analysis of labile dissolved organic carbon. Marine Ecology 118: 283-294.

Tranvik, L.J. and S. Bertilsson. 2001. Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. Ecology Letters 4: 458-463.

Tranvik, L.J., Downing, J.A., and J.B. Cotner. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnology and Oceanography 54: 2298-2314.

United States Geological Survey (USGS). National Water Information System. http://waterdata.usgs.gov/nh/nwis/rt.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., and C.E. Cushing. 1980. The river continuum concept. Canadian Journal of Fisheries and Aquatic Science 37: 130-137.

Webster, J.R. and J.L. Meyer. 1997. Organic matter budgets for streams: A synthesis. Journal of the North American Benthological Society 16: 141-161.

Weishaar, J.L, Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R. and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environmental Science and Technology 37: 4702-4708.

Wetzel, R.G., Hatcher, P.G., and T.S. Bianchi. 1995. Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism. Limnology and Oceanography 40: 1369-1380.

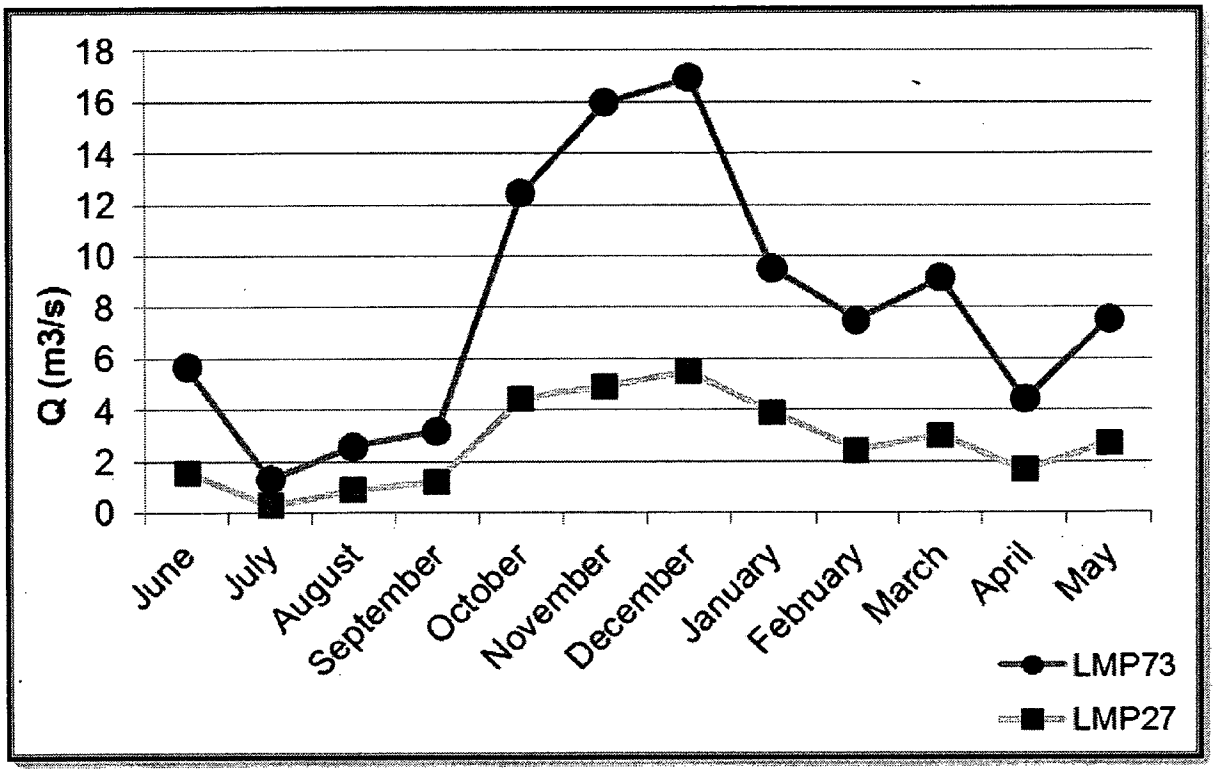
Wiegner, T.N. and S.P. Seitzinger. 2001. Photochemical and microbial degradation of external dissolved organic matter inputs to rivers. Aquatic Microbial Ecology 24: 27-40.

Wiegner, T.N. and S.P. Seitzinger. 2004. Seasonal bioavailability of dissolved organic carbon and nitrogen from pristine and polluted freshwater wetlands. Limnology and Oceanography 49: 1703-1712.

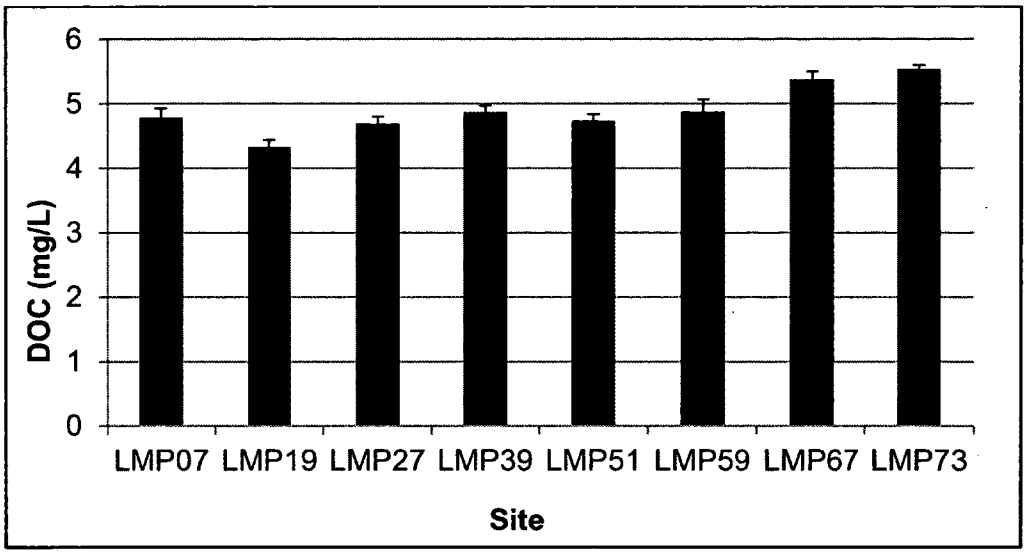
Wiegner, T.N., Seitzinger, S.P., Glibert, P.M., and D.A. Bronk. 2006. Bioavailability of dissolved organic nitrogen and carbon from nine rivers in the eastern United States. Aquatic Microbial Ecology 43: 277-287.

APPENDICES

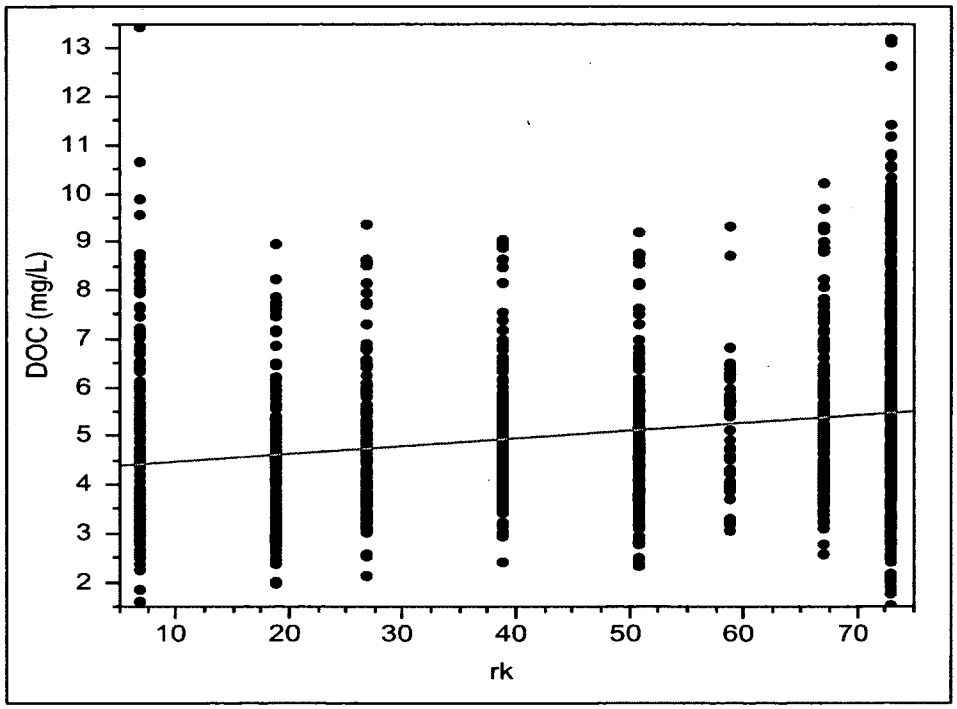
APPENDIX A. Mean monthly discharge for sites LMP27 and LMP73 during the 12 month study period.



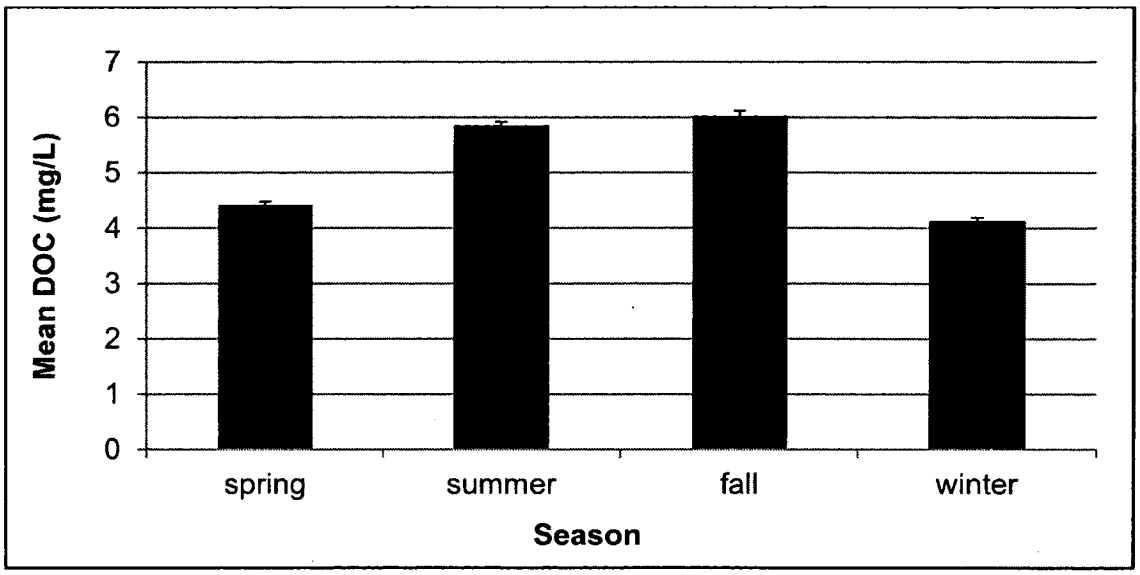
APPENDIX B. Historical trends in DOC concentration for the eight main stem sites on the Lamprey River from 2000-2011.



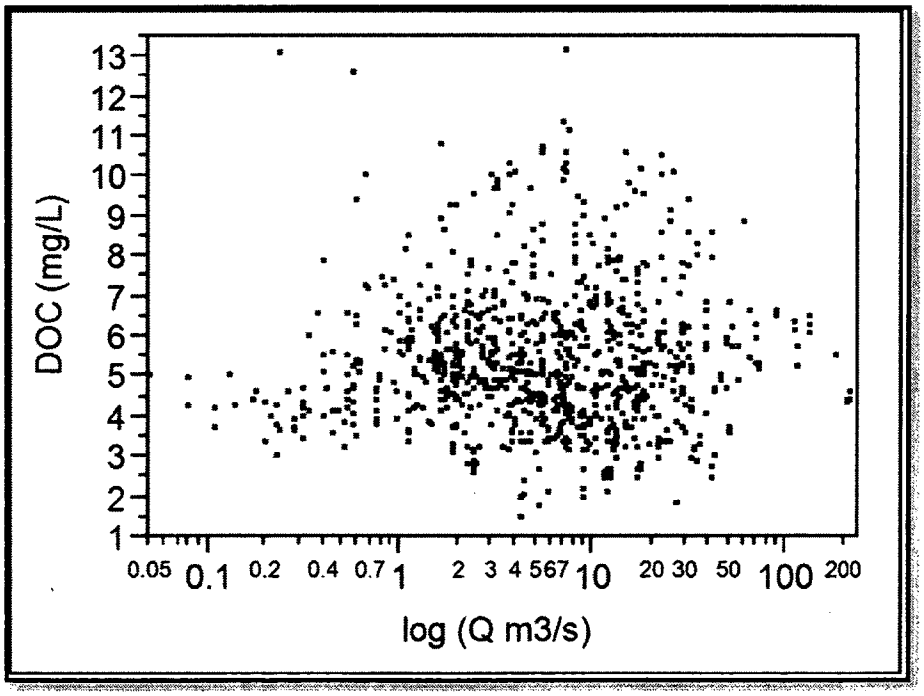
B-1. Mean DOC concentration for the eight main stem sites on the Lamprey River from 2000-2011. Error bars show one SE from the mean.



B-2. DOC concentration from 2000-2011 by river kilometer showing a significant trend in increasing concentration ($R^2 = 0.05$, $P<0.0001$).

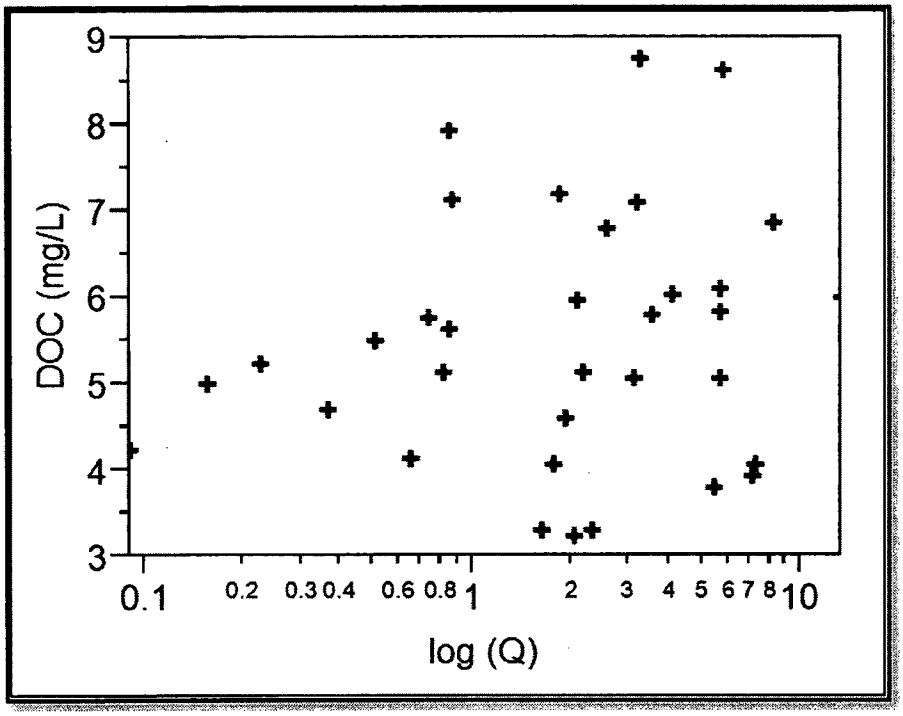


B-3. Seasonal trends in mean DOC concentration for the eight main stem sites on the Lamprey River from 2000-2011. Mean represents all eight sites for each season. Error bars show one SE from the mean.

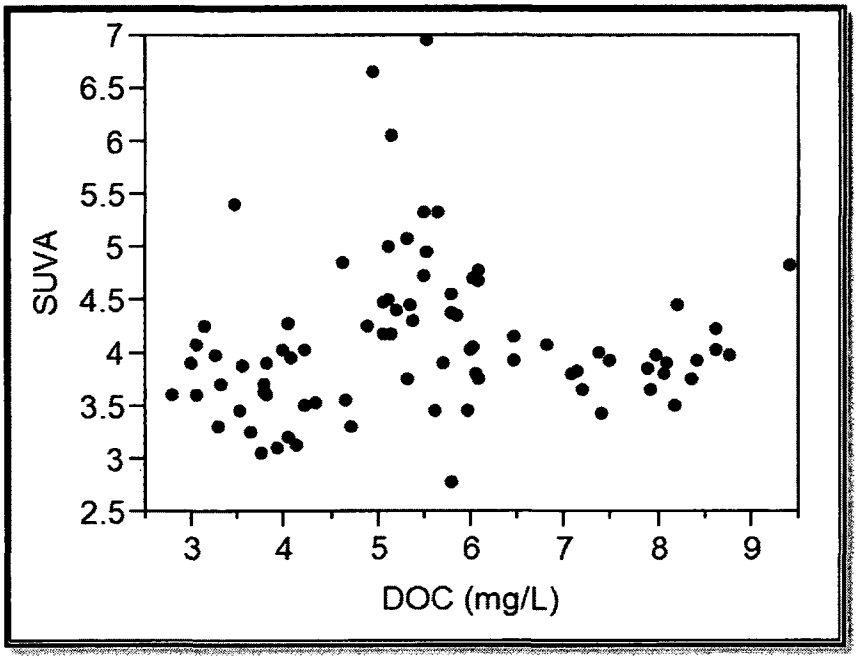


B-4. Relationship between DOC concentration and log (Q m3/s) from 2000-2011.

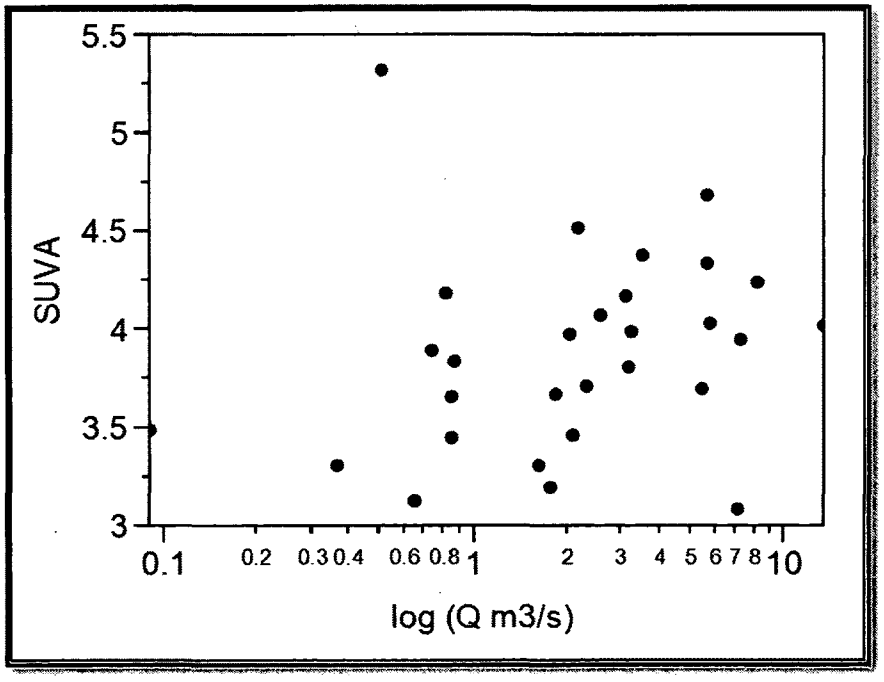
APPENDIX C. Relationship between log (Q) and DOC concentration for the two main stem sites where discharge is measured by USGS gage (LMP27 and LMP73).



APPENDIX D. Relationships between SUVA and other parameters for all sites during the study period.

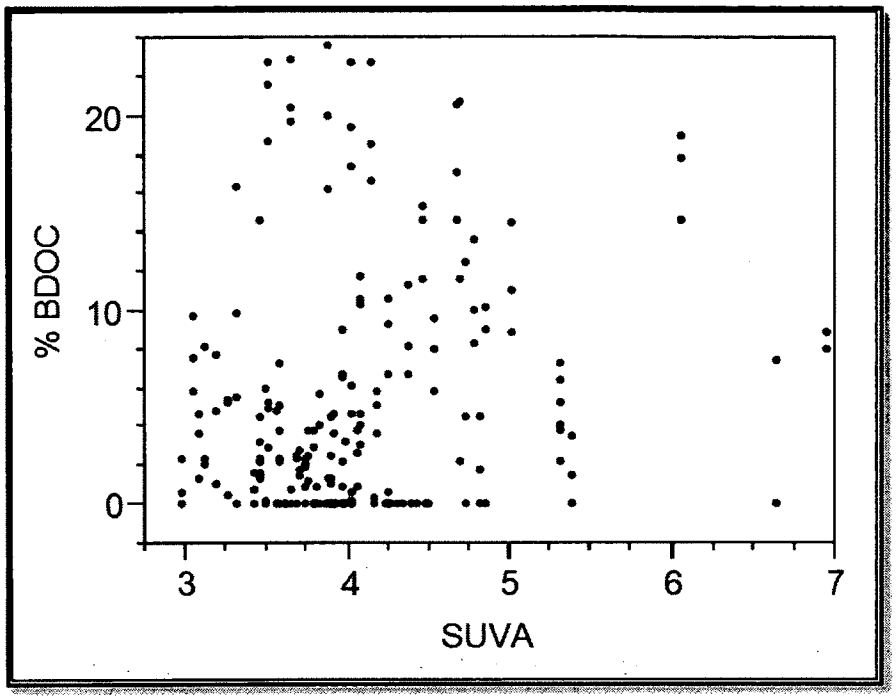


D-1. Relationship between initial DOC concentration and SUVA.

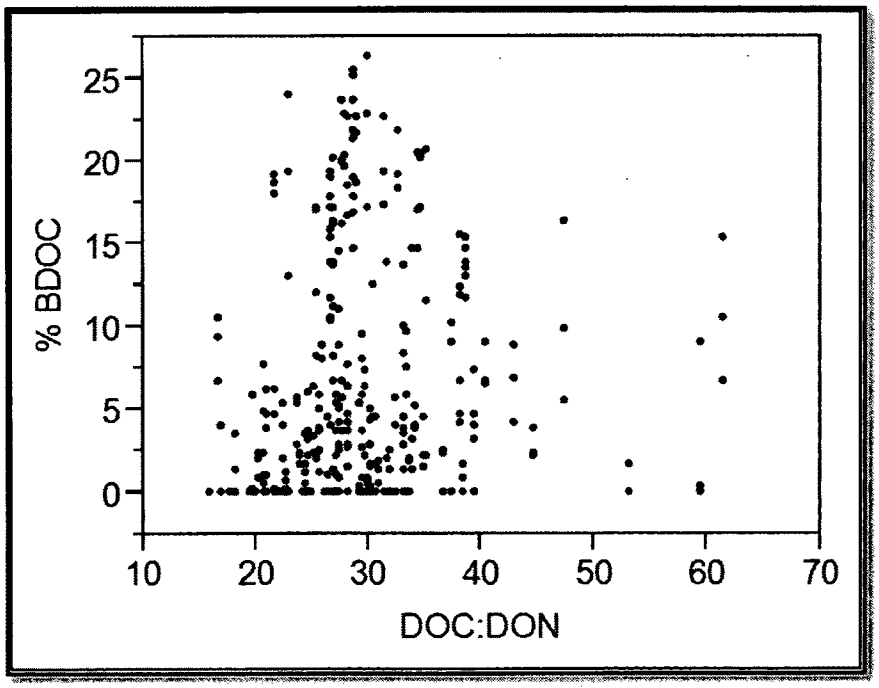


D-2. Non-significant relationship between log (Q) and SUVA throughout the study period. Only includes sites where discharge was being directly measured (LMP27, LMP73).

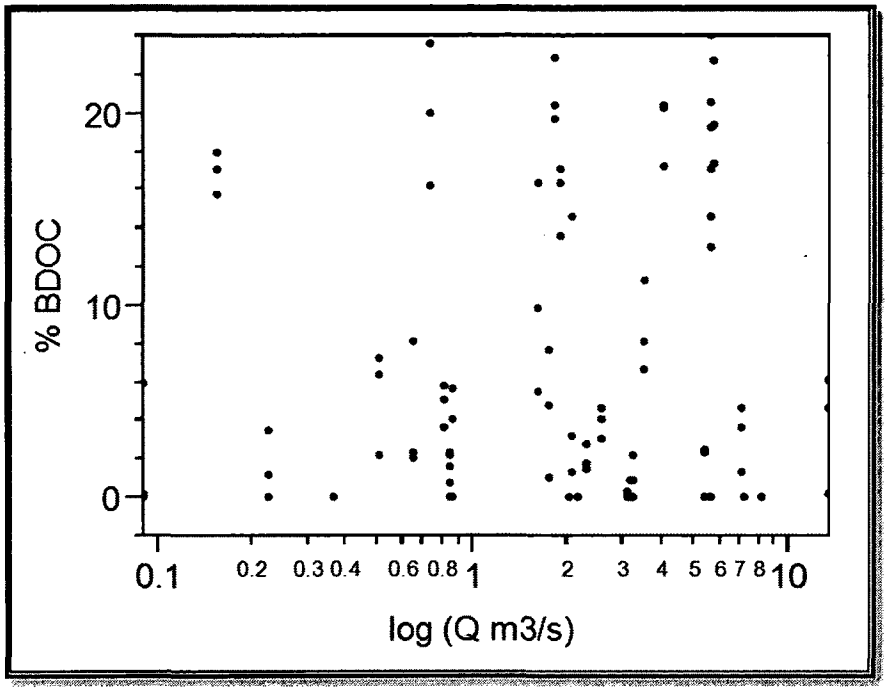
APPENDIX E. Bivariate relationships between BDOC and other in-stream characteristics.



E-1. Bivariate relationship between SUVA and BDOC.

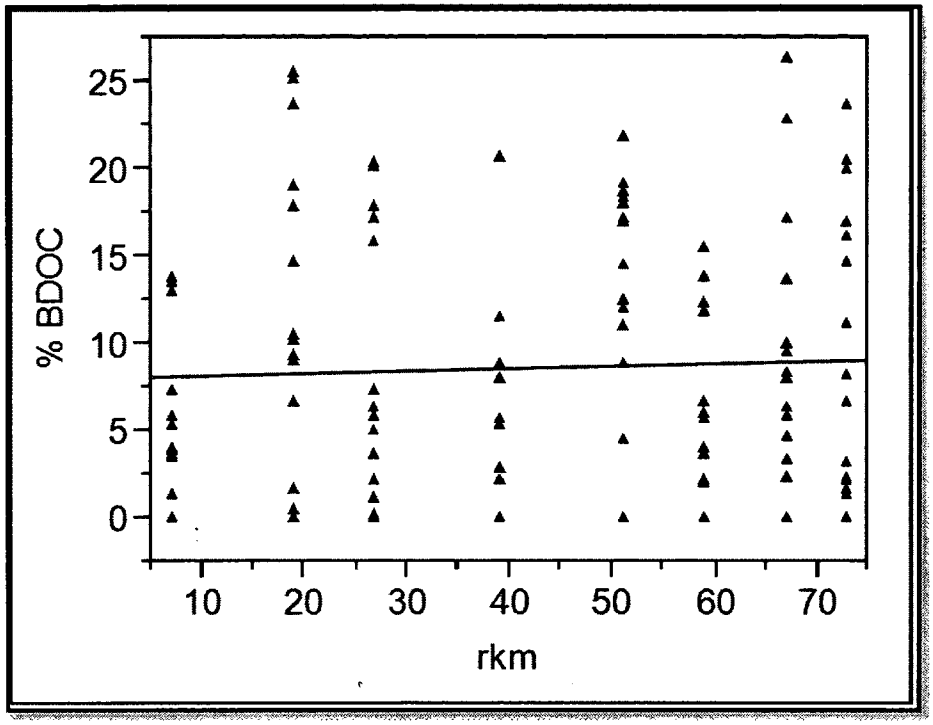


E-2. Bivariate relationship between initial DOC:DON ratio and BDOC.

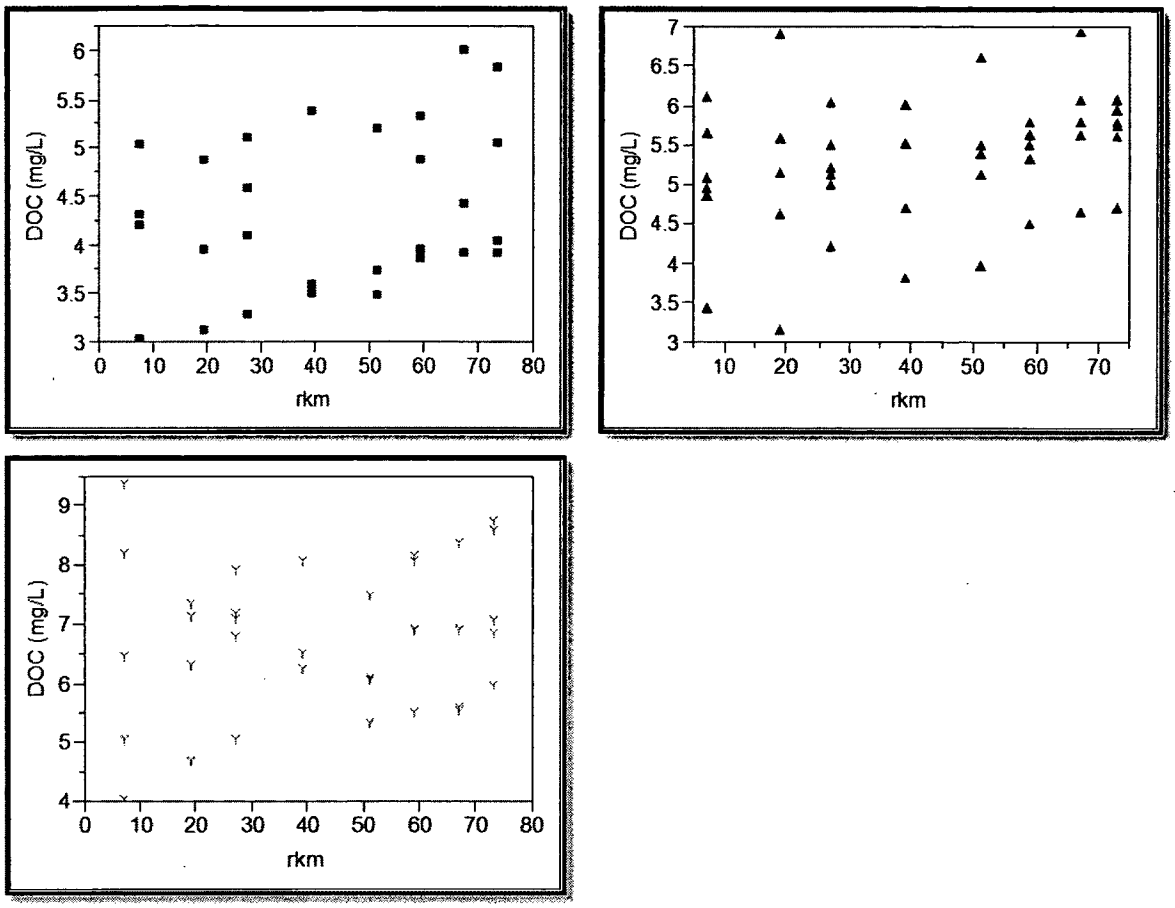


E-3. Bivariate relationship between flow and BDOC.

APPENDIX F. Seasonal spatial variation in various stream solutes.



F-1. BDOC by river kilometer during the summer months (June, July, August).



F-2. Seasonal DOC concentration by river kilometer during the study period. Seasons represented as spring (■), summer (▲), and fall (Y).