Water Resources Research Institute of The University of North Carolina

Report No. 438

NITROGEN RETENTION IN URBAN STREAMS: IMPLICATIONS FOR ECOLOGICALLY BASED STREAM RESTORATION

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UNC-WRRI-438

The research on which this report is based was supported by funds provided by the North Carolina General Assembly and/or the US Geological Survey through the NC Water Resources Research Institute.

WRRI Project No. 70256
September 2013

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ABSTRACT

Altered hydrology and increased pollutant loads in urban areas have led to degraded streams and increased pollutant transport. Ecologically based stream restoration practices seek to improve both form and function by stabilizing the channel, reconnecting floodplains and increasing geomorphologic heterogeneity within the stream. While the primary goals of restoration are often to reduce flooding and decrease sediment loss, nutrient retention via uptake and assimilation by microbial communities in transient storage zones (e.g. hyporheic zones, deep pools) can be enhanced as well. Specifically, channel complexity can increase biogeochemical processes by increasing contact between nutrients in stream water and biologically active, carbon-rich sediments.

The extent to which stream restoration increased transient storage, nitrogen retention and nitrogen removal via denitrification was investigated in restored and unrestored streams in North Carolina. Transient storage and reach-scale nitrate and phosphate uptake were measured using concomitant releases of chloride (nonreactive tracer), nitrate and phosphate; denitrification rates were measured via acetylene block. Our study found that background nutrient concentrations and instream geomorphic features (e.g., rock cross vanes, root wads, constructed riffles) were important predictors of reach scale nutrient retention and patch scale denitrification. Uptake of nitrate and phosphate was positively influenced by water column concentration and hydrogeomorphic characteristics of the reach. Uptake velocity (V_f), which is the velocity at which a nutrient moves through the water toward the sediment, was similar to values other urban streams nutrient ($V_{f\text{-}NO3}$ range of 0.02-3.55; $V_{f\text{-}PO4}$ range of 0.014-19.1 mm min^{-1}). Uptake velocity for both nitrate and phosphate was positively correlated with instream velocity suggesting the potential for increased pumping and delivery of stream water nutrients to the streambed during high flow. In three of the study sites, significantly greater denitrification rates were measured near instream structures (e.g., cross-vanes), which created channel heterogeneity, provided habitat for microbial colonization and potentially enhanced hyporheic exchange. Reach scale results also supports the importance of channel complexity with greater NO_3-N uptake observed throughout the year in the restored reach at LSC with greater heterogeneity compared to the unrestored section. Denitrification rates were significantly higher in restored (312±263 μmol m^{-2} h^{-1}) compared to unrestored (237±200 μmol m^{-2} h^{-1}) streams.

Our study suggests a need to reconsider the classification of streams based solely on land use. By lumping all urban streams together, high variability in watershed characteristics (e.g. stormwater infrastructure, point and non-point source pollutant inputs) and channel morphology (e.g. riparian cover, geomorphic complexity) are overlooked which can have far-reaching implications for conclusions derived from the study. This is particularly critical in urban streams where the variability is vast. Inclusion of metrics in future studies that classify streams in terms of geomorphology (e.g. habitat complexity, sediment size distribution, channel incision) would facilitate interpretation of complex and highly variable results.

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ACKNOWLEDGEMENTS

Many individuals and organizations contributed to the successful completion of this project. We'd like to the thank Charlotte-Mecklenburg Stormwater Services, City of Durham Stormwater and the City of Raleigh Stormwater for access to field sites and background geomorphological and water quality data. We thank Sandra Clinton for helpful comments and suggestions on an earlier version of this manuscript. We also thank A. Jefferson, F. Birgand, A. Apple, B. Blue, E. Darr, N. Garris, L. Haithcock, W. Kimbrell, C. Lattimore, B. Long and B. Marvel for assistance in the field and lab; K. Hall, J. Schrum and J. Karl of Charlotte-Mecklenburg Stormwater Services for assistance with design plans and site selection and access; C. Miller at Wildlands Engineering, C. Tomsic at Baker Engineering and B. Doll at NCSU for helpful discussions involving stream restoration project design and construction. Finally, we thank the Water Resources Research Institute for funding this research.

1. INTRODUCTION

1.1 Urbanization

Watershed disturbances stemming from urbanization, including an increase in impervious surface area and altered hydrology, have been the subject of several studies. These disturbances, coupled with an increased in fertilizer use and combustion of fossil fuels, result in excessive nutrient loading to aquatic ecosystems (Aber et al. 1989, Bernot and Dodds 2005, O'Brien et al. 2007, Inwood et al. 2005, Rabalais 2002, Earl et al. 2006, Walsh 2005). This increase causes eutrophication of rivers and estuaries, acidification of freshwater ecosystems, fish kills, and shifts in community structure (Howarth et al., 1996). With over one-third of the rivers in the United States listed by the Environmental Protection Agency (EPA) as impaired, many due to the aforementioned issues, addressing the problem of stream degradation is of utmost importance (U.S. EPA, 2000).

Hydrologic modification (i.e. increased impervious surface area, soil compaction, deforestation, storm water management infrastructure) in urban landscapes leads to increased flashiness of storm hydrographs, thereby contributing to rapid geomorphic adjustments within urban channels. Widening and deepening of the active channel is a common symptom, as streams respond to changes in streambed sediment loads and historically unprecedented flow regimes (Wolman 1967). This leads to decreased habitat heterogeneity and generally degraded ecosystem functions (Groffman et al. 2005; Meyer et al. 2005; Paul and Meyer 2008, Walsh et al. 2005).

Stream restoration ''Based on the principles of the Rosgen geomorphic channel design approach is most commonly accomplished by restoring the dimension, pattern, and profile of a disturbed river system by emulating the natural, stable river'' (Rosgen 2007). This Natural Channel Design (NCD) approach is often an extremely invasive process, requiring heavy construction equipment to re-grade riparian banks and reshape stream channels to mimic a geomorphically stable reference condition, based on a classification method of natural streams (Rosgen 1994). Ideally, channel reconfiguration increases floodplain connectivity and sinuosity in low gradient alluvial valley streams; however, the urban landscape poses challenges to this approach due to space limitations created by constraining infrastructure and private property. Thus, grade control structures are used to achieve the desired slope gradient rather than meander bends. These in-stream structures can be designed to improve habitat value, reduce flow velocities, and direct thalweg energy away from banks, resulting in decreased sediment export and improved channel stability.

Structures typically intended for grade control and flow direction (e.g., boulder vanes and cross vanes, log vanes, rock weirs, constructed riffles) vary widely in form and function, based on the restoration goals, available materials, and design standards. Challenges lie in transferring the discretion and intentions of the design engineer's plans from paper to the site, which could result in structures becoming either ineffective or destructive to the project goals (Endreny and Soulman 2011), and may require considerable investment of post-project time for reassessment and maintenance. A great deal of contention exists between the stream restoration industry and scientists working within fluvial systems, with proponents and critics of NCD in both camps (Lave 2009). One major criticism of the approach is an exaggerated emphasis of channel form as an oversimplified indicator of natural processes (Kondolf 1998; Niezgoda and Johnson 2005).

Advancing the theory and practice of stream restoration requires effective evaluations of projects (Kondolf 2007) and collection of comparative biophysical data (Palmer and Filoso 2009) to inform innovation in ecological landscape design.

A commonly stated goal of stream restoration is to reestablish ecological and hydrological function of streams through manipulation of the channel and floodplain morphometry. Current practices generally focus on improving stream stability, minimizing flooding and restoring geomorphic form (e.g. meanders and bends, sloped banks). Restoration strategies that increase contact between nutrient-rich stream water and biologically active streambed sediments, promote groundwater-surface water interactions, and increase carbon availability, are predicted to positively impact on instream nutrient retention (Craig et al. 2008, Aldridge et al. 2009). Instream structures such as debris dams, woody debris additions, step-pool and riffle-pool sequences have the potential to enhance these functions, however, quantitative assessment of their efficiency in restored urban streams is largely untested.

Considering this, urban stream restoration aims to repair hyporheic exchange by increasing geomorphic heterogeneity with meandering channels, instream structures, debris dams, and heterogeneous bed materials in efforts to increase nutrient retention and removal capability (Claessens et al. 2010, Bukavekas, 2007, Hall and Tank 2003, Mulholland et al. 1997). At present, quantitative data to present urban stream restoration as an effective method for repairing the intrinsic ability of a stream to retain and remove nutrients are inconclusive (Sudduth et al. 2011, Bukaveckas 2007, Klocker et al. 2009, Doyle et al. 2003, Roberts et al. 2007, Selvakumar et al. 2010, Sivirichi et al. 2011, Filoso and Palmer 2011).

1.2 Theory and background of nutrient spiraling

Nutrient spiraling metrics were developed to describe and quantify the transport of nutrients in a unidirectional flow system. The method developed by Newbold et al. (1981) and standardized in the Stream Solute Workshop (1990) enables the calculation of three nutrient spiraling metrics: uptake length (S_w), uptake velocity (V_f), and uptake rate or flux (U). Uptake length is the length traveled downstream by a nutrient ion before being removed from the water column. This parameter is dependent on background water chemistry, channel width and volumetric flow rate (Q). A short S_w (m) is indicative of high nutrient retention or removal. Uptake rate, U, is the mass of nutrient removed from the water column per unit area per unit time (mg m^{-2} h^{-1}). It is dependent on the uptake velocity and background chemistry of the stream, and thought to follow a 1st-order kinetic model increasing with increasing nutrient concentration. Uptake velocity, V_f (mm min^{-1}), describes the vertical velocity at which nutrients move from the water column to a site of storage or removal. Since it is independent of Q it is a useful parameter for comparison across different stream sites. High values of both U and V_f indicate high removal and retention capabilities of a stream reach. Equations 1-3 describe how each metric is related to the others.

$$S_w = \frac{1}{k} \tag{1}$$

$$U = V_f C_o \tag{2}$$

$$V_f = \frac{Q}{wS_w} \tag{3}$$

Where k is the 1st-order uptake rate coefficient (L^{-1}), Q is stream discharge ($L^3 T^{-1}$), C is the nutrient concentration ($M L^{-3}$).

1.3 Transient Storage

Transient storage is the temporary retention of solutes within portions of a stream characterized including both in-channel areas (e.g., pools, eddies, backwater areas) and in the hyporheic zone, which is the porous boundaries of the streambed and banks (Packman and Bencala, 2000). Coupling nutrient additions with the addition of a conservative solute allows for characterization of transient storage. Analysis of the solute breakthrough curve provides the following information: the transient storage area (A_s), storage zone exchange coefficient (α), and dispersion coefficient (D). These can then be used along with the surface water cross-sectional area (A) to calculate additional transient storage parameters, as described in Webster et al. (2003), in equations 4-7 below.

$$T_w = \frac{1}{\alpha} \tag{4}$$

$$T_s = \frac{As}{A} \times \frac{1}{\alpha} \tag{5}$$

$$S_h = T_w u \tag{6}$$

$$HRF = \frac{As}{Q} \tag{7}$$

The turnover time in the water (T_w) is the inverse of the storage zone exchange coefficient and represents the average time a parcel of water spends in the water column before entering transient storage zones. Similarly, the turnover time in transient storage (T_s) represents the average time water spends in transient storage before reentering the water column. The hydraulic uptake length (S_h) refers to the longitudinal distance a parcel of water spends in the water column before entering transient storage and is a product of T_w and stream velocity (u). (Packman and Bencala 2000). The hydraulic retention factor (HRF) allows for comparison of transient storage areas across sites by normalizing for Q. It is the average time water spends in transient storage per unit length of stream (Morris et al. 1997). These parameters coupled with the nutrient spiraling metrics give a fuller picture of the nutrient retention processes and facilitate comparison among stream types and potential controlling factors (Bukaveckas 2007, Harvey and Wagner 2000).

The goals of this study were to (1) quantify the differences in nutrient retention between restored and degraded reaches and (2) understand the influence of instream engineered structures on nutrient retention in low-order urban streams within North Carolina. We focused both on reach scale (reach scale nitrate and phosphate uptake) and patch scale (denitrification rates in stream sediments) effects. The study examines the influences of the age of a restoration project, the restoration strategies used (e.g. riffle –pool sequences, re-meandering streams), geomorphological characteristics of the stream including in-stream transient storage parameters, and background biogeochemical data.

2 METHODS

2.1 Site Descriptions

Low order urban streams in the Piedmont region of North Carolina were selected for this study. Three are located in Raleigh, NC, USA and three in Charlotte, NC, USA (Table 1). Site selection was conducted in consultation with the North Carolina Ecosystem Enhancement Program (EEP) and stormwater agencies in Raleigh, Durham and Charlotte. In addition, local stream restoration experts were consulted to select stream reaches that were of similar size based on watershed area and included a range of restoration ages. While not possible at all sites, an unrestored reach immediately upstream of each restored reach was included (Table 1).

Rocky Branch (RB) is a 1st order stream that was restored in 2002 and bisects the North Carolina State University (NCSU) campus. The majority of the watershed is mostly located on campus and is 99.2% developed and 35% impervious (Sudduth 2011). Restoration strategies included boulder step-pool sequences, constructed riffles, floodplain bench creation, and planting of a riparian buffer with an average canopy cover of 85% as measured via densiometer. The riparian corridor is narrow, averages 25m wide and is flanked by a road on one side and institutional buildings on the other. The stream has a gravel bed and an overall slope of 1.1%. The average wetted width and depth of the 48 m reach during baseflow were 1.21 m and 0.04 m respectively.

Abbot Creek (ABT) is a 2nd order stream and includes paired restored and unrestored reaches in a medium density residential neighborhood in Raleigh, NC with 18% imperviousness (Sudduth 2011). The restored section flows through a wide vegetated floodplain, which was once a large pond before development in mid-20th Century. Restoration was completed in 2001, making this the oldest of the restored streams in this study. The stream has a meander pattern providing a stable riffle-pool sequence and is well connected to the floodplain. Canopy cover was 40% during leaf-out. Other features include root-wads on outside meander bends and small cross-vanes and constructed riffles along straight reaches. The substrate is gravel in the riffles and sand on the pointbars and pools. The average wetted channel width during baseflow was 1.88 m and depth was 0.03 m. The channel slope is 0.79%. The unrestored reach of Abbot Creek (ABT UR) is located upstream of the restored section and separated by a road culvert. While land use in the contributing watershed is similar to the restored section, encroaching lawns narrow the riparian zone to <6 m on either side but maintain shading of the stream surface. It is deeply incised, disconnected from the floodplain, overwidened, and straightened with an average wetted width of 1.31 m and depth of 0.03 m. It is characterized by long riffles and runs. The slope is steeper than its restored counterpart at 1.2 %, however substrate characteristics are similar. North Creek (CENT) at Centennial Campus at NCSU in Raleigh, NC includes a reach restored in 2008 and a paired unrestored reach just upstream. The watershed includes grassed and wooded areas as well as institutional buildings resulting in 34% imperviousness. The restored section has a wide floodplain (50-70 m) flanked by wetlands on the left bank. With only a slight meander pattern, cross-vanes were utilized for flow variation and stabilization. The average wetted channel width during baseflow was 1.26 m and the depth was 0.03 m; riffle sections included inner berms narrowing the wetted width to 1.2 m. Channel substrate consisted of gravel in the riffle sections and sandy pools/glides/runs. The channel slope was 1.3%. Vegetative cover consisted primarily of herbaceous grasses and newly planted deciduous trees with a canopy density of 20% during

leaf-out. The unrestored reach of North Creek (CENT UR) is directly upstream of the restored reach. The average wetted width and depth during baseflow were 2.9 m and 0.06 m respectively. It is disconnected from the floodplain and characterized by steep rip-rap cascades with two large pools. The overall slope is steeper than the restored section at 3.0%. Substrate in this section is primarily gravel with sand in the pools. Though the floodplain is not connected, the mature riparian vegetation shades about 75% of the stream surface during leaf-out.

Dairy Branch at Sedgefield Park (SP) is located in Charlotte, NC. The restored section, constructed in 2006, is located in a municipal park heavily utilized for public recreation. The watershed extends above the municipal park into commercial and residential districts, with an overall 38% impervious. The reach includes a partial canopy of deciduous shrubs and trees as well as herbaceous grasses and sedges in the periodically mowed reconnected floodplain. Geomorphic restoration included creating a meandering pattern with riffle-pool sequences along the profile with rock sills for grade control, and regraded banks to allow access to a floodplain. Channel substrate is dominated by large gravel in the riffle sequences overlaying native sands. The average wetted width during baseflow was 0.87 m and the depth was 0.06 m with an overall slope of 1.2%.

Little Sugar Creek at Hidden Valley Ecological Park (HV) in Charlotte, NC includes paired restored and unrestored reaches and is located in an urban residential and commercial watershed with average impervious area of 29%. The restored reach was constructed in 2004. A narrow replanted riparian zone is composed of mostly deciduous trees, and shrubs, framed by a maintained mowed grass pathway for public access. The floodplain is reconnected with several intermittent wetlands between highly sinuous meander bends. During baseflow, the average wetted width and depth were 1.27 m and 0.10 m respectively. The high sinuosity creates a low overall slope of 0.13%. While prominent log vanes for grade and erosion control exist at this project, they are not included in the reach studied due to their proximity to low velocity pools with low hydraulic conductivity clay bed material and wide and deep channel dimension that made solute tracer experiments less feasible. One log vane structure was included at the end of the studied reach, however the performance of the structure became increasingly limited through the study period as sand gradually deposited and buried any observable significant bed-elevation changes. The unrestored reach of Little Sugar Creek (HV UR) has similar watershed characteristics to the restored section. The geomorphology of the unrestored reach was a straightened incised channel. A road crossing separates the restored and unrestored reach with an open bottom box culvert. The restored reach included a lateral scour pool with armoring boulders at the outside margin of one meander bend, and substantial overhanging vegetation providing 50% canopy cover during leaf out. The average wetted channel width during baseflow was 1.1 m and the depth was 0.08 m. It is disconnected from the floodplain and overall slope is 0.1%.

Muddy Creek (MC) is a recently completed restoration project (2010) in Charlotte, NC that had ongoing work and adjustments during the study period. Muddy Creek was restored from the headwaters to its confluence with a larger tributary, which precluded inclusion of a paired unrestored reach for this site. Watershed land use is primarily residential with an overall imperviousness of 19%. Dense riparian herbaceous vegetation was established in the spring, along with the installation of live stakes and saplings in the riparian area. It features natural channel design, riffle/step/pool sequences, and floodplain reconnection with average wetted

channel dimensions of 1.58 m wide and 0.2 m deep during baseflow. It has an overall slope of 1.2%. Channel substrate is a mixture of clay, small cobble, and sand. Recent planting of riparian vegetation (Spring 2011) is a mix of herbaceous forbs and grasses, held in place with coir netting and live stakes. At the time of field experiments, no riparian canopy cover by deciduous trees was established.

Toby Creek (TC) is an incised and degraded stream on the campus of UNC Charlotte in Charlotte, NC. The watershed includes both forested and high impervious commercial and residential land use with a total imperviousness of 16%. The study reach features nearly complete canopy cover (80-90%) and banks incised several meters above the streambed. Substrate is primarily sand and the overall slope is 0.25%. Average wetted channel width and depth during baseflow were 3.1 m and 0.26 m respectively.

Gar Creek (GC) in Charlotte, NC is a minimally impacted stream with a primarily forested watershed, including some low density residential and agricultural (pasture) land use. Overall imperviousness in the watershed is 2%. The reference reach has partially incised banks, full canopy cover, and several natural riffles and pools are features of the study reach. Substrate is characterized by sand, large gravel, small boulders and cobble. Average wetted channel dimensions during baseflow were 5.3 m wide and 0.2 m deep, with an overall slope of 2.7%

Table 1: Stream and watershed characteristics. Mean values (± standard deviation) for baseflow discharge (Q), water depth (h) and wetted channel width (w).

Site	Stream order	Year Restored	Length (m)	Slope (%)	Q, L/s	u, m/s	h, m	w, m
Reference								
Gar Creek (GC)	2	-	84	2.7	12.6±5.6	0.01±.004	0.26±0.01	5.3±00
Restored								
Muddy Creek (MC)	1	2010	40	1.2	2.19±1.32	0.017±0.01	0.18±0.02	1.58±0.19
North Creek at Centennial (CENT)	1	2008	72	1.3	1.50±0.39	0.045±0.03	0.03±0.01	1.24±0.37
Dairy Branch at Sedgefield Park (SP)	1	2006	61	1.2	1.02±0.29	0.021±0.01	0.06±0.02	0.87±0.23
Little Sugar Creek at Hidden Valley (HV)	2	2004	37	0.5	6.35±4.92	0.047±0.04	0.10±0.04	1.27±0.42
Rocky Branch (RB)	1	2002	48	1.0	0.89±0.86	0.028±0.03	0.04±0.02	1.16±0.43
Abbot Creek (ABT)	2	2001	44	0.8	2.33±1.06	0.04±0.02	0.03±0.00	1.89±0.07
Unrestored								
Abbot Creek (ABT-UR)	2	-	55	1.2	1.8	0.05	0.03	1.31
North Creek at Centennial (CENT-UR)	1	-	63	3	2	0.01	0.06	2.9
Hidden Valley (HV-UR)	2	-	41	0.1	5.98±6.90	0.06±0.05	0.08±0.01	1.1±0.42
Dairy Branch at Sedgefield Park (SP-UR)	1	-	61	1.2	0.61±0.59	0.02±0.01	0.06±0.02	0.87±0.23
Toby Creek (TC)	3	-	67	0.25	9.06±12.4	0.03±0.00	0.26±0.02	3.10±0.00

2.2 Site Characterization

Longitudinal surveys were performed in winter 2010 at each site to obtain the overall slope and characterization of geomorphic features. Cross-sectional surveys provided information on depth and width of the overall channel. Stream shading by riparian vegetation was estimated in spring and summer via canopy densiometer. Watershed land use was characterized using land use data from Wake and Mecklenburg Counties, NC.

Discharge, representative wetted cross-sectional area and background water chemistry were measured one day prior to each nutrient addition experiment at a stable cross section within the reach. A Flo-Mate model 2000 portable flowmeter was used at the Raleigh sites, and a SonTek FlowTracker ADV was used at the Charlotte sites. Velocity measurements were taken at 60% of the depth every foot across the stream to get an accurate flow measurement. When this method was not appropriate, specifically during times of low flow, a salt slug method was used to determine discharge. Background conductivity was measured using a YSI conductivity meter. The wetted cross-sectional area was estimated from average water depth and width measurements.

Sediment samples were collected prior to each nutrient addition experiment to determine sediment characteristics and measure denitrification rates. Sediment was sampled to a depth of 5 cm at targeted depositional locations within the stream reach using plexiglass core tubes with a diameter of 3.8 cm (area = 11.3 cm^2, volume = 56.7 cm^3). Previous studies (García-Ruiz et al. 1998a; Inwood et al. 2007) have shown that the greatest denitrification activity occurs within the top 1-5 cm of sediments in lotic systems. Sediments were collected upstream and downstream from engineered steps, at depositional locations within riffles, in pools, and in unrestored reaches with less distinct geomorphic complexity. Six cores were taken at each cross-section, with two cross-sections used to represent the geomorphic conditions at each sampling location (for a total of 12 cores). These cores were stored in watertight Whirl-Packs, and placed on ice in a cooler for transport back to the lab (within 3 hours). Sediment samples were homogenized and 25 cm^3 was used to measure percent organic carbon content (%C) and ash free dry mass (AFDM). Samples were dried at 60 °C, weighed, burned at 500°C for 4 hours, and re weighed to determine the %C and ash-free-dry-mass (AFDM) at each sampling location.

Stream water samples were collected and analyzed for background carbon and nutrient concentrations. Water samples for nutrient analysis were filtered within 4 hours of collection (ashed 0.7 um Whatman GF/F) and frozen immediately at -20°C after transport back to the lab. Concentrations of NO_3-N and PO_4-P were determined on a Lachat QuikChem 8500 (Hach Inc., Loveland, Colorado), using the cadmium reduction (QuikChem Method 10-107-04-1-A; detection limit 0.016 mg NO_3-N L^{-1}) and ascorbic acid methods (QuikChem Method 10-115-01-1-A; detection limit = 0.001 mg PO_4-P L^{-1}), respectively (APHA, 2005). Dissolved organic carbon (DOC) concentrations were analyzed on a Shimadzu TOC-TN analyzer (Shimadzu Inc., Kyoto, Japan) using high-temperature combustion (detection limit = 0.08 mg L^{-1}). Additionally, unfiltered stream water was collected at the site for use with the denitrification assay.

2.3 Nutrient Addition Experiments

Nutrient addition experiments were performed seasonally under baseflow conditions from June 2010 through April 2011 in order to quantify whole stream nitrate (NO_3^-) and phosphate (PO_4^{2-})

uptake (Stream Solute Workshop, 1990; Payn et al., 2005). Targeted experiments were also conducted before and after leaf fall to investigate effects of enhanced carbon supply on rates of nutrient retention. A spring study was not completed at HV because of backwater resulting from a recently constructed beaver dam on the site. Also, maintenance to instream structures occurred at SP in spring 2011, preventing an experiment at that time. Uptake measurements were made concurrently in paired restored and unrestored reaches at HV. Nutrients were injected at a location upstream of the unrestored reach of the stream forming one continuous study.

Nutrients and conservative tracer (NaCl) were added to distilled water in the laboratory and separated into two 18.9 L Mariotte jars connected in series. The solution was allowed to drip into the stream at a known rate (50-120 ml/min, depending on discharge and background water chemistry) to raise the instream nutrient concentrations above the background concentration. Plateau samples were collected in triplicate using acid washed 250 ml plastic bottles. For each reach, water samples were collected at 5-8 cross-sections chosen at specific places along the reach in order to provide information about geomorphologic effects on nutrient retention. For example, samples were collected immediately up- and downstream of instream structures (e.g. constructed riffle, cross-vane, debris dam).

After sample collection, the injection was stopped and conductivity recorded until background levels were reached. Nutrient spiraling metrics were calculated based on water chemistry of samples collected at plateau. Uptake length (S_w) was calculated from the slope of the linear regression of the ln-corrected nutrient concentration versus downstream distance (Stream Solute Workshop, 1990). The remaining nutrient spiraling metrics (U and V_f) were calculated using equations 2 and 3.

2.4 Transient Storage Parameters

A mass balance model (OTIS; Bencala and Walters (1983)), was used in this study to estimate storage parameters from the conductivity data collected during each nutrient injection experiment. Measured data were compared to model output to visually calibrate the model and estimate the following parameters: stream channel cross-sectional area (A), storage zone cross-sectional area (As), dispersion coefficient (D) and storage zone exchange coefficient (α). These parameters were then used to calculate the additional metrics in Equations 4-7.

2.5 Denitrification Assays

Denitrification rates were measured using the chloramphenicol amended acetylene block method on sediment slurries in anoxic microcosms (Yoshinari and Knowles 1976; Tiedje et al. 1989). In this method, acetylene gas blocks the activity of nitrous oxide reductase, effectively preventing the conversion of N_2O to N_2 gas (Balderston et al. 1976). The addition of chloramphenicol mediates the short term microbial response by preventing new enzyme production (Balderston et al. 1976). Sediment cores were homogenized and split into 25 cm^3 (30-45 g dry mass) subsamples (n = 3 per sampling location per day). These were placed in acid-washed narrow-mouthed 160 mL glass bottles. 50 mL of unfiltered ambient stream water was added to complete the slurry. Chloramphenicol was added to reach a concentration of 0.3-0.4 mM to minimize the interference with existing enzymatic pathways caused by the antibiotic, while preserving the inhibitory effects on de novo protein synthesis (Wu and Knowles 1994). These bottle "microcosms" were fitted with new air tight rubber septa caps.

Oxygen in the microcosm headspace and slurry was removed by purging the bottles with helium; vacuum and helium were cycled at 1 minute intervals for a total of 8 minutes. Pure acetylene gas (produced by the reaction of calcium carbide with water) was injected into the bottle through the sealed septa cap to achieve a concentration of 10% by total volume. Bottles were shaken vigorously after the addition of acetylene to equilibrate with dissolved gasses in the slurry.

Gas samples were taken within 10 minutes of the first injection using a 500uL gas-tight needle and sampled hourly. Gas samples were analyzed by Gas Chromatography (GC) on a Shimadzu GC-2014 fitted with a ^{63}Ni electron capture detector, and 2 m Porapak Q column, (flow rate 15 mL/min, at °100 C). A mixture of 95% Argon and 5% methane was used as the carrier gas. For calibration of the GC, pure USP grade (99%) N_2O gas was used to create a calibration curve by serial dilution, with concentrations ranging from 0.98-625 ppm by volume.

Within each bottle, the linear rate of N_2O production was used to determine denitrification rate, and the average of these rates from the 3 replicate microcosms was used to represent the denitrification rate for an individual sampling location. Because of potential interference by bottle effects (Tiedje et al. 1989), observed rates were not always linear for the entire course of the experiment (6-8 hours). Points representative of the linear portion of N_2O production were selected. When possible, the headspace of sediment microcosms (500 µL samples) were analyzed real time, to monitor the progress of the reaction, and to minimize the number of samples taken after bottle effects begin to depress rates. Otherwise, 5mL samples were placed in 3mL evacuated exetainer vials (LabCo, UK) with butyl septa caps. The positive pressure within the exetainer vials minimized the risk of contamination from outside air. The 5 mL sample volume was immediately replaced with 10% C_2H_2 in He in the microcosm headspace.

Total mass of N_2O in the headspace was calculated using the headspace N_2O concentrations and total microcosm volumes. Concentrations were correction for N_2O solubility in the aqueous phase with temperature-dependent Bunsen coefficient based on ambient laboratory temperature (Knowles 1982). The mass of N_2O produced over time was converted to areal rates (µmol N m^{-2} hr^{-1}) using sediment sample volume and depth (25 cm^3/5 cm).

2.6 Statistical analyses

Relationships between transient storage and nutrient spiraling metrics and hypothesized causal variables were tested using linear regression and ln transformed when required to satisfy the assumption of normality. That is, for all statistical analyses, the data were first tested to determine if they came from a normal distribution. If not, the data were transformed by taking the natural log (ln) of the values. Transient storage and nutrient spiraling metrics were compared among streams using one-way ANOVA with site as a single factor. Where the overall effect was significant, pairwise Tukey-Kramer post hoc comparison of means was used to test for differences. Reported statistics were determined to be significant at $\alpha = 0.05$. Ranges and means of measured and modeled values are presented with error shown as the standard deviation. Outliers beyond the 95% confidence interval were excluded (i.e., NO_3^- metrics at RB during Winter)

Denitrification rates ($x^{0.25}$ transformation) were compared using a one-way ANOVA with site as a single factor. Denitrification rates were also normalized for ambient nitrate concentration to correct for influences of nitrate limitation. This was accomplished by calculating (1) residuals of

regression of denitrification with nitrate and (2) z-scores. The residuals (observed value - predicted value) from a linear regression between nitrate and denitrification rates were used to compare denitrification rates among different watersheds. Residuals were placed into groups and means compared via one-way ANOVA and Tukey-Kramer post hoc comparison of means at a level of significance of $\alpha = 0.05$. To compare locations (e.g. individual geomorphic features) within a single site across multiple dates, the z-score was calculated for each set of replicate microcosms for that date.

$$z\ score = \frac{x-\mu}{\sigma} \tag{8}$$

Where x is the value of a single sample (one microcosm), μ is the mean of all samples from the site and σ is the standard deviation of the same population. This standardized our comparisons as relative differences between each location. A z score of zero would indicate that the sample was close to the population mean for that day. We used a one-way ANOVA and Tukey-Kramer post hoc comparison of means to compare the z-scores of consistent sampling locations. All statistical analyses were performed using SAS (version 9.2, SAS Institute, Inc.) and JMP (version 9.0.0 SAS Institute Inc.)

3 RESULTS

3.1 Physical and Hydraulic Characteristics

Baseflow discharge was relatively low across the 11 sites ranging from 0.3-24 L/s with an average of 5.1 ± 6.4 L/s (Table 1). Velocities ranged from 0.004-0.092 m/s with an average of 0.034 ± 0.025 m/s. Discharge and velocity did not vary significantly among sites or seasons during this study. Channel depth and width were correlated with discharge which is largely a function of watershed area (h: R^2=0.282, p=0.016; w: R^2=0.456, p=0.0011). For all restored streams, depth and width were not statistically different from each other. Values for channel width ranged from 0.6-5.3 m, depth from 0.02-0.27 m and slope from 0.79 to 2.7%.

To standardize transient storage to stream size, transient storage ratio (A_s/A) was calculated by dividing transient storage area (A_s) by surface water cross-sectional area (A). This ratio ranged from 0.04-2.4 with an average of 0.45±0.53 (Table 2). Dispersion (D) and storage zone exchange (α) ranged from 0.001-0.3 $m^2\ s^{-1}$ and 1.0 $x10^{-5}$-0.03 s^{-1} respectively. Transient storage normalized to stream cross-sectional area (As/A) was positively correlated with stream velocity (R^2=0.389, p=0.0075) based on linear regression analysis. Dispersion was negatively correlated with discharge (R^2=0.275, p=0.025) and stream depth (R^2=0.511, p=0.0013). Based on one-way ANOVA ($p<0.05$), A_s, A_s/A, alpha and D were statistically different among the sites, but no distinct pattern was observed.

Additional hydraulic factors descriptive of transient storage behavior, as outlined by Webster et al. (2003) were calculated from modeled and measured data. Turnover time in the water column (T_w), the inverse of α, ranged from 33 s to 2.8 hr. The longest turnover time was at SP, and the shortest on the restored reach of CENT however differences among sites were not statistically different. The average time water spends in transient storage (T_s) ranged from 20 s to 42 min

and was 26 min shorter than T_w on average. The longitudinal distance water travels downstream before entering transient storage, S_h, was 34 ± 37m on average and ranged from 1.3-120.0 m. When transient storage area is normalized for discharge, the resulting hydraulic retention factor (HRF) describes the time discharge spends in transient storage per meter of stream. Based on ANOVA of ln transformed data, HRF was highest at CENT (40±12 m s^{-1}) and lowest at TC (6.0±0.79 m s^{-1}) (Table 2).

3.2 Water chemistry

Concentrations of NO_3-N measured during the study experiments ranged from 65 µg NO_3-N L^{-1} at ABT-UR to 1070 µg NO_3-N L^{-1} at RB with an average concentration across all sites and dates of 340 ± 247 µg NO_3-N L^{-1} (Figure 1). The concentration of PO_4^{2-} ranged from 8 µg PO_4-P L^{-1} at MC in spring to 85 µg PO_4-P L^{-1} at HV in summer with an average concentration across all sites and dates of 35 ± 22 µg PO_4-P L^{-1}. Concentrations were measured during baseflow under steady state conditions with no influence from prior storm events. Ambient concentrations of PO_4^{2-} varied significantly across seasons (p=0.0348) with highest concentrations observed during the summer (56±19 µg PO_4-P L^{-1}) and lower concentrations throughout the rest of the year.

3.3 Nutrient Spiraling Metrics

A total of 20 nutrient spiraling experiments were completed at the 5 restored sites in this study. Two experiments at MC (NO_3-N uptake in spring; PO_4-P uptake post leaf fall) did not show a statistically significant change in solute concentration. These measurements are listed as zero uptake (Tables 2 and 3) and were excluded from further statistical analysis. Nutrient spiraling metrics for NO_3-N or PO_4-P were similar across sites and seasons with the exception of $U_{NO3\text{-}N}$ which had the highest measured values at SP and lowest at NC (p=0.02, Tables 3 and 4). Nitrate uptake length ($S_{w\text{-}NO3}$) ranged from 34.4 m to 2668 m (Table 3) and was not correlated with any measured environmental parameters. Uptake velocity for NO_3-N ($V_{f\text{-}NO3}$) ranged from 0.02-3.55 mm min^{-1} (Table 3) and U_{NO3} ranged from 1.36-116.4 mg m^{-2} h^{-1}. $V_{f\text{-}NO3}$ was positively correlated with stream velocity (R^2=0.53, p=0.0006) and U_{NO3} was positively correlated with ambient NO_3-N concentrations (R^2=0.26, p=0.025, Figure 2).

Phosphate uptake was correlated with concentration for all three measured nutrient spiraling metrics (Figure 2). Uptake length ($S_{w\text{-}PO4}$) ranged from 12.4-571.7 m (Table 4); $V_{f\text{-}PO4}$ ranged from 0.14-19.11 mm min^{-1} (Table 4); and U_{PO4} ranged from 1.06-422.7 mg m^{-2} h^{-1} (Table 4). Additionally, linear regression revealed that $V_{f\text{-}PO4}$ and U_{PO4} were positively correlated with ambient PO_4-P concentrations (R^2=0.26, p=0.025 and R^2=0.21, p=0.048, respectively) and $V_{f\text{-}PO4}$ was positively correlated with stream velocity (R^2=0.46, p=0.002).

Table 2: Annual average transient storage metrics ± SD for restored sites. HV not included due to unsuccessful OTIS model calibration.

Site	A_s, m^2	A_s/A	α, s^{-1}	D, m^2 s^{-1}	T_w, min	T_s, min	S_h, m	HRF
MC (n=3)	0.063±0.058	0.25±0.11	0.004±0.002	0.014±0.011	7.8±7.7	2.3±2.7	5.9±5.2	29.9±18.2
CENT (n=5)	0.068±0.015	0.69±0.47	0.004±0.004	0.083±0.051	9.2±6.1	5.6±4.5	32.9±40.2	40.0±12.2
SP (n=3)	0.023±0.015	0.43±0.29	0.002±0.003	0.060±0.017	38.1±30.2	18.1±21.3	56.9±42.6	13.2±9.95
RB (n=2)	0.045±0.007	0.051±0.016	0.002±0.000	0.19±0.16	8.3±0.0	0.4±0.13	2.0±0.34	5.96±1.50

Table 3: NO_3-N uptake metrics for restored sites by season: uptake length, $S_{w\text{-}NO3}$ (m), uptake velocity, $V_{f\text{-}NO3}$ (mm min^{-1}), and uptake rate, U_{NO3} (mg m^{-2} h^{-1}). Dashes (-) indicate experiments not completed (e.g. flooding by debris dams, construction).

	Summer			**Pre-leaf fall**			**Post-leaf fall**			**Winter**			**Spring**		
Site	$S_{w\text{-}NO3}$	$V_{f\text{-}NO3}$	U_{NO3}	$S_{w\text{-}NO3}$	$V_{f\text{-}NO3}$	U_{NO3}	$S_{w\text{-}NO3}$	$V_{f\text{-}NO3}$	U_{NO3}	$S_{w\text{-}NO3}$	$V_{f\text{-}NO3}$	U_{NO3}	$S_{w\text{-}NO3}$	$V_{f\text{-}NO3}$	U_{NO3}
MC	-	-	-	74.3	0.42	1.76	75.98	0.43	4.86	472.1	0.29	8.86	0.0	0.00	0.0
CENT	38.7	1.26	7.95	85.9	0.88	6.51	59.12	1.82	6.43	214.5	0.08	1.36	136.2	1.04	18.4
SP	35.3	3.33	108.0	428.4	0.17	6.3	63.4	0.98	34.0	100.6	0.77	24.5	-	-	-
HV	348.6	1.33	29.5	95.4	0.86	6.34	-	-	-	241.3	1.10	12.5	-	-	-
RB	44.3	0.47	22.0	-	-	-	150.1	0.11	4.74	2668	0.02	1.51	34.4	3.55	116.4

Table 4: PO_4-P uptake metrics for restored sites by season: uptake length, $S_{w\text{-}PO4}$ (m), uptake velocity, $V_{f\text{-}PO4}$ (mm min^{-1}), and uptake rate, U_{PO4} (mg m^{-2} h^{-1}). Dashes (-) indicate experiments not completed (e.g. flooding by debris dams, construction).

	Summer			**Pre-leaf fall**			**Post-leaf fall**			**Winter**			**Spring**		
Site	$S_{w\text{-}PO4}$	$V_{f\text{-}PO4}$	U_{PO4}	$S_{w\text{-}PO4}$	$V_{f\text{-}PO4}$	U_{PO4}	$S_{w\text{-}PO4}$	$V_{f\text{-}PO4}$	U_{PO4}	$S_{w\text{-}PO4}$	$V_{f\text{-}PO4}$	U_{PO4}	$S_{w\text{-}PO4}$	$V_{f\text{-}PO4}$	U_{PO4}
MC	-	-	-	73.2	0.43	1.79	0.00	0.00	0.00	129.3	1.06	32.4	120.5	0.66	3.24
CENT	40.3	1.21	7.64	59.4	1.28	9.42	21.82	4.93	17.42	76.2	0.24	3.83	47.1	3.01	53.1
SP	100.0	1.17	38.1	79.4	0.91	34.2	139.4	0.4	15.5	421.1	0.18	5.85	-	-	-
HV	24.3	19.1	422.7	571.7	0.14	1.06	-	-	-	250.2	1.06	12.1	-	-	-
RB	12.4	1.66	78.4	-	-	-	72.5	0.23	9.80	112.5	0.56	35.9	41.3	2.96	97.0

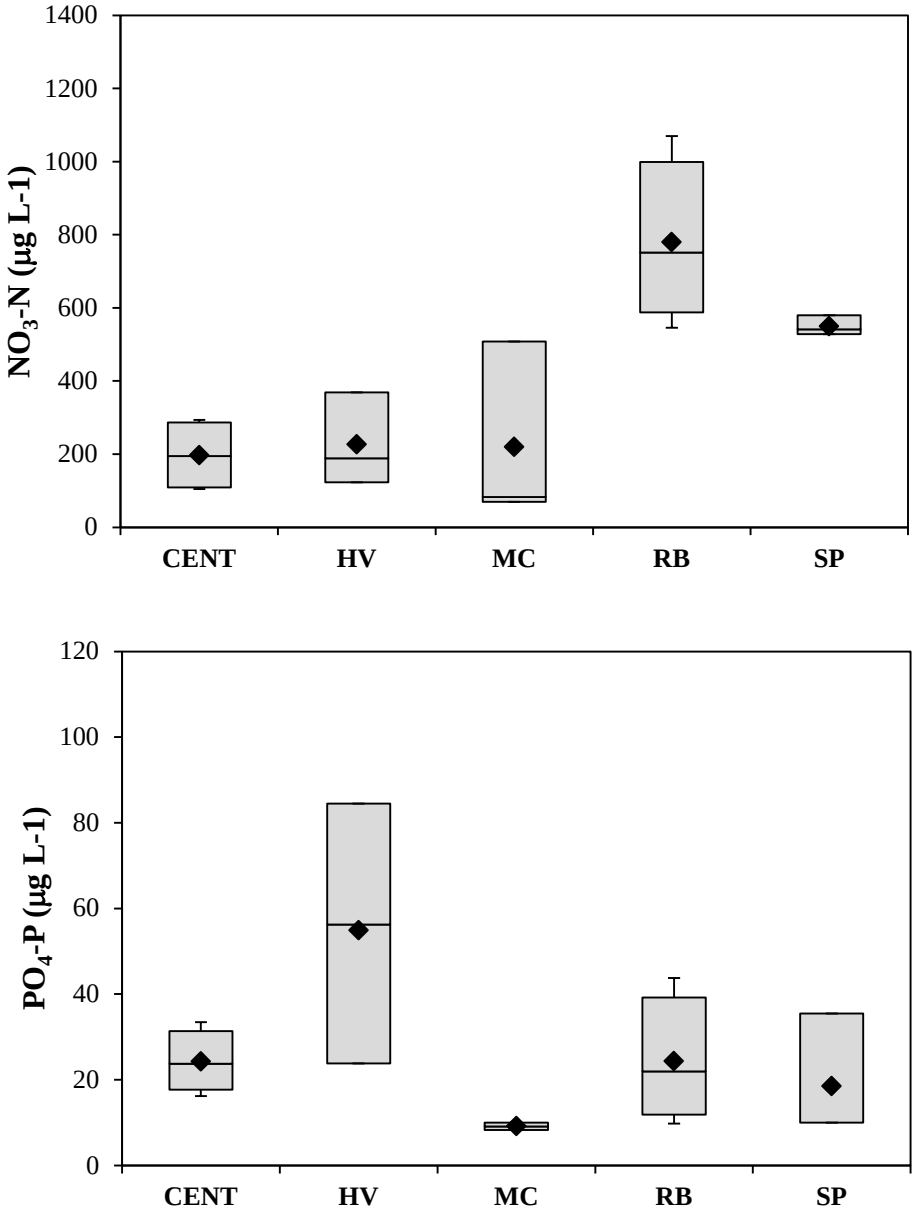

Figure 1: Ambient concentrations (µg L^{-1}) of NO_3-N and PO_4-P at the restored site. Box plots display 25th, 50th and 75th percentiles; extents display minimum and maximum values; dot denotes average value.

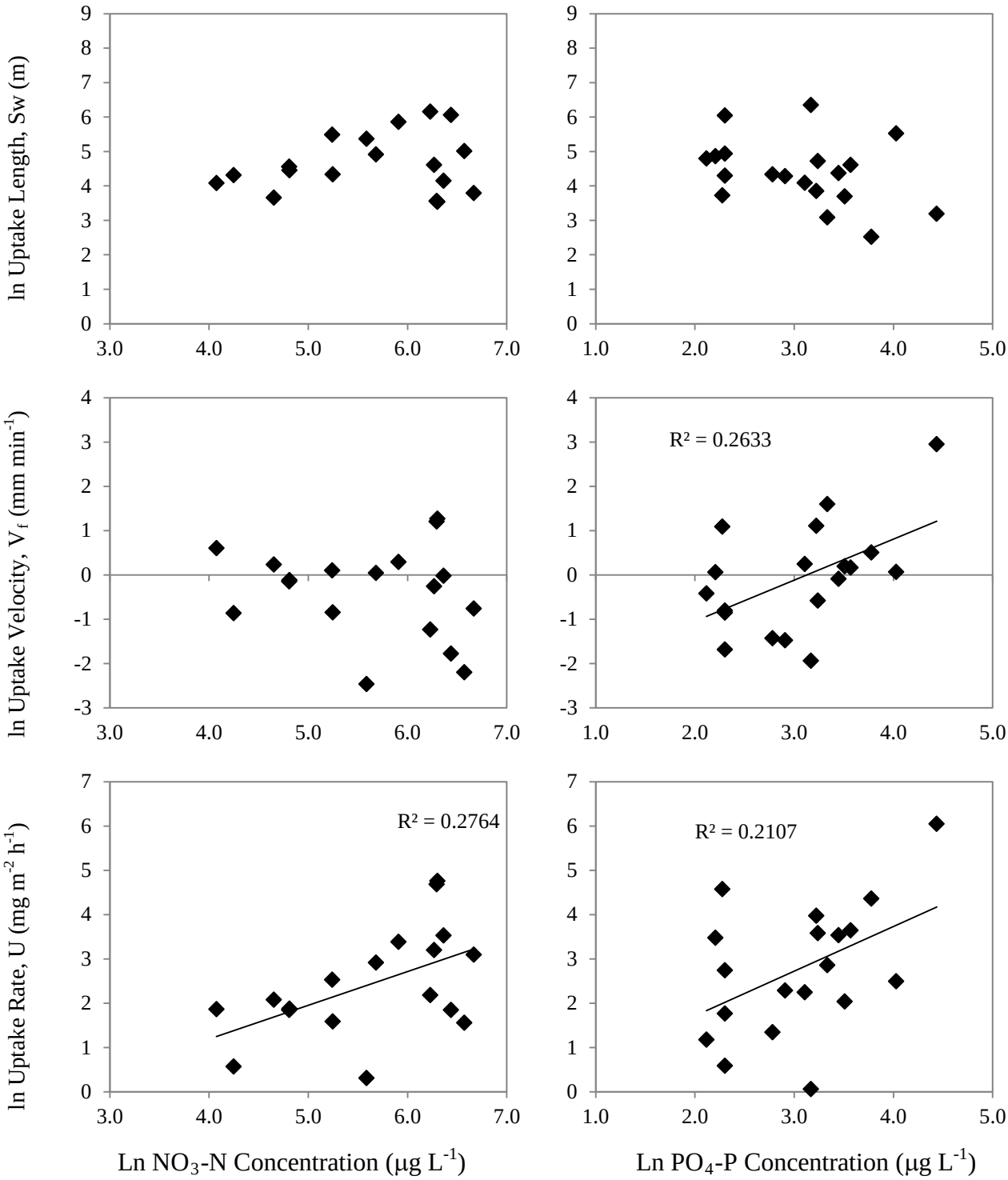

Figure 2: Relationships between nutrient concentration (μg L^{-1}) and nutrient uptake length (Sw, m), uptake rate (U, mg m^{-2} h^{-1}) and uptake velocity (V_f, mm min^{-1}). All data were ln transformed to achieve normality. Nutrient concentrations are those at the time of uptake measurements. Lines represent significant linear regressions.

3.3.1 Paired restored and unrestored

Nitrate and phosphate uptake experiments were conducted at HV in an unrestored reach immediately upstream. This approach minimized watershed influences (e.g. water chemistry, discharge) on nutrient retention by keeping these conditions similar in connected stream reaches. The uptake rate (U) in the restored reach was divided by U in the unrestored reach to calculate relative U across seasons. Greater instream retention is indicated by V_f values greater than one. Significantly greater $V_{f\text{-}NO3}$ across seasons was observed in the restored reach (p=0.02) while differences in $V_{f\text{-}PO4}$ were not significant (Figure 3). The predictive power of this analysis was limited by the small sample size (n=3).

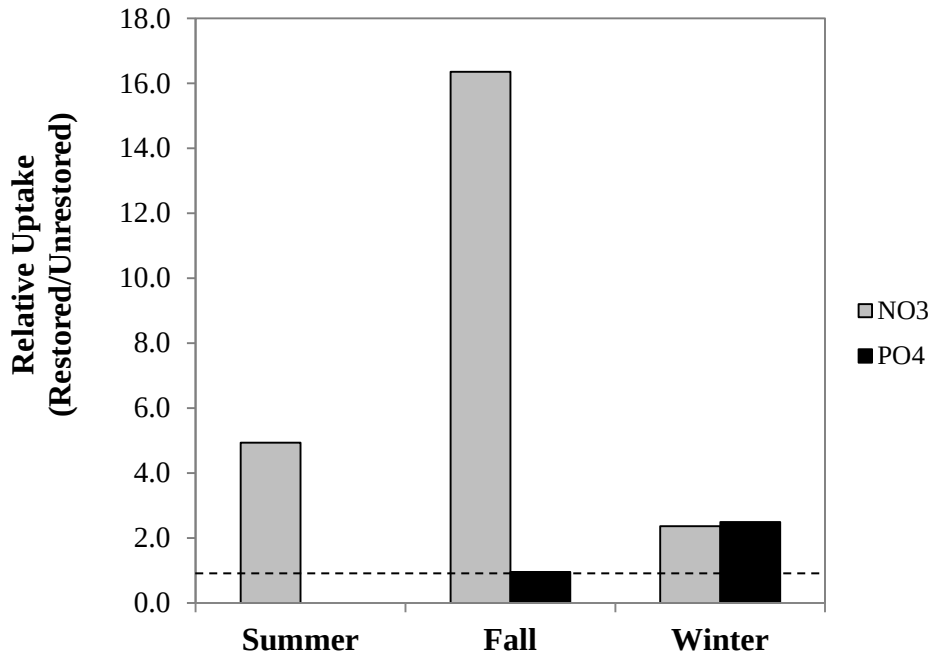

Figure 3: Relative nitrate uptake in paired restored and unrestored reaches at LSC (June 2010-February 2011; measurements were not made in Spring 2011 because of extensive beaver dams). Greater instream retention is indicated by V_f values greater than one. Dashed line at relative uptake of 1 is shown for visual comparison.

3.4 Denitrification rates

Denitrification rates were highly variable, but were significantly greater in restored (312±263 μmol m^{-2} h^{-1}) versus unrestored (237±200 μmol m^{-2} h^{-1}) in streambed sediments when compared using the z scores, which normalized for site-specific differences (e.g., watershed characteristics, water chemistry) (p=0.014, Figure 4). The wide range of observed rates at any single location limited the significance of site specific differences, however important trends were noted. Significantly greater rates were observed at (SP = 585 ± 214) compared to the other sites (with the exception of SP-UR). The lowest rates were measured at unrestored ABT-UR (97 ± 58) (Figure 5, Table 5). Denitrification rates also varied seasonally as determined by one-way ANOVA on transformed data (p<0.001). The highest rates across all sites were observed in the summer and winter averaging 315 ± 223 and 452 ± 315 respectively (Figure 6).

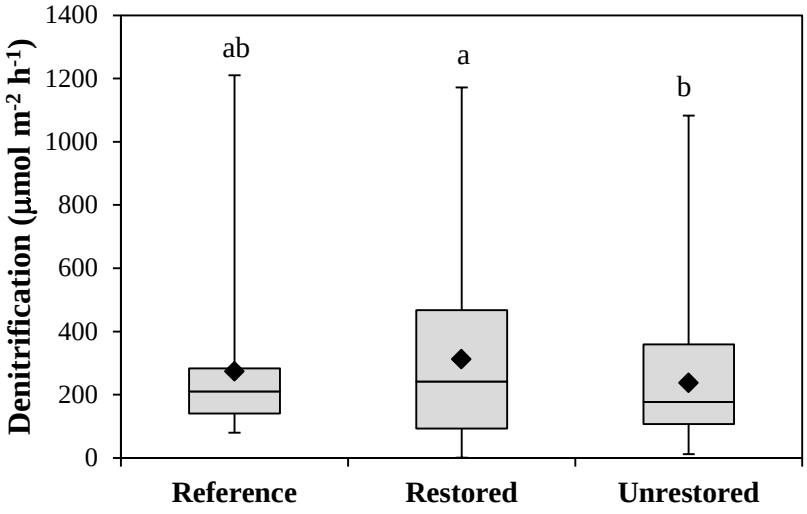

Figure 4: Denitrification rates (µmol N m^{-2} h^{-1}) measured in stream sediments as a function of restoration status. Box plots display 25th, 50th and 75th percentiles; extents display minimum and maximum values; marker denotes average value. Site categories are listed in Table 1. Groups that are significantly different from each other are indicated with letters.

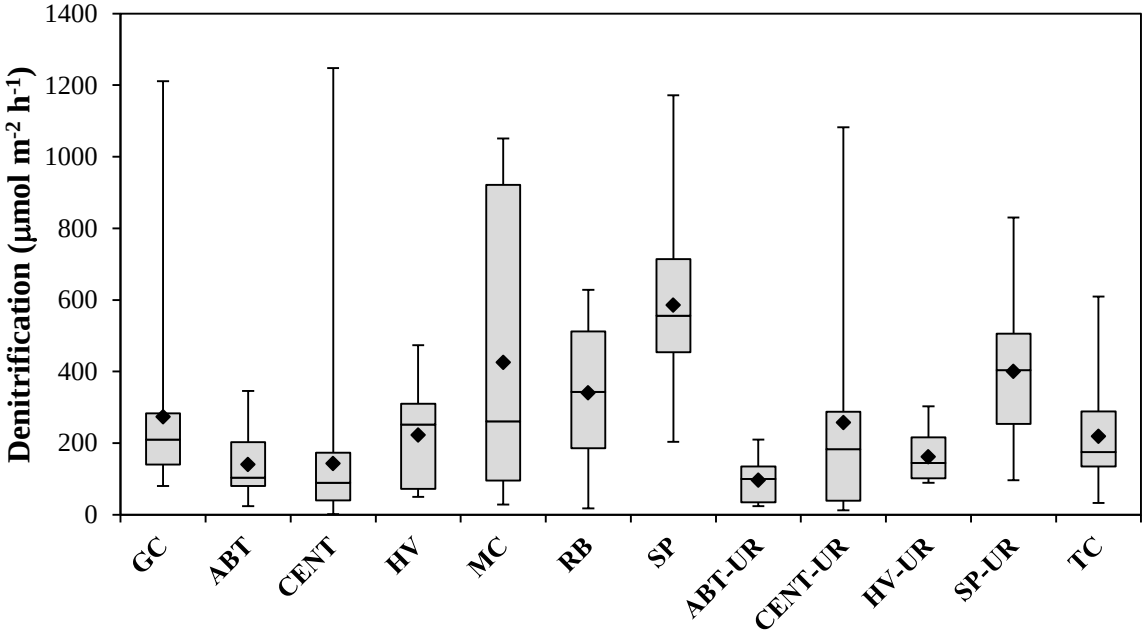

Figure 5: Denitrification rates (µmol N m^{-2} h^{-1}) measured in stream sediments at each site. Box plots display 25th, 50th and 75th percentiles; extents display minimum and maximum values; marker denotes average value. Site codes are listed in Table 1. Summary statistics for these comparisons are in Table 5.

Table 5: Average of observed denitrification rates (μmol N m^{-2} h^{-1}) ± SD for one year (June 2010-June 2011). Means compared via one-way ANOVA on transformed data and Tukey-Kramer post hoc comparison of means ($p<0.05$). Groups that are significantly different do not share the same letter. Site codes are listed in Table 1.

Site	Denitrification rate (μmol N h^{-1} m^{-2})	Significance	Sample size (n)
SP-R	585 ± 214	a	61
SP-UR	401 ± 172	ab	19
MC	402 ± 371	bc	30
RB	356 ± 185	bc	33
GC	273 ± 219	bc	49
TC	219 ± 130	cd	42
HV-R	223 ± 131	cd	27
CENT-UR	258 ± 322	cde	17
HV-UR	162 ± 81	bcde	6
ABT-R	140 ± 93	de	54
CENT-R	128 ± 197	e	39
ABT-UR	97 ± 58	e	19

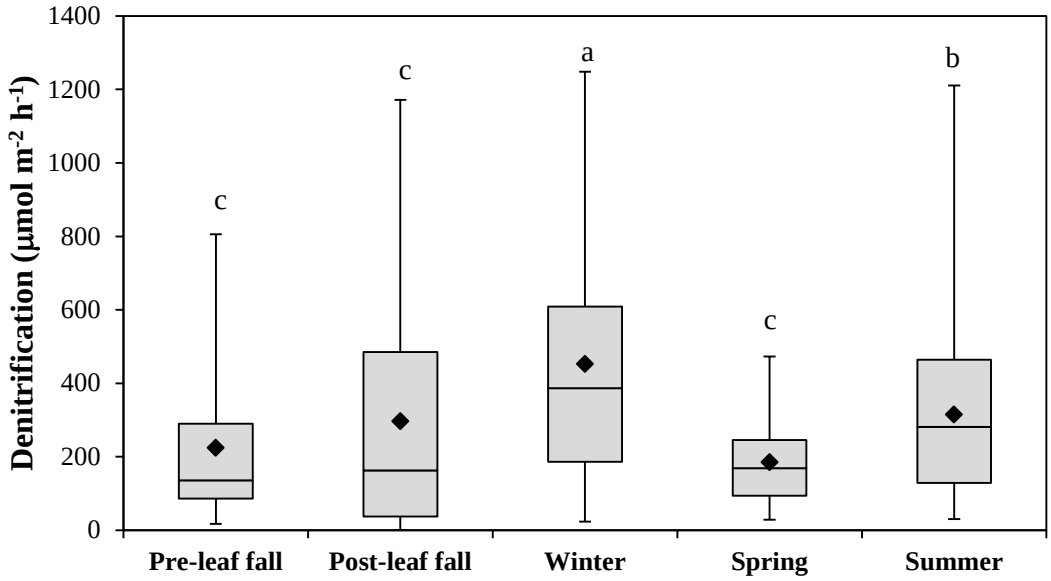

Figure 6: Seasonal denitrification rates (μmol N m^{-2} h^{-1}) across all sites with highest rates in winter, followed by summer. Box plots display 25th, 50th and 75th percentiles; extents display minimum and maximum values; marker denotes average value. Transformed denitrification rates were compared; groups that are significantly different from each other are indicated with letters.

3.4.1 Controls on Denitrification Rates

When the entire dataset of z scores of denitrification rates was lumped together (restored n=226, unrestored n=87, and reference n=49), rates of denitrification were significantly greater in restored compared to unrestored sites (p=0.014). Using the residuals of the nitrate-denitrification regression, paired restored were greater than unrestored sites at SP and ABT (p<0.01).

Variation in denitrification rates was primarily correlated by ambient stream nitrate concentrations ($p < 0.0001$, $R^2 = 0.391$, n=362). SP had consistently high ambient stream water nitrate concentrations (μ= 0.67 ±0.15 mg/L; Figure 1), which partially explains higher denitrification rates compared to the other sites. A linear regression performed on a plot of ln NO_3^- and ln denitrification explained 56% of the variation in the dataset ($p < 0.0001$, $R^2= 0.562$; Figure 7).

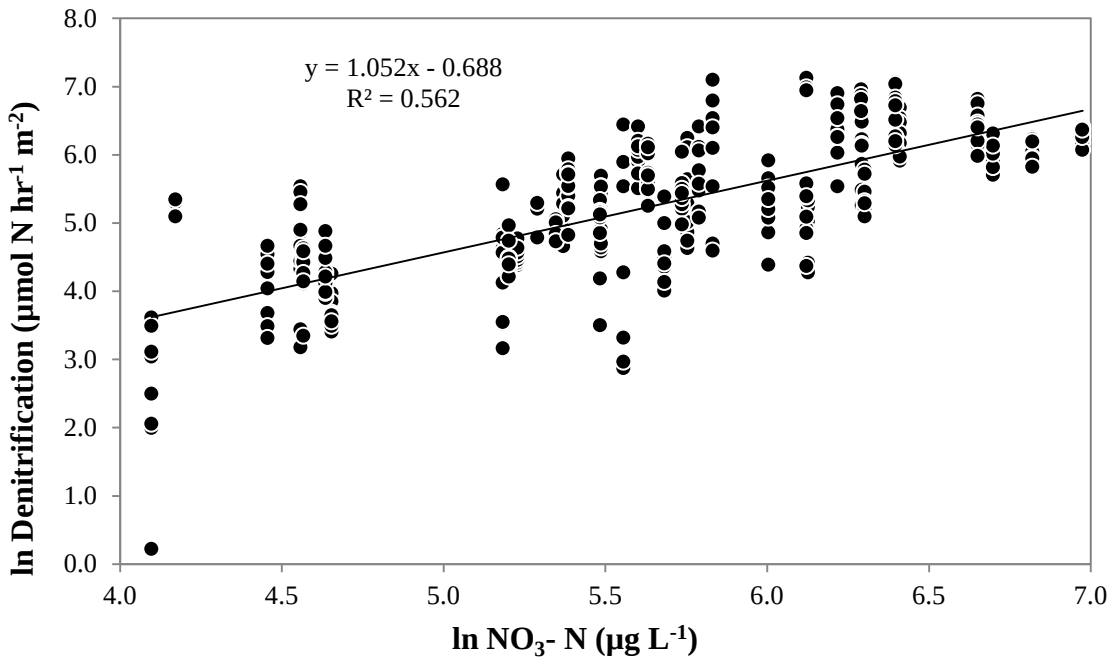

Figure 7: Linear regression between ln transformed ambient stream NO_3-N (mg L^{-1}) and denitrification rates (μmol N m^{-2} h^{-1}) (p<0.0001, n=362).

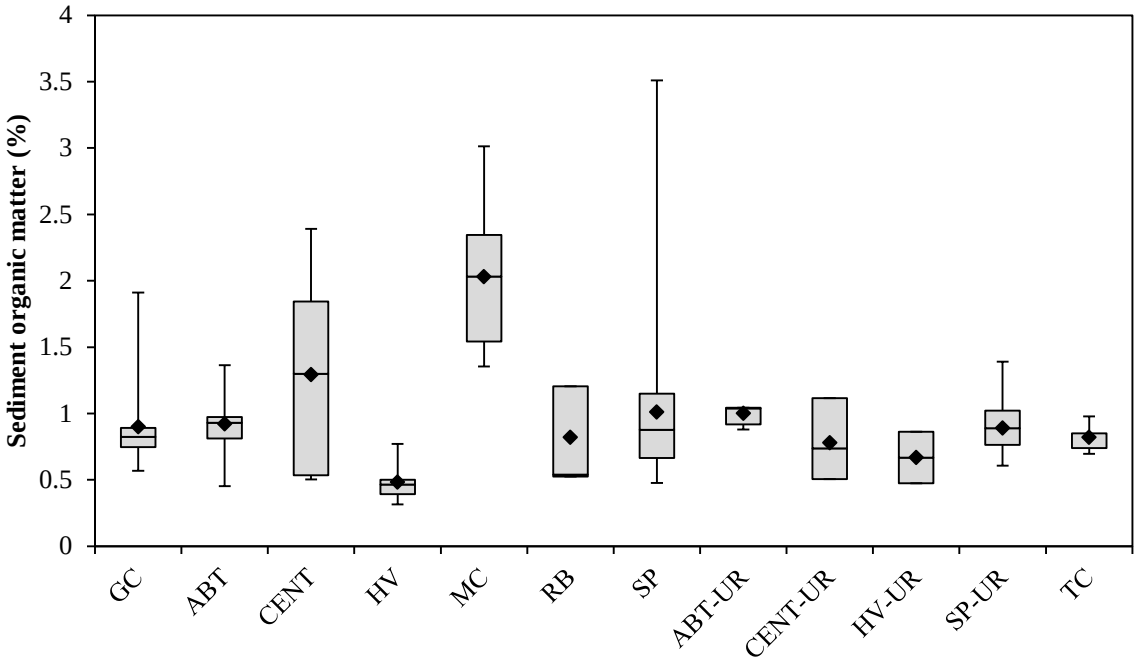

Figure 8: Distribution of sediment organic matter (%) among sites. Box plots display 25th, 50th and 75th percentiles; extents display minimum and maximum values; marker denotes average value. Site codes are listed in Table 1.

To better understand the effect of streambed heterogeneity on rates of denitrification, we compared the Z-scores of denitrification rates within each site at different sampling locations corresponding to distinct geomorphic features (e.g. pools, riffles). Using the Z score removes the bias of nitrate concentration and preserves the spatial variability within the site without the influence of other sampling events. In this way, we can make within site comparisons across sampling dates among geomorphic features. Data for TC is not compared due to the instability of streambed geomorphology (periodic avulsions and changing patterns of scour and deposition) so sediment sampling locations, while based on consistent positions within the reach, did not consistently relate to a stable feature in geomorphic bedform. Additionally, unrestored reaches (UR) contained little heterogeneity and were treated as a unique geomorphic category.

No differences were observed among geomorphic features at ABT, CENT, HV and MC as determined by one-way ANOVA with Tukey-Kramer post hoc comparison of means on the Z-scores for each location. However, significant differences based on geomorphology were demonstrated at RB, GC and SP (Figure 9). At RB, denitrification rates measured at the USS location (USS = immediately upstream of the instream grade control structure, e.g., cross vane) were significantly higher than those measured in the pool. At GC and SP, the reverse was true with highest rates observed at DSS (DSS = immediately downstream of the instream structure) and lower rates at USS. Surprisingly, the lowest rates were measured in the pool at RB in the fall, (18.6 μmol N h^{-1} m^{-2}) where higher accumulation of organic matter was expected. At one site (SP), rates measured in UR were significantly lower than those downstream of instream structures (DSS) and in pools.

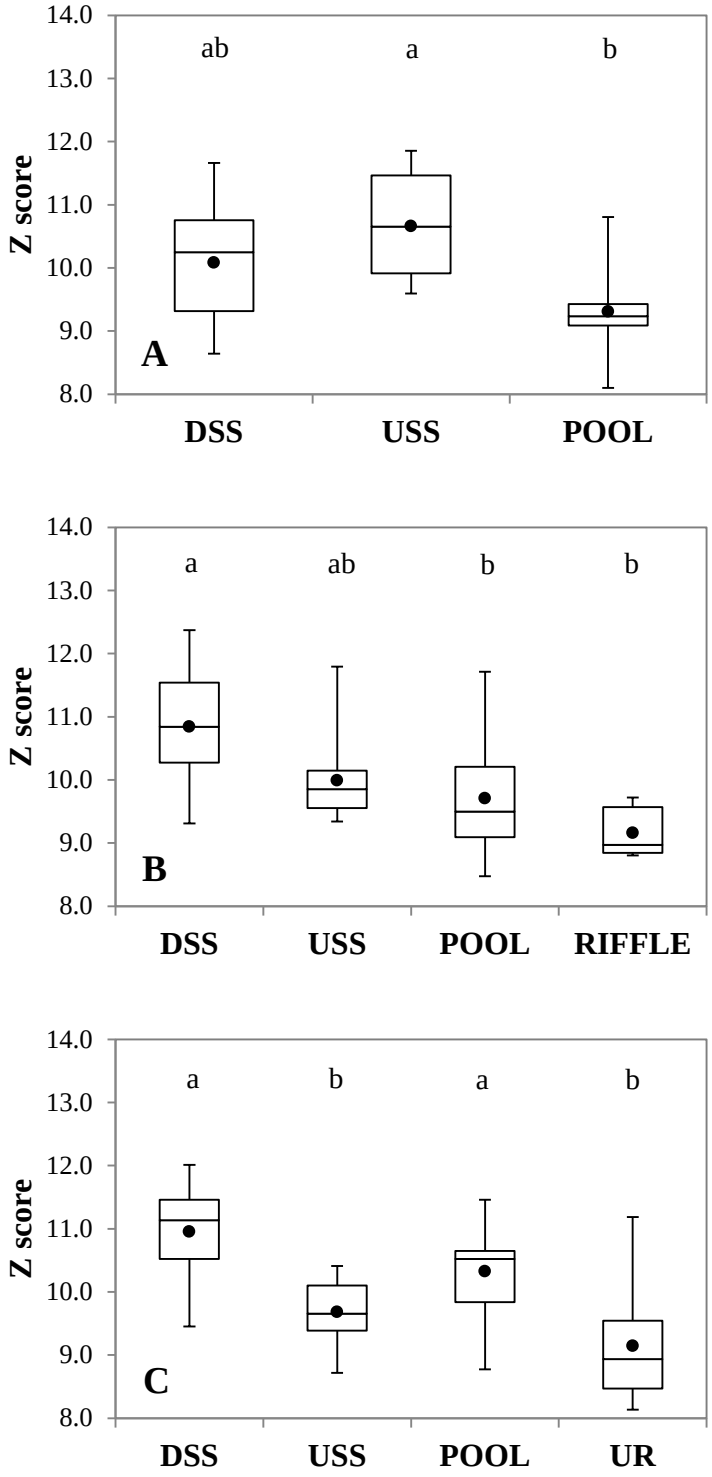

Figure 9: Z-scores are compared for distinct geomorphology at each sediment sampling location. (A) RB, (B) GC and (C) SP. Vertical axis is z-score +10. Groups that are significantly different from each other do not share a letter, as determine by ANOVA and Tukey-Kramer post-hoc comparison ($\alpha = 0.05$). DSS = downstream of the instream grade control structure (e.g., cross vane), USS = upstream of the instream structure, UR = unrestored.

4 DISCUSSION

4.1 Controls on reach scale nutrient retention

In restored streams, engineered instream structures are designed to increase benthic habitat, reduce shear stresses on stream banks and also improve water quality. Deep pools are designed to trap fine sediment and grade control structures can enhance groundwater-surface water interactions. By improving flow of stream water through transient storage in hyporheic zones, the potential to enhance nutrient transformations exists. A number of studies have demonstrated the importance of the hyporheic zone in regulating nutrient transformations in streams (Grimm and Fisher 1984, Holmes et al. 1996). We expected to see a strong relationship between transient storage and instream nutrient uptake in the restored streams in this study, but this was not realized with our results. However, these trends have been observed in other studies (e.g. Marti et al. 1997, Butturini and Sabater 1998, Webster et al. 2003). Hall and others (2002) found only a weak relationship between nitrate uptake and transient storage in forested streams in Hubbard Brook and no relationship between phosphorus uptake and transient storage. Because transient storage zone area (A_s) does not distinguish between surface and subsurface storage, these results alone cannot be used to identify flowpaths.

Comparison of the water uptake rate (S_h) to the nutrient uptake rate (S_w) can indicate whether nutrient uptake occurs at the same spatial scale as water uptake into transient storage zones. A value of S_h/S_w greater than one suggests that nutrient uptake is occurring in surficial biofilms prior to entering transient storage (e.g. hyporheic zones, deep pools) (Webster et al. 2003, Ensign and Doyle 2006). In all but two experiments, the ratio of S_h:S_w was less than one for nitrate (0.49±1.16) and phosphate (0.39±0.54) which suggests that nutrient uptake was more closely coupled with retention and removal processes occurring in transient storage zones rather than the water column. The two measurements of S_h:S_w values greater than one (CENT, SP) took place late fall after the addition of leaf litter to the streams which often serves as a surface for biofilm colonization and a labile carbon source for bacterial communities. These assemblages assimilate nutrients from the water column and can be areas for enhanced denitrification.

The influence of channel geomorphology has been well documented with headwater streams identified as hot spots for nutrient retention owing to shallow depths and increased contact between streamwater and biochemically active sediments (Alexander et al. 2000, McClain et al. 2003). Similar to other studies of low order streams, we found high variability in uptake lengths of nitrate (Sudduth et al. 2011, Klocker et al. 2009, Grimm et al. 2005) and phosphate (Davis et al. 1999, Mulholland et al. 1985, and Bernot et al. 2006).

Of the nutrient spiraling metrics, uptake velocity (V_f) has been shown to be the most robust indicator of uptake for comparison because it corrects for the effects of both discharge and concentration (Doyle et al. 2003, Hall et al. 2002). Uptake velocity can be conceptualized as the velocity at which a nutrient moves through the water toward the sediment and represents the demand for nutrients relative to the concentrations in the water column. In this way, it is a measure of uptake efficiency relative to availability. We found an average $V_{f\text{-}NO3}$ of 1.16 mm min-^{1} with a range of 0-5.45 mm min^{-1} which is similar to than that found in other studies of urban stream nutrient retention (Klocker et al. 2009, Grimm et al. 2005, Sudduth et al. 2011).

Nitrate uptake in our streams was similar to uptake in forested systems (Davis et al. 1999, Ashkenas et al. 2004), and generally lower than agriculturally influenced streams (Bernot et al. 2006, Royer et al. 2004). Uptake velocity for both nitrate and phosphate was positively correlated with instream velocity suggesting the potential for increased pumping and delivery of stream water nutrients to the streambed under conditions of increased discharge velocity (Endreny et al. 2011).

In a study of nitrate removal across 72 streams in 8 regions, Mulholland et al. (2008) demonstrated a decrease in V_f and increase in U as concentration increased. Although excess nitrate resulted in increased uptake per area of streambed, their streams became less efficient at doing so. In our study, similar patterns were observed in uptake rates with higher water column concentrations correlated with increased uptake of both nitrate and phosphate. However, uptake velocities for nitrate did not decrease with concentration, which was likely attributed concentrations that varied across a much smaller range. Phosphate nutrient spiraling metrics (U_{PO4} and $V_{f\text{-}PO4}$) were positively correlated with concentration indicating that these streams were not saturated with respect to phosphate. This also showed that increased concentration not only increased the uptake per unit of streambed area, but did not adversely affect the efficiency at which the uptake occurred. Nutrient uptake in both restored and unrestored streams in our study was directly correlated with instream concentration for both nitrate (U_{NO3}) and phosphate (U_{PO4} and $V_{f\text{-}PO4}$).

4.2 Controls on denitrification

Denitrification converts dissolved nitrate to nitrogen gas (N_2) as heterotrophic bacteria use NO_3-N for respiration, utilizing dissolved carbon to fuel energy metabolism. Denitrification requires that specific environmental conditions be met: (1) NO_3^- supply, (2) near zero oxygen concentrations, (3) organic matter as a carbon source and (4) active populations of denitrifying bacteria. The limitation of denitrification by nitrate is well documented in streams (Holmes et al. 1996; García-Ruiz et al. 1998c; Martin et al. 2001; Mulholland et al. 2008). Variation in denitrification rates in our study was primarily driven by nitrate concentrations. The importance of labile carbon to heterotrophic microbial metabolism becomes more evident as nitrate concentrations reach saturation of denitrification enzymes (Knowles 1982). A wide range of half saturation constants (0.2-1.3 mg/L) is reported in the literature for benthic stream sediments (Seitzinger 1988; García-Ruiz et al. 1998b; Arango et al. 2007). This range corresponds directly with observed stream nitrate concentrations in our study. In many cases, a relationship of denitrification with sediment organic matter is not observed until nitrate concentrations exceed the half-saturation constant (Arango et al. 2007). This constant may be unique to the *in situ* microbial community (Holtan-Hartwig et al. 2000), or dependent upon coupled elemental cycles (Burgin et al. 2011). While our data did not indicate a relationship between percent organic matter and denitrification, bulk measurements of carbon (such as water column DOC or sediment percent organic matter) are not robust indicators of the presence of labile carbon. In addition, because of the spatial heterogeneity of denitrification hot spots within stream sediments, accurate reach-scale estimates of denitrification based on a small number of samples is difficult to assess (Groffman et al. 2009).

The relative importance of denitrification for nutrient removal is emphasized in headwater streams (Mulholland et al. 2008), because of their close proximity to terrestrial landscapes, high

inputs of organic material, increased interactions between surface water and groundwater, and contact with microbial biofilms. However, urbanization has altered the drainage density of stream networks, reduced the prevalence of perennial low-order streams and removed floodplain connectivity (Paul and Meyer 2008). Restoration elements (e.g. log vanes, boulder weirs) that increase contact between nitrogen in stream water and biologically active, carbon-rich streambed sediments can have a positive impact on instream nitrogen retention. Other studies of denitrification in relation to geomorphic features in urban environments found the highest denitrifying activity and highest percent organic matter near organic debris dams (Groffman et al. 2005; Harrison et al. 2012). In our study, we found higher denitrification rates near both natural and constructed steps compared to other locations in the reach. However, these rates were not correlated with organic matter accumulation, which differs from the previous studies. The fact that we observed increased denitrification activity near artificial structures, despite the absence of elevated percent organic matter in these locations, indicates that geomorphology itself may be another important regulator of the richness and extent of the biofilm community.

Other factors, such as microbial abundance and diversity (Cavigelli and Robertson 2001, Harrison et al. 2012), affinity for nitrate (García-Ruiz et al. 1998b), and sediment grain size (García-Ruiz et al. 1998a) all contribute to variation in microbial activity. Harrison et al (2012) found that the most important predictive metrics for denitrification potential were microbial biomass nitrogen and percent organic matter, which also highlight the importance of a robust microbial community in regulating denitrification.

Weir-like restoration structures that create rapid changes in water surface water elevation enhance hyporheic exchange flow through the difference in head gradient and slope (Hester and Doyle 2008; Crispell and Endreny 2009). Additionally, complex subsurface flowpaths created by turbulence associated with the downward force of flow and subsequent hydraulic jump (Endreny et al. 2011) create spatial patterns of upwelling and downwelling that vary by structure due to the unique morphology and flow dynamics at each site (Crispell and Endreny 2009). The dynamic hydraulic conditions near structures also affect patterns of sediment deposition and scour, influencing grain size distribution. Finer grained sediments are reported as demonstrating higher denitrification potential, owing both to the available surface area (Inwood et al. 2007), and higher the tendency toward porewater anoxia (Groffman and Tiedje 1989). In our study, downwelling near weir-like structures was observed using peizometers during baseflow conditions in the summer of 2010 at GC and SP (data not shown). This demonstrates the potential for spatial variation of denitrification rates partially attributed to hydraulic conditions and temporal variation to differences in ambient stream water nitrate in response to season, anthropogenic nitrogen inputs, and watershed hydrology.

4.3 Restored vs. Unrestored

It is difficult to compare the effectiveness of restoration on nutrient uptake using restored and unrestored streams in different watersheds due to natural variance in ecological function between any two streams. An ideal study would compare pre- and post-restoration similar to that of Bukaveckas (2007) who observed increased ammonium retention post restoration compared to pre-restoration in a Kentucky stream, which was attributed to an increase in transient storage and retention time. However collection of nutrient retention prior to restoration is often infeasible due to logistical constraints of project timing and coordination with restoration professionals.

One of the sites (LSC) in our study was directly connected to an upstream reach that was unrestored. This afforded us the opportunity to directly compare nutrient retention as a function of restoration since watershed inputs and other confounding variables were similar. Greater NO_3-N retention was measured in the restored reach during each measurement period.

The channel morphology of the restored reach was relatively homogenous compared to the other restored streams but much greater than the incised and simplified unrestored channel. In restored streams, engineered instream structures (e.g. boulder cross-vanes, log weirs/J-hooks, riffles and pools) are designed to increase benthic habitat, provide grade control and reduce shear stresses on stream banks but can also influence hyporheic exchange and biogeochemical fluxes (Hester and Doyle 2008; Lautz and Fanelli 2008; Crispell and Endreny 2009; Gordon et al., 2013). While it is uncertain whether the patterns we observed would remain across all seasons, these results highlight the influence of riparian vegetation on energy inputs (e.g. heat, organic matter) and on nutrient retention.

We expected changes in channel geomorphology related to restoration to influence patch scale rates of denitrification. Where significant differences were observed, differences between restored and unrestored reaches were driven by the increased denitrification near grade control structures (SP, RB, GC). Our results suggest that the inclusion of grade control structures at restored sites may encourage the development of more active denitrifying communities, but does not guarantee nutrient removal enhancement due to the unique eco-hydrological conditions at each site. The effectiveness of a structure at achieving vertical hyporheic exchange flow could be a major determining factor. Construction practices during stream restoration projects use heavy equipment to reshape the channel, regrade stream banks and install instream structures for grade control and habitat diversity. These practices have the potential to compact streambed sediments and effectively block surface-subsurface exchanges.

Caution must be taken in using nutrient spiraling experiments as a basis for evaluating the success of restoration projects. Nutrient spiraling experiments, while providing valuable information on instream nutrient dynamics, do not give the entire picture. One of the restoration strategies at restored reaches in this study was floodplain reconnection but its function was not assessed with the methods used in this study. The floodplain is a biologically active area capable of denitrification and retention of nutrients (Baker and Vervier 2004). Since nutrient concentrations are often highest during storm events (Filoso and Palmer 2011) when overbanking is likely to occur, biogeochemical processes in the floodplain may be of equal importance to instream processes. For example, in a restoration project at Sandy Creek in Durham, NC, where wetlands were constructed in the floodplain, significant reductions in nitrogen (64%) and phosphorus (28%) loads were estimated during storm events (Richardson et al. 2010).

5 CONCLUSIONS AND RECOMMENDATIONS

In a study of nutrient retention in restored and unrestored urban streams in the Piedmont of NC, we found that the instream geomorphic features and streamwater chemistry were important predictors of reach scale retention and patch scale denitrification. Denitrification rates were

significantly higher in restored (312±263 μmol m^{-2} h^{-1}) compared to unrestored (237±200 μmol m^{-2} h^{-1}) streams. Low instream velocities, particularly through long deep pools precluded measurement of reach scale uptake in 3 of the 4 unrestored streams. However, reach scale NO_3-N uptake at LSC was greater throughout the year in the restored reach with greater heterogeneity compared to the unrestored section supporting the importance of channel complexity. Comparisons of uptake metrics and environmental conditions in all restored reaches showed that uptake of nitrate and phosphate were influenced by background nutrient concentrations and hydrogeomorphic characteristics of the reach.

In three of the study sites, significantly greater denitrification rates were measured near instream structures (e.g., cross-vanes), which created channel heterogeneity, provided habitat for microbial colonization and potentially enhanced hyporheic exchange. Increased geomorphic heterogeneity results in flowpath complexity near instream structures contributing to robust microbial communities and delivery of stream water nutrients to the subsurface. Results from restored and unrestored reaches of LSC also support the importance of channel complexity with greater NO_3-N uptake observed throughout the year in the restored reach with greater heterogeneity compared to the unrestored section. Denitrification rates were significantly higher in restored compared to unrestored streams.

Our study suggests a need to reconsider the classification of streams based solely on land use. By lumping all urban streams together, high variability in watershed characteristics (e.g. stormwater infrastructure, point and non-point source pollutant inputs) and channel morphology (e.g. riparian cover, geomorphic complexity) are overlooked which can have far-reaching implications for conclusions derived from the study. This is particularly critical in urban streams where the variability is vast. Inclusion of metrics in future studies that classify streams in terms of geomorphology (e.g. habitat complexity, sediment size distribution, channel incision) would facilitate interpretation of complex and highly variable results.

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APPENDIX A: ABBREVIATIONS

ABT – Abbot Creek
ABT-UR – Unrestored branch of Abbot Creek
α - Transient storage exchange coefficient
A – wetted stream area
A_s – Transient storage area
A_s/A – Transient storage ratio
CENT – North Creek at Centennial Campus
CENT-UR – Unrestored branch of North Creek at Centennial Campus
CPOM – coarse particulate organic matter
D – Transient storage Dispersion
d – wetted stream depth
DOC – dissolved organic carbon
FPOM – fine particulate organic matter
GC – Gar Creek
HRF – Hydraulic Retention Factor
HV – Little Sugar Creek at Hidden Valley Ecological Park
HV-UR – Unrestored branch of Little Sugar Creek at Hidden Valley Ecological Park
MC – Muddy Creek
RB – Rocky Branch
SP – Dairy Branch at Sedgefield Park
$S_{w\text{-}NO3}$ – Nitrate uptake length
$S_{w\text{-}PO4}$ – Phosphate uptake length
S_h – Hydraulic uptake length
T_s – Average time spent in transient storage
T_w – Turnover time in the water column
U_{NO3} – Nitrogen uptake rate
U_{PO4} – Phosphorus uptake rate
$V_{f\text{-}NO3}$ – Nitrate uptake velocity
$V_{f\text{-}PO4}$ – Phosphorus uptake velocity
w – wetted stream width

APPENDIX B: PUBLICATIONS & PRESENTATIONS

McMillan, S. K., A. K. Tuttle, G.D. Jennings, , and A. Gardner (2013). “Influence of restoration age and riparian vegetation on reach-scale nutrient retention in restored urban streams.” Journal of the American Water Resources Association. *Accepted*.

McMillan, S. K. (2012). “Influence of riparian vegetation and channel complexity on coupled biogeochemical cycles in restored urban streams”. American Water Resources Association, Riparian Ecosystems Specialty Conference. Invited plenary presentation. Denver, CO

McMillan, S. K. (2012). “Nutrient retention in restored streams: Influence of channel complexity and floodplain connectivity.” Stream Restoration in the Southeast: Innovations for Ecology. Invited plenary presentation. Wilmington, NC

McMillan, S. K. (2011). “Assessing ecosystem function of urban streams: Influence of restoration on nutrient retention.” Virginia Tech, Department of Civil and Environmental Engineering Seminar Series. October 2011

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