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FACTORS CONTROLLING DISSOLVED ORGANIC CARBON LABILITY AND ECOLOGICAL FATE IN THE EAST BRANCH SWIFT RIVER, MASSACHUSETTES

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FACTORS CONTROLLING DISSOLVED ORGANIC CARBON LABILITY AND ECOLOGICAL FATE IN THE EAST BRANCH SWIFT RIVER, MASSACHUSETTES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University.

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List of Abbreviations

Pg: Petagram

OC: Organic Carbon

DOC: Dissolved Organic Carbon

DON: Dissolved Organic Nitrogen

EBSR: East Branch Swift River

Chl*a*: Chlorophyll *a*

LTER: Long Term Ecological Research

GFF: Glass Fiber Filter

STR: Short Term Decay Rate

LTR: Long Term Decay Rate

ACC: Amount of Carbon Consumed

PLC: Percentage of Labile Carbon

k: DOC Consumption rate

STP: Short Term Percentage

LTP: Long Term Position

DIC: Dissolved Inorganic Carbon

DIN: Dissolved Inorganic Nitrogen

DEM: Digital Elevation Model

TP: Total Phosphorous

TN: Total Nitrogen

Abstract

FACTORS CONTROLLING DISSOLVED ORGANIC CARBON LABILITY AND ECOLOGICAL FATE IN THE EAST BRANCH SWIFT RIVER, MASSACHUSETTES

Fluvial systems have been estimated to transform, transport, or store 2.75 petagrams (Pg) of Organic Carbon (OC) per year. Although approximately 1Pg per year of terrestrial carbon is fluxed to the atmosphere through inland waters, little is known about the factors regulating its eventual ecological fate. 28 day lability incubations were conducted concurrent with the measurement of several environmental parameters including discharge, nutrient concentration, $DO^{13}C$, and DOC:DON at several sites along Bigelow Brook and the East Branch of the Swift River, Massachusetts. Temporal and spatial variation of DOC, DOC:DON and $DO^{13}C$ were explored. Two distinct DOC consumption rates, short and long term, as well as overall consumption rate (k), were evaluated to determine the interactions with source, quality, and nutrients. Dissolved organic nutrient concentrations significantly increased long term consumption rates but had little effect on short term rates suggesting that short term rate may be tightly coupled to local, in stream, processes. The short term rate was significantly correlated to k. Interestingly, few significant relationships were found between various rate metrics and the source or quality of the DOC. A large recalcitrant DOC pool persisted after the 28 day period suggestive of downstream export of a large fraction of initial DOC pool.

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INTRODUCTION

Three major reservoirs govern the global carbon budget: terrestrial, oceanic, and atmospheric. Within these reservoirs carbon is unevenly distributed and turns over on varying time scales (Cole et al., 2007). Most of the world's carbon is sequestered in rocks and sediments, followed by deep ocean sequestration; however, the turnover time in these reservoirs is on the order of thousands to millions of years. Often overlooked in calculating the global carbon cycle are inland waters which may turn over carbon on a much faster time scale relative to sediments and the deep ocean, with residence times of some fluvial systems ranging from days to weeks (Battin et al., 2008). Inland water systems may have an influence on contemporary carbon cycling which is disproportionate to their size. This omission could potentially leave significant gaps in our understanding of the global carbon cycle (Cole et al. 2007, Battin et al., 2008, Tranvik et al., 2009). Previously, inland waters were conceptualized as a passive conduit that provided passage for fluvial carbon to an eventual marine end member. More recently a model incorporating processes where carbon is biologically utilized, transformed, stored, or transported was proposed (Cole et al., 2007). It was estimated by Cole et al. (2007) that only half of the carbon that enters inland aquatic systems is exported to the sea. Battin et al. (2008) incorporated streams into the Cole et al. (2007) model and estimated that 2 petagrams (Pg) of terrestrial organic carbon (OC) per year were transformed, transported, or stored by rivers and streams. Further, in a recent review Aufdenkampe et al. (2011) upwardly revised that figure in excess of 2.75 Pg C y^{-1}.

Dissolved organic carbon (DOC) is a major component of fluvial organic matter that must be taken into account when investigating carbon transfer within fluvial networks (Battin et al., 2008). DOC, a complex mixture of organic compounds, can exhibit variable lability due to its chemical heterogeneity (Guillemette and del Giorgio, 2011). This lability directly impacts the ability of the microbial community to metabolize DOC and thus partially regulates its ecological fate. Several biogeochemical and physical processes should be taken into consideration when accounting for DOC lability and transport within fluvial networks. The metabolic fate of DOC includes both microbial consumption leading to biomass production (Guillemette and del Giorgio, 2011), and fluvial respiration that may release CO_2 back into the atmosphere (Battin et al., 2008). In addition, sedimentation/flocculation may remove DOC from the water column (Cole et al., 2007) and photolytic processes may alter the lability of DOC (McCallister et al., 2005). Further, environmental factors such as nutrient availability and temperature have well defined impacts on the microbial community's ability to consume DOC (Guillemette and del Giorgio, 2011).

Undoubtedly, fluvial networks are supplied with significant allochthonous carbon subsidies from land (Cole and Caraco, 2001; and Prairie, 2005; Tittel et. al, 2008). The lability of allochthonous and even autochthonous subsidies is still being debated (Guillemette and del Giorgio, 2011) and presumably varies on a regional or perhaps local scale. Source, coupled with DOC quality may have significant impact on the metabolic fate of DOC (McCallister et al., 2008). Wiegner and Seitzinger (2004) found that as the DOC to DON ratio decreased bacterial growth efficiency improved, suggesting that DOC:DON may play a significant role in the regulation of bacterially mediated carbon consumption. Further, Raymond and Bauer (2001) suggested that ^{13}C stable isotope analysis may be utilized to decipher carbon source. In this

study DOC:DON and stable isotope analysis was employed to investigate the impact of DOC source and quality on its processing.

Carbon pools are often separated in experimental studies based on differences in their reactivity (Guillemette and del Giorgio, 2011). Pools of differing reactivity are commonly divided into labile (quickly consumable), semi-labile (moderately consumable), and recalcitrant fractions although there is still much ambiguity in the separation of these pools both by definition and differences in experimental methodology (Guillemetter and del Giorgio, 2011; Kirchman et al., 1993; Middleburg et al., 1993; Kragh and Sondergaard, 2004). This provides an interesting challenge for those investigating the lability of aquatic DOC. Elucidating the availability of DOC for microbial metabolism is critical to understanding the processing of carbon within fluvial networks and is the primary focus of this study. However, factors that control or drive the processing of one pool may be distinctly different than factors driving the microbial consumption of pools with different reactivity. Because of this, both short and long term labile pools as well as the total amount of carbon consumed were investigated within processing incubations. In addition to source and quality DOC metrics, several factors such as discharge and inorganic as well as organic nutrient concentrations were investigated. A plethora of measurements taken allowed for not only the elucidation of patterns in DOC lability, but also to uncover clues concerning the ecological fate of fluvial carbon in the East Branch Swift River, Massachusetts. It was the goal of this study to determine the impact of DOC source, amount, and quality, as well as nutrient concentration and discharge on pools of carbon exhibiting different labilities. Deciphering any significant interactive effects was a secondary goal of this study. Further, the characterization of pCO_2 and DIC was also of importance.

EXPERIMENTAL DESIGN AND METHODS

Study Site Description:

The Harvard Forest, a Long Term Ecological Research (LTER) site located in north-central Massachusetts, is a mixed deciduous forest dominated by red oak (*Quecus rubra),* red maple (*Acer rubrum)*, eastern hemlock (*Tsuga canadensis),* white pine (*Pinus strobus,)* and black birch (*Betula lenta).* The hilly terrain averages 1100mm of annual precipitation that is evenly distributed throughout the year. The soils were developed on primarily granitic glacial till deposits. Drainage in the forest ranges from well drained in most areas to some poorly drained swamps (Gaudinski et al., 2000). Within Harvard Forest and the East Branch of the Swift River (EBSR), study sites were chosen along a continuum that encompassed both vegetation and hydrogeomorphological differences critical in achieving our objectives.

The study sites included Bigelow Brook, a headwater stream that originates within Harvard Forest, the EBSR, the largest tributary of the Quabbin Reservoir, which is fed by Bigelow Brook, and the entrance of Quabbin Reservoir (Figure 1). The studied system ranged from 1st through 4th order using the Strahler method of stream ordering and 1st through 34th order using the Shreve ordering method. The Bigelow Brook watershed was forested with its riparian zone dominated by old growth eastern hemlock (D'Amato et al., 2006). The EBSR watershed that feeds the Quabbin reservoir, the end member of the study area, was dominated by deciduous forest cover and also included significant evergreen and mixed forest coverage (Figure 2)

Discharge information was available via stream gages and forest composition, and land use was well documented for Bigelow Brook sites (Foster and Aber, 2004;

http://harvardforest.fas.harvard.edu/data/archive.html). A USGS station located at the end member sampling site (the entrance to the Quabbin reservoir) measured daily discharge values, and eddy-flux towers located within the research area provide data on net ecosystem production and CO_2 fluxes and afforded a terrestrial comparison for the fluvial data.

Sample Collection and Experimental Approach

Water samples and measurements were collected from various sites with hydrogeomorphological and vegetation differences within Bigelow Brook, the East branch of the Swift River, and the Quabbin Reservoir. Eight featured sites were sampled 3 times per year (March, May, and September) from May of 2009 until March of 2011. Abbreviated sampling from other sites along the EBSR was also conducted and incorporated into the data analysis.

Carbon in the system was characterized by isotopic analysis ($\delta^{13}C$) of the DOC which was used as a metric for source and dissolved organic C:N ratios which was used as a metric for quality. *In situ* DOC, inorganic and organic nutrients, and chl *a* concentrations, as well as, pH, pCO_2, and temperature measurements were taken at each site. Incubation experiments were conducted in triplicate over a 28 day period to evaluate the lability of DOC from each site. Pools were classified based on different lability to isolate which pool may contribute to the most DOC metabolism. Relationships between source, quality, and quantity were correlated with different lability metrics to elucidate driving factors. Interactive impacts were also explored to see if any of the aforementioned variables significantly influenced another. In addition, a characterization of pCO_2 and DIC was also completed.

DOC Lability Incubations:

Water samples were collected in acid washed containers and filtered through pre-combusted (525°C, 4 hours) 0.7µm Whatman Glass Fiber Filters (GFF) into pre-washed 1L acid washed brown Nalgene incubation bottles and sub sampled for DOC concentration at various time points. Subsamples were transferred into pre combusted (525°C, 4 hours) 40ml glass vials, acidified and stored at 4°C until analysis. Incubations were conducted at room temperature and run for 28 days as comparable to Guillemette and del Giorgio (2011), thus allowing for the remineralization of the pool of semi-labile of DOC. The total amount of carbon consumed, percent of DOC consumed, consumption rate of DOC (k), short term decay rate (STR), long term decay rate (LTR), and percentage of DOC consumed over short term (days 0-2) and long term (days 7-21) were determined using the following formulas:

(1) Total Amount of DOC Consumed (ACC)= X_I-X_F;

where X_I is the initial amount of DOC and X_F the final amount of DOC.

(2) Percent of DOC Consumed (PLC)= {[X_I-X_F]/ X_I}*100;

(3) DOC Consumption rate (k)= $G_T(t) = G_{Lab}[\exp(-kt)] + G_{Res}$;

where G_T is the initial DOC concentration; G_{Lab} and G_{Res} are the labile and residual pools, respectively; *k* is the first order decay constant; and *t* is time (Guillemette and del Giorgio, 2011).

(4) Short term carbon consumption rate (STR) = Slope of DOC loss between days 0 and 2;

(5) Long term carbon consumption rate (LTR)= Slope of DOC loss between days 7 and 21;

(6) Short term percent of DOC consumed (STP) = {[X_I-$X_{(0-2)}$]/ X_I}*100

(7) Long term percent of DOC consumed (LTP) ={[X_I-$X_{(7-21)}$]/ X_I }*100

The extent of DOC lability was derived from incubations collected for 8 sites (Bigelow Brook (BB) upper, BB lower, Swamp 101, Quaker, Connors Pond (CP), Gate 40, Dana, and BM3) for

March 2010- Sept 2010 sampling periods. In September of 2009 no incubations were conducted for CP and Swamp 101.

Analytical Methods

DOC and DIC

In situ and incubation samples for DOC concentration were filtered using pre combusted (525°C, 4 hours) 142mm 0.7 µm Whatman GFF filters and collected in pre combusted (525°C, 4 hours) 40ml glass vials. Samples were acidified with 100µL of concentrated hydrochloric acid (HCl) and stored at 4°C until measured on a TOC-V CSN Shimadzu analyzer at VCU's Environmental Analysis Laboratory (Wickland et al. 2007). DIC samples were processed as detailed above but were treated with 20µL of mercuric chloride ($HgCl_2$).

$DO^{13}C$ and $DI^{13}C$:

Samples were prepared as detailed above and analyzed at Colorado Plateau Stable Isotope Laboratory on an OI Analytical Total Carbon Analyzer coupled to a Thermo Isotope Ratio Mass Spectrometer (IRMS) for $\delta^{13}C$ analysis. Results for stable isotope values are reported in standard δ notation as

(8) $\delta\,^{13}C=((R_{sample}/R_{standard}) - 1) \times 10^3$

where R is ^{13}C:^{12}C.

Nutrients Analysis:

Approximately 40 mL of sample was filtered through precombusted (525°C, 4 hours) 0.7 µm Whatman GFF filters and stored frozen in acid washed 50ml Corning conical tubes until analysis on a SanSystem Skalar segmented flow auto analyzer in the Environmental Analysis Lab at VCU. Measurements for phosphate, nitrate, ammonia, TN, and TP were run.

Alkalinity:

Total alkalinity was determined by titrating 0.02N sulfuric acid (H_2SO_4) into 20 ml of sample until an equilibrium state at pH 4.3 was reached.

(9) Total Alkalinity (mg/L) = {(ml of titrant)(N)(50)(1,000)}/ ml of sample

pCO_2:

In situ CO_2 was stripped out of the water using a membrane Liquicell filter and analyzed on a PP Systems Environmental Gas Monitor (EGM-4) by infrared detection. For sampling periods when the device was not available $pC0_2$ was calculated using the seacarb package in R from pH and DIC or alkalinity and DIC with a temperature correction.

Chlorophyll a:

Samples were filtered through 0.7 Whatman GFF filters, the volume recorded and stored frozen until analysis. Filters were then placed in a 15ml vial with 10mL of buffered 90% acetone for a period of 24 hours and analyzed on a Turner Designs Fluorometer (TD-700).

Discharge:

Discharge for the EBSR was determined by averaging the discharges from USGS station 01174500 for all of the days during the sampling period (http://waterdata.usgs.gov/usa/nwis/uv?site_no=01174500).

REUSLTS

Seasonal and site comparison of DOC, source, quality, and pCO_2

In May of 2009 an exploratory sampling was conducted during which DOC values ranged from 2.42 mg/L at the headwaters to 7.49 mg/L at Gate 40, which was approximately 16.7 km downstream. In the 7.3 km reach from Gate 40 to the end member BM3, there was a decline in DOC concentrations to 2.59 mg/L. These DOC fluctuations were accompanied by $DO^{13}C$ and Chl a values that ranged from -28.71 to -31.06 ‰ and 0.093 to 2.633 (µg/L), respectively.

The range of DOC concentrations was similar between May of 2009 and September of 2009 (Figure 3), and September 2009 $\delta^{13}C$ signature was slightly more depleted than during the spring ranging from -29.84 to -32.39‰ (Table 1.). Chl *a* values ranged more broadly in September (0.06- 4.74 µg/L) with greatest concentration at CP nearly double the May 2009 maximum.

In March of 2010, the range of DOC concentrations was not as large as previously detected (maximum of 5.08 mg/L at BB lower, minimum of 2.95 mg/L at BM3) (Figure 3) and exhibited a negative relationship with distance from headwaters ($r = -0.75$, $r^2=0.56$, $p = 0.033$). pCO_2 ranged from 1882 ppm at BB lower to 444 ppm at CP (Figure 3) and also exhibited a negative relationship with distance from headwaters ($r = -0.50$, $r^2 = 0.25$, $p = 0.004$). Concomitant with DOC concentrations, the $\delta^{13}C$ signature also exhibited a smaller range of -29.05 to -31.49 ‰ (Table 1). The most negative values were found at the end member location

of BM3 and BB upper, which are the open water and headwater sites, respectively (Table 1). DOC:DON values ranged from 85.1 to 34.2, with sites having open water land covers (BM3, CP, and Swamp) (Hall and McCallister, unpublished data) corresponding with the lowest C:N values. In contrast the highest ratios were at the 1st order sites (BB upper and Lower) and Dana which has a large wetland influence (Table 1).

The range of DOC concentration during May 2010 was similar to those of May 2009 despite significant discharge differences (Table 1, Figure 3). BB upper had a minimum concentration of 1.69 mg/L, while the maximum of 6.25 mg/L was at Quaker. Both BB lower and Swamp 101 had pCO_2 values that exceeded 2000ppm, while Gate 40 and BM3 had values that were below measured atmospheric background of 420 ppm (Figure 3). The associated $\delta^{13}C$ values showed a surprisingly narrow range (-26.44 to -27.80 ‰). DOC:DON was highest at BB upper and lowest at BM3 and Swamp 101, with a range of 72.2 to 17.4 (Table 1).

The range go DOC in September of 2010 was larger than that of 2009 perhaps due to a doubling of discharge (See Table 1, Figure 3), with a maximum of 10.89 mg/L at BB lower and minimum of 2.36 mg/L at BM3. Similar to March of 2010 DOC exhibited a negative relationship with distance from headwaters ($r = -0.88$, $r^2 = 0.78$, $p = .004$). pCO_2 values were all well above atmospheric background, ranging from 1437ppm to 3179ppm (Figure 3). The associated $DO^{13}C$ values, howevere exhibited a smaller range than in September of 2009 falling between -27.28 and -28.40‰ . The DOC:DON ratio at BM3 was the lowest at 14.0 whereas Dana was the highest at 53 (Table 1).

The March 2011 sampling yielded the smallest range in DOC concentration in comparison to other sampling periods and had the greatest discharge (Figure 3, Table 1). pCO_2 was generally higher than the other sampling periods and ranged from 1731 to 4036 (Figure 3).

$DO^{13}C$ and DOC:DON values also had the smallest range compared to all sampling periods, falling between -27.1‰ and -27.6 ‰ and 33.3 to 45.5, respectively, suggesting a homogenization of DOC source and quality during periods of very high flow (Table 1). Chl *a* values ranged from 0.992µg/L at Swamp to 0.012 µg/L at BB upper.

Influence of Discharge

Discharge ranged from 566 L/s in September 2009 to 11864 L/s in March 2011. May 2010 and September 2010 had very similar discharges (1104 and 1132 L/s), whereas May 2009 had a much higher discharge than May of 2010. March of 2010 was also a high discharge period, with an average discharge during the sampling period of 7486 L/s (Table 1).

There was a weak, non significant negative correlation between DOC concentration and discharge with pooled data. Contrary to the trend found with the DOC, DIC exhibited a positive significant correlation with discharge. The same was found for inorganic and organic nitrogen species, where DON significantly decreased with discharge and nitrate, the predominate form of inorganic nitrogen within the system, significantly increased with discharge. There was no trend found with the isotopic signature of the DOC however, the $DI^{13}C$ significantly increased (became less negative) with increasing discharge (Figure 4). The amount of carbon consumed within incubations significantly decreased as discharge increased and the DOC:DON increased with discharge (Figure 5).

Rate metrics and influencing factors.

Lability metrics for September of 2009 (PLC, k, and STR) suggested the highest percentage of labile material for the entire study was found at Gate 40. Although the PLC at BB

upper was the lowest (3.9%), the rate at which this pool of carbon was consumed was still relatively fast (k = -0.428). Gate 40 as well as Quaker also exhibited fast k values. STRs were much higher than LTRs for all sites except for Dana and BM3. Ranges for PLC, k, STR, and LTR were as follows: 3.9 to 34.1%; -0.574 to-0.037; -0.476 to -0.013 and -0.026 to -0.004 (Table 1).

Metrics of carbon lability suggest lower bioavailability in March 2010 compared to September 2009 (Table 1). Although DOC:DON values at BM3 and Dana fell near the maximum and minimum, their associated PLCs were nearly identical (16.4 and 16.2%, respectively) suggesting DOM quality may not be the only driver of its metabolic fate. Similar to September of 2009, BB upper had the lowest PLC, whereas March 2010 BB lower had the lowest k and STR. BM3 had the highest k of -0.408, more than double that of the second highest k value found for the sampling period. STR ranged from -0.014 (BB upper) to -0.128 (BM3) and LTR ranged from -0.005 to -0.0013, with BB lower and Dana as the maximum and minimum, respectively (Table 1).

PLC for May of 2010 had a relatively small range, 11.5% at Dana to 4.1% at BB Lower. The rate of carbon consumption was lowest at BB lower (k = -0.014) and greatest at Dana, (k= -0.828), the highest rate measured in the study. The maximum STR was also associated with Dana (-0.142). The minimum STR (-0.028) was measured at Gate 40, a site that had previously registered the maximum STR in the fall of 2009. LTR ranged from -0.002 at CP and BM3, both open water sites to -0.014 at Swamp 101 (Table 1). In September of 2010, CP had the lowest PLC measured not only for this period but for all periods measured. Quaker had the highest PLC at 12.9% and the two headwater stream sites BB upper and lower had PLCs of 10.1% and 12.0% respectively. September 2010 had the smallest range of k values for any sampling period with a

maximum of -0.101 at Quaker and minimum of -0.004 at Dana. STRs ranged from -0.238 at Quaker to -0.006 at Dana which registered the fastest STR in the May sampling period of the same year. Many LTRs were higher than the maximum values from other sampling periods suggesting an increase in the breakdown of less labile carbon over the incubation period in comparison to the other sampling periods. A doubling in discharge compared to the September2009 sampling may contribute to the accumulation of carbon that is broken down later in the incubation period at multiple sites. BB lower had the highest LTR measured in this study at -0.056, followed by BB upper at -0.036 and Dana at -0.031 (Table 1).

In March of 2011, PLC exhibited the narrowest range of all the sampling periods, from 1.5% at BB upper to 6.2% at Dana. k varied from -0.0025 at BB upper to -0.191 at Swamp 101. Four other sites had k values that fell between -0.17 and -0.179. Maximum STR was found at Swamp 101 and the minimum at BM3. All of the carbon consumed at Swamp 101 was short term labile as the LTR was 0. LTRs for this sampling period ranged from 0 to 0.011, with the maximum found at BB upper.

There was a large recalcitrant pool of carbon that persisted after the 28 day incubation period was completed, with 80% of the initial amount of carbon remaining in all but two of the incubations (Figure 6). The largest percentages consumed were in September of 2009 at Quaker and Gate 40. All sites in May 2010 had a greater amount of consumption in the short term except for Swamp 101. In March 2010 an increase in the amount consumed in the short term can be seen as the distance away from the headwaters increases. September 2010 did not exhibit the same amount of short term consumption as 2009 and generally saw greater percentages of long term consumption, perhaps due to differences in leaf down and sampling date (Figure 6).

Faster LTRs were associated with increases in the initial amount of DOC, TN, and TP with the highest r squared found in correlation with DOC(Figure 7). The dissolved organic species of nitrogen and phosphorous appear to be the driving factors in the relationship with LTR (Shown inset Figure 7.). LTRs exhibited the opposite relationship with the inorganic nitrogen species nitrate, slowing the long term rates ($r^2 = 0.13$, $p = 0.04$). STRs were not correlated with initial DOC or any nitrogen species and exhibited a much weaker correlation with phosphate ($r^2 = 0.17$, $p = 0.02$) . STRs and LTRs were both correlated with k (LTR with k, $r^2 = 0.11$, $p = 0.046$), however the correlation between STRs and k was much stronger (Figure 8). Five of the samples from September sampling periods exhibited higher STRs than the remaining pooled data and are shown with a separate regression line, no such trend was found for LTRs and k.

Combined March data showed that PLC significantly decreased as $DO^{13}C$ became less negative ($r = -0.68$, $r^2=.46$, $p = 0.004$). Combined September data yielded a significant relationship showing that as $DO^{13}C$ became less depleted as k slowed ($r = 0.61$, $r^2=0.37$, $p = 0.021$), whereas the opposite relationship was found with $DO^{13}C$ and LTR ($r = -0.65$, $r^2= 0.42$, $p = 0.012$).

DISCUSSION

Environmental Parameters

Temporal and spatial DOC variation

Few studies have investigated the influence of seasonality on DOC dynamics though it has been suggested that seasonal changes may play a role on DOC availability (Johnson et al., 2009). Ranges and maximum values for DOC (Table 1, Figure 3.) were highest during September and lowest in March suggesting that fall leaf drop and senescence may contribute allochthonous OC to the system consistent with the findings of Mullholland and Hill (1997) in an Eastern Tennessee headwater stream. Large excursion in DOC concentration at headwater stream sites BB upper and lower for September of 2009 (5.17 mg/L) and May of 2010 (4.36mg/L) may result from DOC additions from the wetland area that separates the two sites. Wetland derived DOM has been extensively studied and is thought to be an important source of DOC to streams and rivers (Creed et al., 2002; Mulholland and Kuenzler, 1979; Urban et al., 1989; Eckhardt and Moore, 1990;Hemond, 1990; Koprivnjak and Moore, 1992; Kortelainen, 1993; Clair et al., 1994; Hope et al., 1994; Dillon and Molot, 1997; Mulholland, 1997; Gergel et al., 1999) The same DOC increase between the headwater sites is not seen in sampling periods during high flow or after precipitation events (such as Sept 2010 and March 2011) suggesting increased discharge may dilute the headwater wetlands DOC contribution. Wetlands in 3rd and 4th order stream segments of the EBSR may play a different role. Conceivably this may be due to differences in wetland vegetation and the microbial community which may impact DOM

export and processing. An alternate possibility may be that differences in canopy cover and variations in the amount of open water at each wetland may influence the amount of photochemical breakdown of DOC that can occur. Large increases in DOC (Table 1, Figure 3) are not found at Swamp 101 (4.9km from headwaters) and Dana (18.5 km from headwaters), both of which fall directly after wetlands with larger open water components to their upstream land covers than the headwater wetlands. Reductions in DOC concentration are noted between Dana and BM3 (24.2 km from headwaters) during March (1.06 mg/L), May (1.12 mg/L), and September (4.4 mg/L) of 2010 sampling periods. BM3 has a large open water component to its upstream land cover which may promote photochemical breakdown of DOC, making it more available to bacterial metabolism (McCallister et al., 2005, Smith and Benner, 2005). DOC fluctuations along the system during lower flow sampling periods suggest that the amount of DOC may be dependent on local sources and processes that may be largely connected to terrestrial inputs.

Average DOC for 5 tributaries of the Hudson River (3.3-5.6 mg/L) fell within the ranges measured in this study (Findlay et al.,1998). Average yearly DOC of the EBSR, calculated by averaging DOC concentration at BM3 for March, May, and September, was 5.06 mg/L for 2010 which is higher than all of the averages for several small stream networks measured in PA, MI, ID, and OR (Moeller et al., 1979), and similar to DOC concentrations ranges found by Guillemette and del Giorgio (2011) in a complex drainage basin in southern Quebec. While in past studies it has been well established that DOC amount is related to its processing, investigations into its source and quality may also be crucial in describing DOC input and availability .

Source and Quality

Autochthonous sources in streams and rivers are generally characterized as having a more depleted isotopic signature in addition to lower C:N ratios (McCallister and del Giorgio, 2008, Dodds et al., 2004). Ranges for $DO^{13}C$ were largest in September 2009 (-32.39 to -29.84) and were slightly more depleted than 6 Hudson watershed small streams (Raymond et al., 2004) and 3 sampling sites on non forested headwater stream in Scotland (Palmer et al., 2001). 13C signatures for in the EBSR were similar to many of the rivers sampled by Raymond and Bauer, (2001) including the Amazon (-28‰), York (-28.8‰), James (-28‰), and Potomac (-30.9‰). Average $DO^{13}C$ of 28.81‰ for the EBSR falls within many of the aforementioned ranges. More depleted September 2009 values may be explained by leaf down which was captured more completely in September of 2009 than in September of 2010 due to differences in sampling period and leaf down. Although it has been generally thought that aquatic production produces more depleted signatures, Amiotte-suchet et. al., (2007) found that leaf litter from deciduous leaves could have 13C signatures near the -31 range. Leached coniferous needles, mostly Easter Hemlock from Harvard Forest, have also yielded 13C values in the -31‰ range in litter solutions as well (Hall and McCallister, unpublished data). The headwater sampling sites generally had the highest DOC:DON ratio suggesting these sites are dominated by allochthonous input. Although Dana, a wetland site near the end member, consistently had high DOC:DON as well suggesting wetland DOC contribution that may contain high molecular weight components (Agren et., al. 2008) , or perhaps some biotic removal of DON (Conveney et., al. 2002). Wetland DOM processing can be impacted by slope, soil properties, and differing flow paths (Aitkenhead-Peterson et., al. 2003), all of which may attribute to the differences in wetland DOM processing elucidated in this study. Further, Mullholland (2003), suggests that wetland activity can exhibit seasonal variation. Sites that contained open water components to their

upstream land covers generally had more depleted $DO^{13}C$ isotopic signatures suggesting more aquatic production of DOC (McCallister and del Giorgio, 2008). With the exception of the high flow event in March of 2011, the end member and open water dominated site, BM3 exhibited low DOC:DON ratios (14-36) compared to the rest of the sampling sites. This may be attributed to autochthonous source DOC as phytoplankton derived DOC is thought to have lower C:N ratio (Dodds et. al., 2004). Other open water sites CP and Swamp 101 also followed the same low DOC:DON trend supporting the idea that autochthonous production may be more likely to contribute DOC in reaches with greater open water components. The average DOC:DON of 38.5 falls between the annual averages for 4 Scottish temperate streams ranging from 58 to 21 (Champan et. al., 2000). In addition to amount, the source and quality of DOC is thought to play a major role controlling processing rates.

DOC Consumption Metrics

Percentage of labile carbon

DOC consumption can be measured in a variety of ways and the term lability is an "entirely operational term" (del Giorgio and Davis 2003). In this study percentage and amount of carbon consumed were each measured in addition to rate measurements. Percentage and amount of DOC consumed are common measurements to assess the amount of DOC that is microbially processed within incubations. Average PLC for the ESBR was highest in the September of 2009 (14.6%) sampling followed by March of 2010 (10.75%). September 2010 and March of 2011 yielded PLCs nearly 50% less than of the previous year. These drops in PLC may be explained by increases in discharge for the latter two sampling periods leading to dilution and homogenization of DOC within the system. Kaplan and Newbold (2003) found that

increased flow inhibited glucose uptake rates during in stream glucose injections in the Pennsylvania Piedmont. Only two instances of PLC exceeding 17% were measured suggesting that a large recalcitrant pool of DOC may be exported from the EBSR in comparison to other systems. Sondergaard and Middelboe (1995), in their review of labile DOC across different systems, found that on average 19% (±16%) of DOC was consumed in river systems. Sampling efforts in the EBSR yielded less than half of this with an average of 8.6% (±6.4%), which is less than the average percentage, 10.2 (±4.54), of DOC removed in several rivers in 1 to 3 day incubation periods reviewed by del Giorgio and Davis (2003). Percentages of carbon consumed in this study also fell below ranges found by Fellman et. al., (2009) who reported 3 Alaskan main-stem streams to range from 16.1 to 30.1% carbon lost within their incubations when averaging snow melt (May), summer draw down (June-August) and wet season (August-November) sampling periods. Further, estimates in this study also suggest EBSR contains more recalcitrant DOC than was measured for several lakes, marshes, estuaries, and marine environments (del Giorgio and Davis, 2003).

Rate Metrics

In addition to quantification techniques measuring amount, rate measurements may also provide insight into the reactivity of DOC within aquatic systems. There was no correlation found between k and ACC for pooled data which supports Guillemette and del Girgio's suggestion (2011) that k is not a robust predictor of the size of the labile carbon pool. k values were weakly correlated to LTRs but more strongly correlated to STRs (Figure 8.) suggesting that the short term labile carbon pool drives k values more so than LTRs. Also, further complicating matters, it appears that DOC with two distinct rates can be isolated from the short term labile pool. With the exception of BB lower in March of 2010 STRs were faster than LTRs for all

sampling events further suggesting the separation of pools with different labilities (Guillemtte and del Girgio, 2011; del Giorgio and Pace, 2008). A rapid turnover of a small, highly labile, portion of DOC within incubations (del Giorgio and Davis, 2003) indicates that this short term labile pool may be directly connected to local in stream processes that may be disrupted during the incubation. Kaplan and Newbold (2003) suggest that a rapid replenishment of labile DOM may occur by turbulent mixing within streams. Further, Berggren et., al. (2010) suggest that low molecular weight carbon from terrestrial environments may be turned over rapidly providing continuous supply of labile metabolites. This may account for underestimates in the amount of carbon processed by the stream in this study and other studies with similar incubation methodologies. Few studies have investigated *in situ* carbon processes, however, Kaplan et., al. (2008) found that 82% of labeled DOC added to a Pennsylvania stream was taken up in the first 1.5hrs. Data from this study suggests a large recalcitrant DOC pool remains and is potentially exported out of the fluvial system (Figure 6). However, the Quabbin Reservoir has low DOC concentrations relative to the EBSR (Massachussettes Department of Conservation and Recreation, 2006) suggesting that the large recalcitrant pool may not simply be exported. Although some dilution may occur, most likely abiotic processes such as sediment deposition and photolysis or biotic processes not captured by incubation experiments act to further remove DOC from the system.

Influence of discharge on environmental parameters and carbon consumption

In addition to the impact of discharge on DOC concentrations, discharge may also play a role in the quality and availability of other nutrients crucial in aquatic carbon cycling. A homogenization of DOC is most likely present in periods of high flow accounting for the small

ranges (2.95 to 5.22 mg/L) exhibited in March samplings (Table 1, Figure 4.). The idea that homogenization of DOC occurs during periods of high discharge is further supported by the smallest DOC:DON (33.3 to 45.4) and $DO^{13}C$ (-27.56 to -27.1‰) ranges found concurrent with the highest discharge (11864 L/s). Nitrate and DIC significantly increased as discharge act to accelerate nitrate delivery and amount of DIC exported from the terrestrial landscape to the aquatic environment (Shilling and Lutz, 2004, Oquist et. al., 2009). The opposite trend was seen with DOC and DON although the relationship with DOC and discharge was not significant. These results do not support the trend found by McDowell et,. al. (1988) who observed increases in DOC concentrations with increasing discharge at Hubbard Brook, NH, but similar to trends discovered by Eimers et., al. (2007) who suggest that relationships with temperature and dilution induced by discharge may lower DOC concentrations at high discharges . An alternative view might indicate rapid mineralization processes occurring to remove organic nutrient species from the system during high flow in the EBSR. There was no similar indication that changes in discharge influence shift source of carbon based on $DO^{13}C$ measurements other than its homogenization at the highest discharge value. $DI^{13}C$ exhibited equilibration toward atmospheric levels as discharge increased indicating that periods of high flow may allow for more terrestrial derived organic carbon to be transferred to the atmosphere. This is also supported by maximum pCO_2 values found concurrent with the highest flow in March of 2011 at all but one site, Swamp 101 (Figure 3.). Further, Butman and Raymond (2011), found that CO_2 evasion is positively correlated with annual precipitation in rivers and streams which they partly attributed to the flushing of CO_2 from soils. The amount of carbon potentially consumed decreased during these periods of DOC homogenization (Figure 5.) further suggesting that localized source and processing is prevalent at lower discharges but may be negated during

periods of high discharge. This may be due to the input of more recalcitrant terrestrial carbon during high flow and disruption of locally driven in stream processes producing short term labile carbon sources.

Environmental Influences on rate metrics

Although source and supply have also been proven to impact aquatic microbial metabolism (Lennon and Pfaff, 2005), source and quality data in the form of $DO^{13}C$ and DOC:DON had no significant impact on any carbon consumption metrics measured in the study when pooling the data for all seasons, and very few relationships when the data was analyzed seasonally. March data showed that PLC decreased as $DO^{13}C$ became less negative(r^2=.456, p = 0.004) suggesting that more depleted carbon sources promoted more consumption. Interestingly, in September k slowed as $DO^{13}C$ became more depleted suggesting that terrestrial input has a significant impact on fall carbon processing rates. This indicates that seasonal factors may play large roles on carbon transformation and export in this fluvial system. While amount of DOC exhibited a positive trend with k, the results were not significant. del Giorgio and Davis (2003) found in their review of DOM labilities that source and quality were critical in determining lability. $DO^{13}C$ and DOC:DON measurements may not be the best indicators of source and quality as Qualls and Haines (1992) found relationships with percent DOC loss using humic and hydrophilic neutral fractions of the initial DOC pool. Furthermore, Fellman et. al., (2009) presented linkages between biodegradable DOC and tyrosine and tryptophan like components. This indicates that composition of DOC rather than isotopic signature and DOC:DON may play a large role in its eventual fate. Short term rates were weakly correlated to DOC and DOP concentrations while k rates were not influenced significantly by any of the measured

environmental parameters further suggesting they are tightly coupled to local in stream processes. LTRs were influenced by the amount of DOC as well as by total nitrogen and phosphorous (Figure 7). del Giorgio and Davis (2003) suggest that inorganic nutrients limitation may play a role in DOM degradation. Results from this study suggest that the more recalcitrant pool may rely on available organic, rather than inorganic, nutrients to drive the breakdown of the While inorganic nutrient limitation has been extensively studied in various ecosystems, organic nitrogen and phosphorous studies are less frequent. Data from this study suggest that the role of organic nutrients on DOC consumption may be as, if not more important than inorganic nutrients in the EBSR. However, data from this study also suggest that nutrient limitation may be overridden when looking at shorter time scales by the quick cycling of what may be low molecular weight DOM turned over rapidly within the EBSR.

Conclusions

It appears that the factors controlling carbon consumption may indeed differ based on the reactivity of the carbon. In addition, it appears that even within the different fractions, different labilities may exist, further complicating studies that investigate factors controlling DOC consumption. Elucidating factors that control carbon consumption will allow for more appropriate management techniques in dealing with fluvial carbon export. Studies like this will also aid in filling gaps within carbon models concerning fluvial systems. Future studies in the Harvard Forest and EBSR watershed should include investigations into influences of land cover, photochemical breakdown, and nutrient additions to the system. It is also of interest to explore the export of both DOC and DIC from the EBSR in relationship to the net ecosystem production of the area.

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Tables

Month	Site	DOC (mg/L)	$DO^{13}C$ (‰)	DOC:DON	PLC %	k (d^{-1})	STR (mg C L^{-1} d^{-1})	LTR (mg C L^{-1} d^{-1})
Sept '09	BB upper	2.63 (.02)	-32.39	-	3.9(.04)	-0.428	-0.020	-0.004
566 L/s	BB lower	7.80 (.02)	-29.96	-	6.9 (2.1)	-0.144	-0.066	-0.009
	Swamp101	6.85 (.13)	-30.39	-				
	Quaker	7.24 (2.02)	-29.84	-	27.1 (4.7)	-0.250	-0.310	-0.026
	CP	5.29 (.02)	-30.89	-				
	Gate 40	6.27 (.13)	-30.07	-	34.1(3.9)	-0.574	-0.476	-0.008
	Dana	5.05 (.02)	-31.2	-	5.2 (.5)	-0.077	-0.018	-0.010
	BM3	5.09 (.03)	-30.32	-	10.4 (3.6)	-0.037	-0.013	-0.019
Mar '10	BB upper	4.72 (.13)	-31.49	85.1	4.7 (.7)	-0.001	-0.014	-0.005
7486	BB lower	5.08 (.07)	-29.07	74.9	8.1 (1.6)	-0.040	-0.033	-0.013
L/s	Swamp101	3.96 (.06)	-29.05	38.0	9.9 (2.5)	-0.137	-0.041	-0.011
	Quaker	5.09 (.14)	-30.07	-	12.6 (3.0)	-0.068	-0.056	-0.012
	CP	4.08 (.12)	-31.11	34.2	9.3 (3.4)	-0.062	-0.051	-0.009
	Gate 40	4.13 (.02)	-30.68	43.1	8.8 (2.6)	-0.150	-0.073	-0.006
	Dana	4.01 (.03)	-29.73	84.4	16.2 (.5)	-0.114	-0.062	-0.013
	BM3	2.95 (.28)	-31.42	36.1	16.4 (7.1)	-0.408	-0.128	-0.012
May '10	BB upper	1.69 (.01)	-26.44	72.2	6.2 (1.0)	-0.328	-0.039	-0.003
1104	BB lower	6.05 (.13)	-27.79	42.8	4.1 (2.2)	-0.014	-0.050	-0.007
L/s	Swamp101	4.78 (.02)	-27.80	17.4	11.2 (2.3)	-0.132	-0.074	-0.014
	Quaker	6.25 (.06)	-27.45	26.2	5.7 (1.1)	-0.068	-0.056	-0.007
	CP	4.37 (.09)	-27.24	24.6	6.4 (4.5)	-0.397	-0.099	-0.002
	Gate 40	3.65 (.12)	-26.58	26.0	7.1 (1.9)	-0.043	-0.028	-0.004
	Dana	3.73 (.14)	-27.01	40.8	11.5 (2.9)	-0.828	-0.142	-0.005
	BM3	2.61 (.04)	-27.12	18.6	6.7 (1.2)	-0.472	-0.044	-0.002
Sept '10	BB upper	9.48 (.21)	-27.28	35.0	10.1 (1.3)	-0.064	-0.173	-0.036
1132	BB lower	10.89 (.24)	-27.69	35.1	12.2 (3.0)	-0.026	-0.194	-0.056
L/S	Swamp101	7.85 (.08)	-28.34	22.1	6.4 (0.9)	-0.052	-0.020	-0.017
	Quaker	6.75 (.14)	-27.97	30.1	12.9 (2.2)	-0.101	-0.238	-0.029
	CP	4.59 (.02)	-28.40	21.1	2.7 (1.1)	-0.072	-0.023	-0.004
	Gate 40	5.63 (.03)	-28.24	25.4	6.9 (.1)	-0.005	-0.028	-0.023
	Dana	6.76 (.04)	-28.04	53.2	8.1 (0)	-0.004	-0.006	-0.031
	BM3	2.36 (.07)	-28.29	14.0	3.6 (1.6)	-0.005	-0.018	-0.005
Mar '11	BB upper	3.17 (.04)	-27.10	43.3	1.5 (3.9)	-0.003	-0.052	-0.004
11864	BB lower	4.27(.09)	-27.25	45.1	3.7 (3.8)	-0.113	-0.005	-0.011
L/s	Swamp101	4.23 (.14)	-27.46	36.5	4.4 (2.8)	-0.191	-0.067	-
	Quaker	5.22 (.07)	-27.23	33.3	4.0 (2.5)	-0.17	-0.007	-0.007
	CP	3.94 (.07)	-27.28	34.3	5.0 (.83)	-0.079	-0.051	-0.0002
	Gate 40	4.27 (.12)	-27.37	42.5	5.7 (3.1)	-0.179	-0.024	-0.001
	Dana	4.15 (.16)	-27.43	40.3	6.2 (4.3)	-0.173	-0.048	-0.008
	BM3	4.79 (.04)	-27.56	45.4	4.7 (5.0)	-0.175	-	-0.009

Table 1. Mean DOC concentration (mg/L) and standard deviation shown in parentheses, $DO^{13}C$ (‰), DOC:DON, Percentage labile carbon (PLC) and standard deviation are shown in parentheses. Mean rate of carbon consumption (k), and short and long term carbon consumption rates (STR, LTR) are shown for September of 2009 to March 2011 sampling periods. Discharge is shown in L/s underneath the sampling period.

Figures

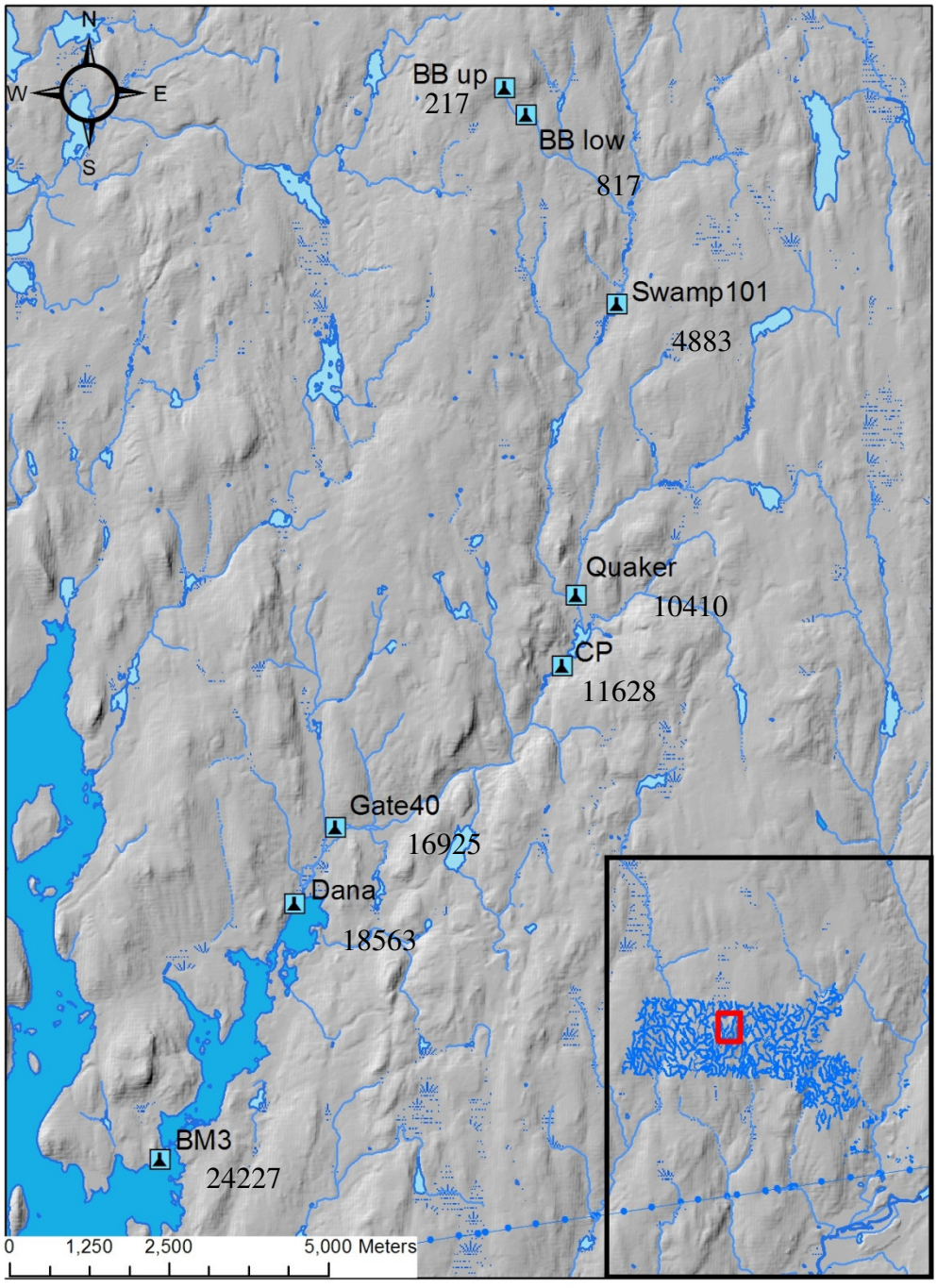

Figure 1. Sampling sites of the East Branch Swift River with distance of each site from headwaters in meters. Study area shown in inset map in the red square (bottom right).

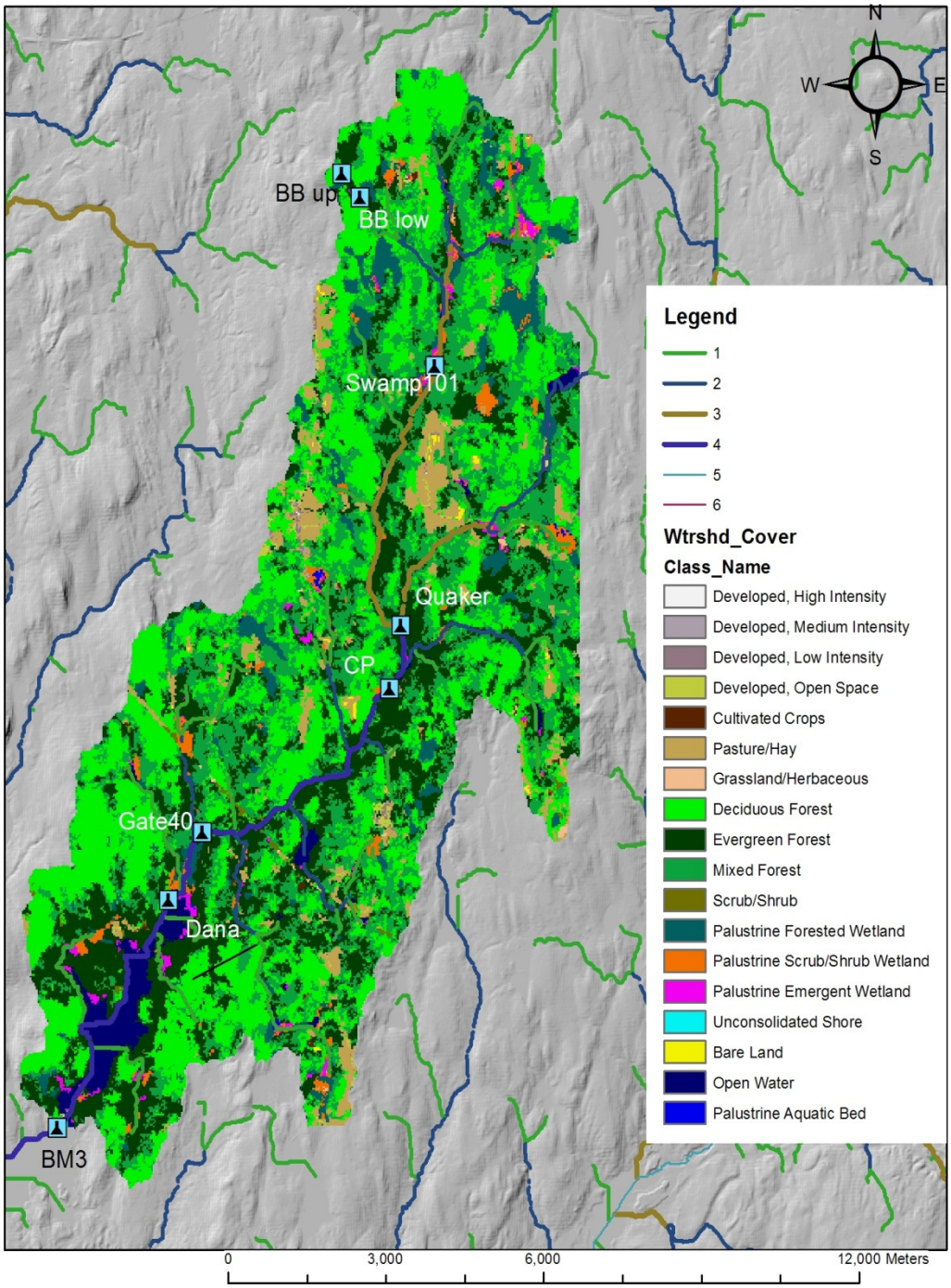

Figure 2. Land cover for the entire watershed before reclassification and Strahler stream order for the entire watershed.

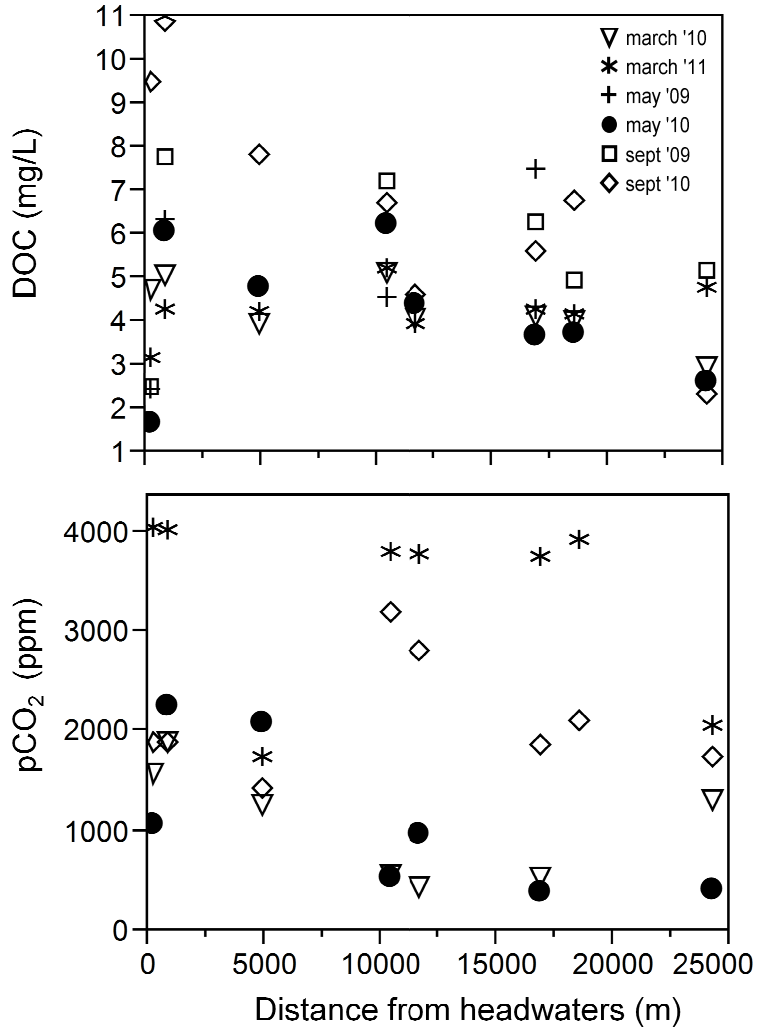

Figure 3. DOC (mg/L) and pCO_2 (ppm) displayed as a function of distance away from headwaters each sampling period with a unique shape. Standard deviation for DOC values can be found in Table 1.

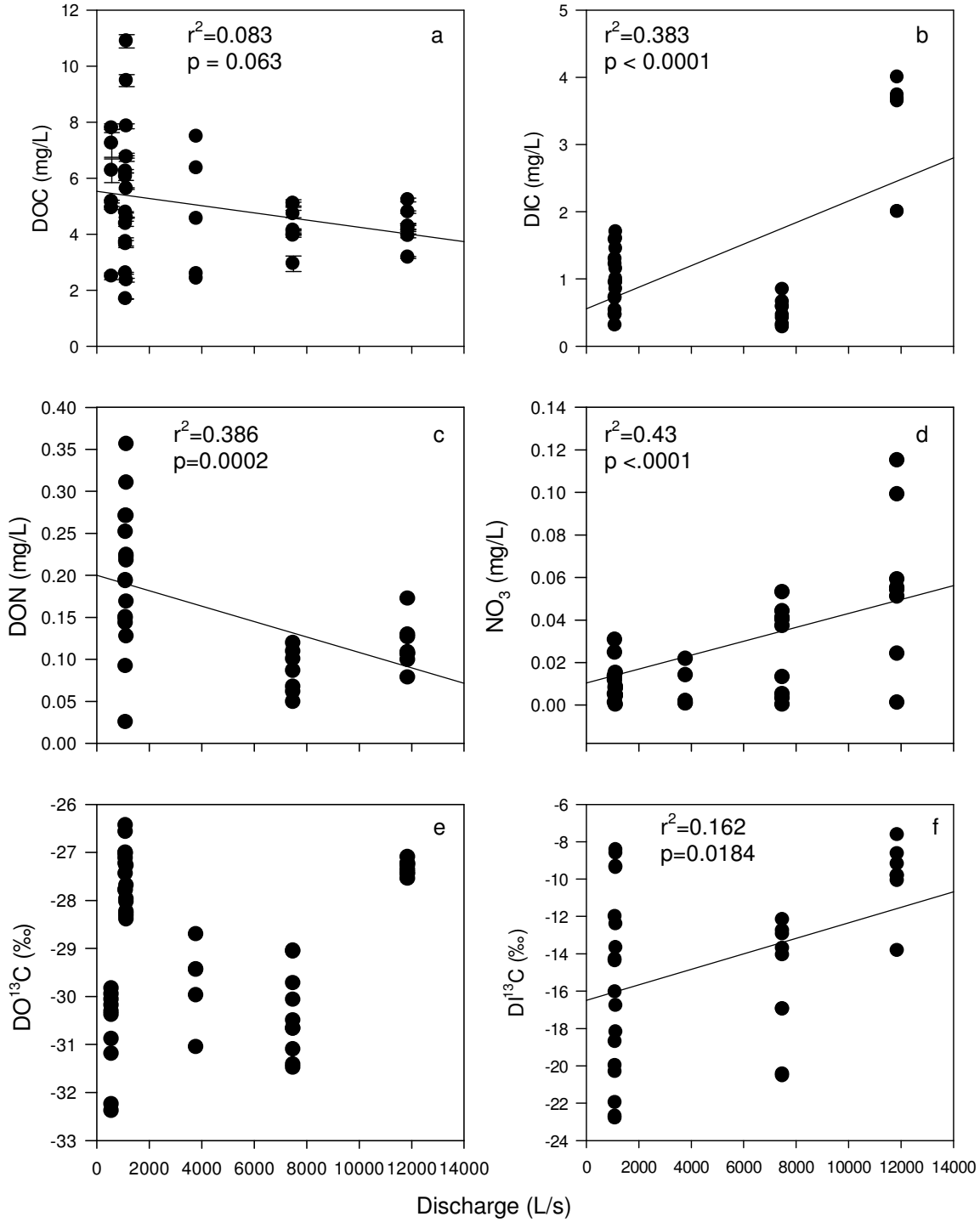

Figure 4. The influence of discharge on various factors. Standard deviations for isotopic measurements are < 0.32 ‰ for $DI^{13}C$ and <0.1 ‰ for $DO^{13}C$.

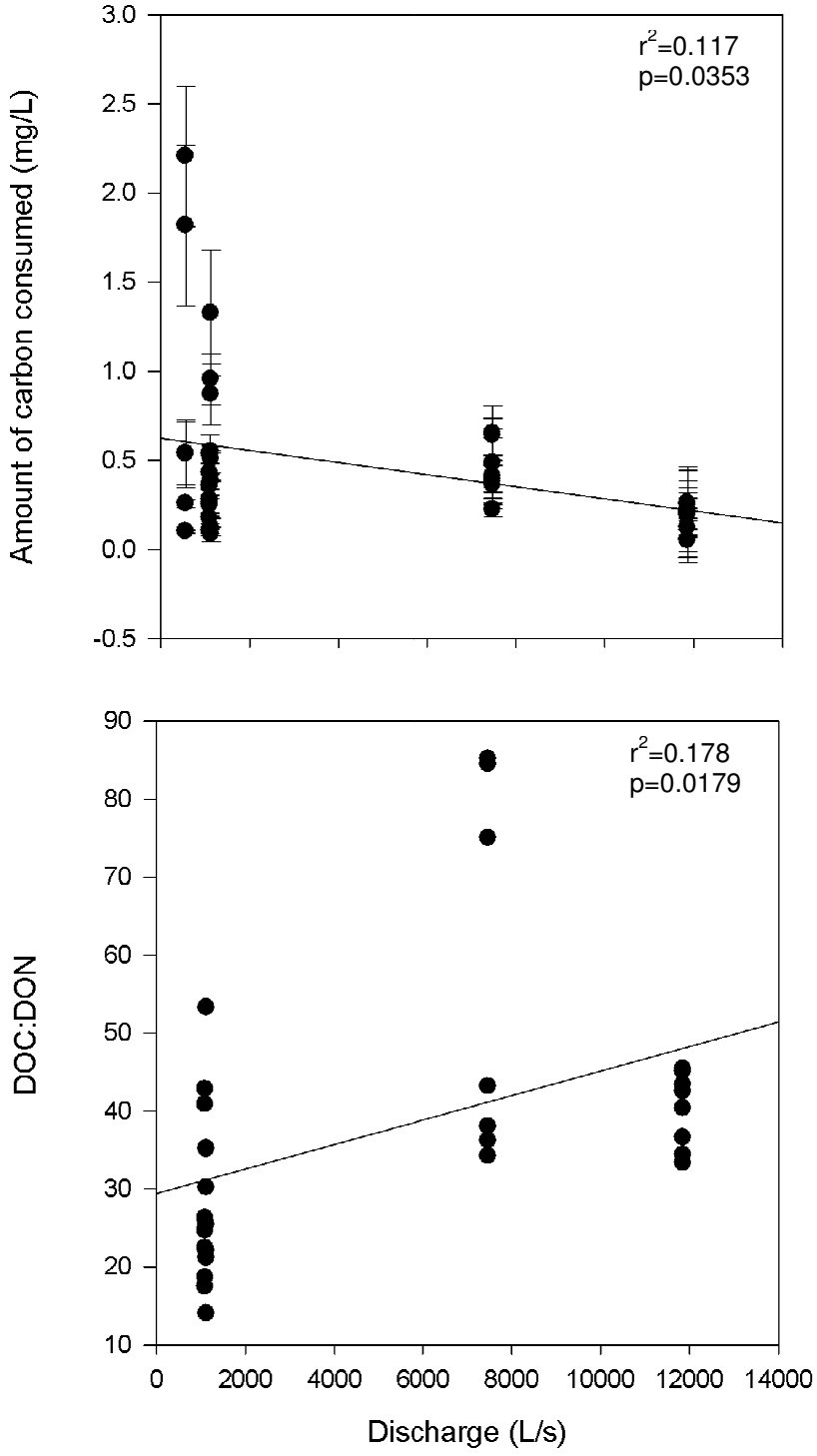

Figure 5. The influence of discharge on the amount of carbon consumed (mg/L) and the DOC:DON quality.

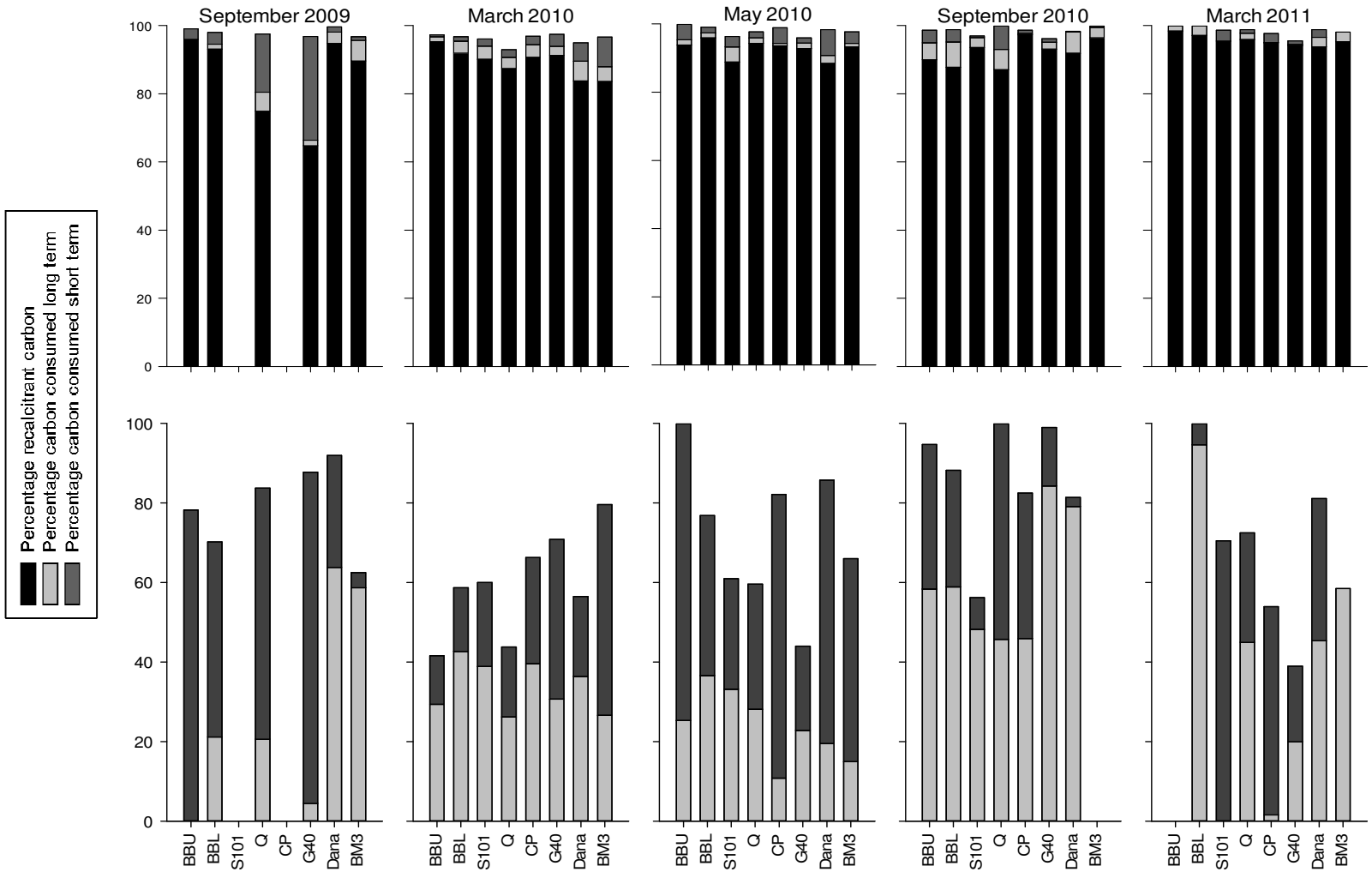

Figure 6. (Top row) The percentages of recalcitrant carbon, carbon consumed within the long term (7-21 days), and carbon consumed in the short term (0-2 days) for each site during each time period. (Bottom Row) Percentages of the total percent consumed shown as short term labile and semi-labile fractions.

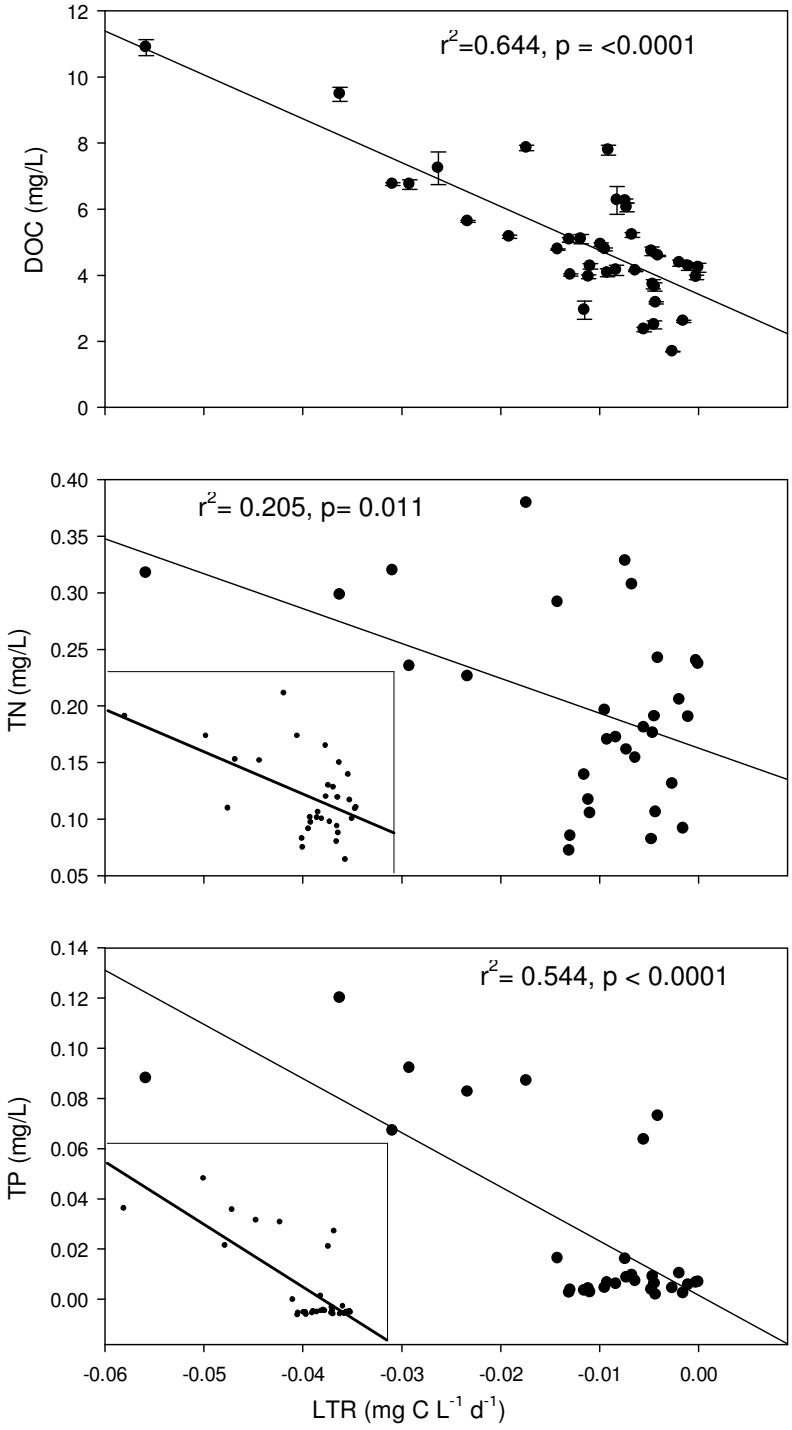

Figure 7. The influence of DOC, total nitrogen (TN) and total phosphorous (TP) on LTR. Inset figures show DON (r^2=0.287, p = .0014) and DOP (r^2=0.565, p < 0.0001) respectively.

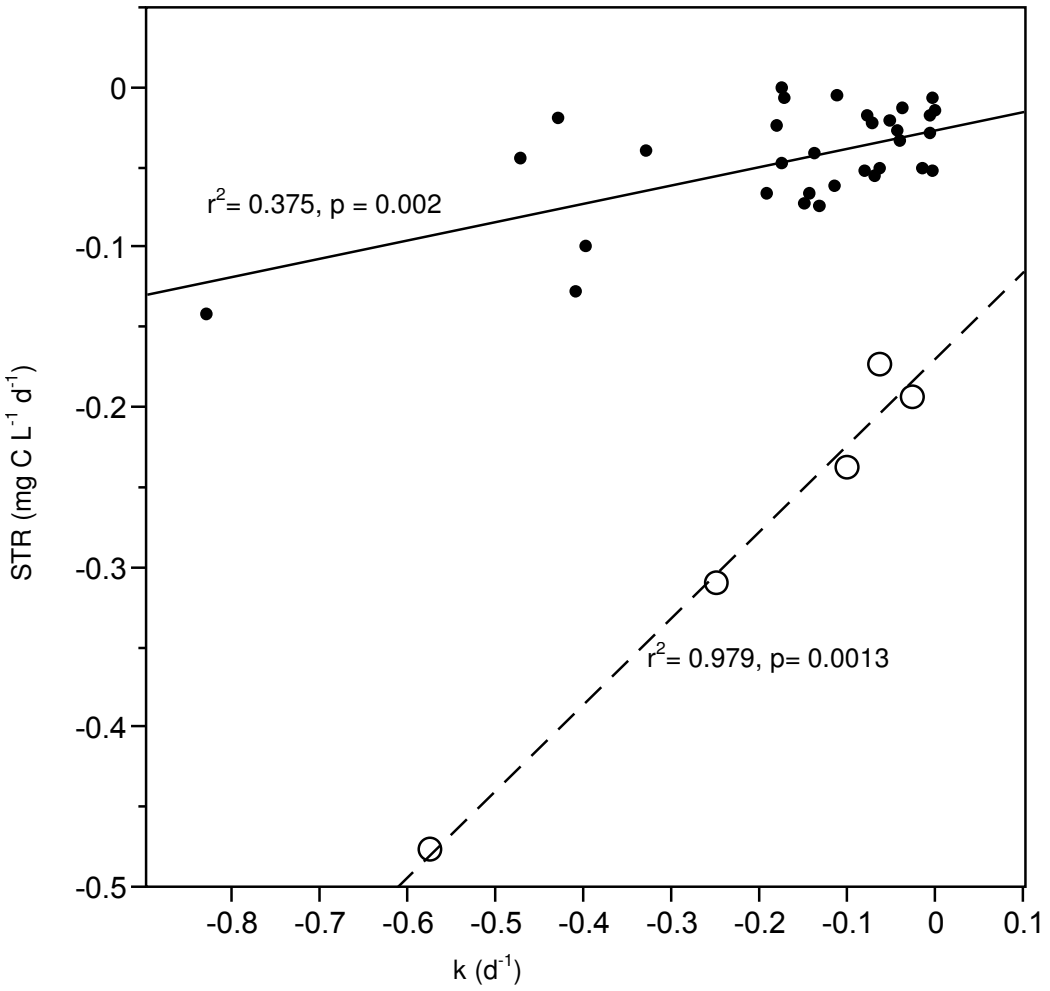

Figure 8. Short term rates as a driver of overall consumption rates (k). Open circles denote samples from September that exhibit a faster consumption of labile material in the short term relative to the rest of the pooled data represented by dark circles.

Vita

Eric Hall was born on May 25, 1987 in Watertown, NY. He graduated from General Brown High School in 2005 and moved to Cortland, NY later in 2005 to attend SUNY Cortland from which he graduated in 2009 with a B.S. in Biomedical Sciences. Mr. Hall matriculated at Virginia Commonwealth University in August 2009 to pursue a M.S. degree in Biology and began his research in the fall of 2009 in the Biogeochemistry Lab. After graduation, Eric has been offered a position in the Integrative Life Sciences at VCU where he plans to continue his study.