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The biogeochemical influences of nitrate, dissolved oxygen, and dissolved organic carbon on stream nitrate uptake

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The biogeochemical influences of nitrate, dissolved oxygen, and dissolved organic carbon on stream nitrate uptake

BY

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DEDICATION

This thesis is dedicated to my family for making my journey a joyful one. I would like to give special thanks to my parents for raising me in a loving environment, and to Amanda for her endless love and support.

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ABSTRACT

THE BIOGEOCHEMICAL INFLUENCES OF NITRATE, DISSOLVED OXYGEN AND DISOLVED ORGANIC CARBON ON STREAM NITRATE UPTAKE

by

Joseph A. Thouin

University of New Hampshire, September, 2008

Streams are important hotspots for the retention and removal of nitrogen (N), an element that contributes to eutrophication and threatens the stability of coastal ecosystems. Nitrate (NO_3^-) is the most mobile form of N, and understanding the causal mechanisms that foster optimal NO_3^- retention and removal in stream systems is critical from both predictive and conservation standpoints. Dissolved organic carbon (DOC) is hypothesized to be a major control of instream NO_3^- concentrations, but dissolved oxygen (DO) is also an important control of NO_3^- removal processes. Assessing the individual impacts of NO_3^-, DO, and DOC concentrations on stream NO_3^- removal is difficult due to the natural interdependencies of these nutrients in the carbon and nitrogen cycles. This study took an experimental approach to quantifying the influences of NO_3^-, DOC, and DO on NO_3^- transport within two headwater streams of the Ipswich and Parker River watersheds, MA, with contrasting levels of DOC and DO. In a first set of experiments we added increasing levels of NO_3^- to address how uptake kinetics differed in a low DO/high DOC stream (Cedar Swamp Creek) versus a high DO/low DOC stream (Cart Creek). In a second set of experiments, we manipulated for the first time at the reach scale both DO and DOC in a factorial experiment. DO was added to the low DO stream by injecting oxygen, and removed from the high DO stream by adding sodium sulfite. DOC was added both alone and in combination with the DO manipulations. Results from the NO_3^- enrichments suggest NO_3^- concentration is an important control of NO_3^- vertical velocity. Results from the DOC and DO manipulations suggest that DO determines whether a stream has net nitrate uptake or production, and that DOC magnifies these processes. Addition of DOC by itself did not lead to increased nitrate uptake, suggesting that inverse relationships between nitrate and DOC may arise from complex interactions among DOC, DO and nitrate concentrations and how they influence dominant stream processes. In addition to these findings, we also observed organic matter "priming effects" (Kuzyakov et al. 2000) not previously reported in stream systems.

Keywords: nitrate, nitrate uptake, dissolved oxygen, dissolved organic carbon, net nutrient uptake, solute addition, priming effect

CHAPTER I

Introduction

Nitrogen (N) is a naturally occurring element that is essential to life on earth, and often controls productivity in terrestrial (Tamm 1991) and marine ecosystems (Vitousek and Howarth 1991). Excessive anthropogenic N inputs from sources such as atmospheric deposition, fertilizer use, and septic systems are exceeding terrestrial demand over many parts of the world, causing nitrogen concentrations to increase in river systems (Aber et al. 1989, Boyer et al. 2002, Driscoll et al. 2003). Once in river systems, inland nitrogen pollution has the potential to be translocated to coastal zones with deleterious effects (Howarth et al. 2002, Rabalais 2002). Currently more than 40% of U.S. coastal waters suffer from excess nutrient inputs (Bricker et al. 1999), leading to the outbreak of algal blooms (Glasgow and Burkholder 2000). Upon senescence, these blooms increase the biological demand for oxygen, decreasing its availability and creating areas of anoxia that negatively impact coastal biota (Dodds 2006).

Nitrate (NO_3^-) plays a significant role in coastal eutrophication. Due to its mobility, nitrate is the most common form of dissolved inorganic nitrogen reaching the coastal zone (Howarth et al. 1996). To mitigate the negative impacts of nitrogen entering the coastal zone, it is necessary to understand how nitrate is loaded into and then processed and transported within river systems.

Although rivers may constitute an important transport route for nutrients originating in terrestrial ecosystems, they are hardly passive conduits (Alexander et al. 2000, Cole et al. 2007). Streams and rivers may retain or remove anthropogenic N inputs through abiotic and biotic in-stream processes, which include adsorption to sediments, sediment burial, assimilative uptake by plants and algae, immobilization by microbes during the breakdown of organic matter, and anaerobic respiratory pathways of bacteria, i.e., denitrification (Bernot and Dodds 2005, Seitzinger et al. 2006). Peterson et al. (2001) found that nitrogen uptake in headwater streams can reduce up to half of the nitrogen that is introduced from the adjoining terrestrial ecosystem. With total river length in most watersheds dominated by small streams (Leopold and Maddock 1953), headwater systems have the potential to play an integral role in buffering nitrogen exports to coastal waters.

Supported by the stream nutrient spiraling paradigm (Newbold et al. 1981), a number of studies have quantified N uptake in streams using standard solute addition methodology (Stream Solute Workshop 1990). Stream spiraling techniques have been used to determine N dynamic metrics such as areal uptake (U, mass removal of a nutrient per unit area of the streambed per time) and vertical velocity (υ_f, the speed at which a nutrient is removed from the water column) (Stream Solute Workshop 1990) during N enriched conditions using solute additions (Dodds et al. 2002, Payn et al. 2005) and under ambient conditions using isotopically labeled N (Webster et al. 2003, Mulholland et al. 2004). To determine the effects of variable biotic and abiotic conditions on stream nitrogen uptake, significant effort has been invested in quantifying and comparing nitrogen retention and removal across sites (Wollheim et al. 2001, Mulholland et al. 2002, Webster et al. 2003). Fewer studies have determined the influence of hydrologic and biogeochemical factors on nitrogen uptake by manipulating physical and chemical conditions in individual stream systems (Bernhardt and Likens 2002, Ensign and Doyle 2005).

Whereas inter-site comparisons enable general relationships to be formulated linking watershed characteristics and stream biogeochemistry, short-term stream reach manipulations offer the opportunity to gain better insight into the causal mechanisms responsible for observed variability. This is important insofar as streams are prone to variable conditions over both spatial and temporal domains, which together significantly influence nitrogen retention and removal (Simon et al. 2005). Among the spatially and temporally heterogeneous biogeochemical controls that can significantly alter demand for NO_3^- are NO_3^- concentration (Dodds et al. 2002), dissolved oxygen (DO) concentration (Kemp and Dodds 2001), and dissolved organic carbon (DOC) concentration (Webster et al. 2000).

NO_3^- concentrations are a primary influence on NO_3^- uptake rates. Dodds et al. (2002) suggest that biotic uptake is directly related to NO_3^- concentration, and as such NO_3^- uptake will increase with increasing NO_3^- concentration. Recent findings indicate that nitrate removal rates do not increase linearly with increasing concentrations across sites (Mulholland et al 2008). Within individual streams, N removal rates have been assumed to follow Michaelis-Menten kinetics (Mulholland et al. 2002, Payn et al. 2005). These studies suggest that uptake efficiency declines with increasing concentration.

NO_3^- dynamics in streams may in part be attributed to biotic processes that are dependent on DO, such as nitrification and denitrification. Oxygen concentrations have been found to be positively correlated with nitrification (Kemp and Dodds 2001), and thus can lead to increased NO_3^- in the water column. Furthermore, DO provides an electron acceptor for carbon respiration, leading to the remineralization of organic nitrogen as ammonium (NH_4^+) via ammonification (Scott and Binkley 1997), which can also elevate rates of nitrification (Ollinger et al. 2002) and produce higher levels of NO_3^-. Low DO concentrations are generally known to decrease NO_3^- concentrations, by inhibiting nitrification, and providing conditions instead favorable to denitrification (Seitzinger et al. 2006), which removes NO_3^- from streams.

A recent review article, focusing on data from streams of the northeastern U.S., shows that DOC levels are inversely related to NO_3^- concentrations (Goodale et al. 2005), suggesting that DOC may increase stream NO_3^- retention. DOC is a significant energy source for stream ecosystems (McDowell and Fisher 1976, Wiegner et al. 2005), and is tied to the nitrogen cycle through its use by heterotrophic bacteria (Meyer et al. 1988). Furthermore, strong coupling of carbon and nitrogen has been demonstrated in empirical studies of both soils (Swerts et al. 1996, Ollinger et al. 2002) and streams (Bernhardt and Likens 2002, Starry and Valett 2005). The experimental addition of DOC in streams led to increased NO_3^- uptake (and hence loss from the water column) by increasing heterotrophic immobilization (Bernhardt and Likens 2002) and denitrification (Inwood et al. 2005). Because heterotrophs can out-compete nitrifiers for NH_4^+, DOC is also known to inhibit nitrification (Straus and Lamberti 2000), which would have the net effect of reducing NO_3^- in the water column. Through its metabolism, DOC can also affect DO levels (Sand-Jensen and Pedersen 2005), and thus indirectly exert influence on nitrification and denitrification.

The overall goal of this study was to better understand how NO_3^- dynamics in headwater streams of the Ipswich and Parker River, MA watersheds (Figure 1) are controlled by concentrations of NO_3^-, DO, and DOC in the water column. These watersheds, which drain to the Plum Island Sound ecosystem, are rapidly urbanizing and have elevated nitrogen concentrations and fluxes (Wollheim et al. 2005) that threaten the coastal ecosystem. Furthermore, these basins have a large proportional area of wetlands that contribute high levels of DOC (Raymond and Hopkinson 2003), and also lead to relatively low DO in many reaches. Consistent with the analysis of Goodale et al. (2005), Figure 2 shows an inverse relationship between DOC and NO_3^- concentrations within streams and rivers of the Ipswich and Parker River watersheds. Furthermore, a synoptic survey of water chemistry from streams within the Parker and Ipswich River basins (n=41, data unpublished) provide an inverse relationship between DOC and NO_3^- ($p=0.001$). However, these data also show DOC levels are inversely correlated to concentrations of DO ($p=0.02$, n=41), and concentrations of DO are directly related to NO_3^- levels ($p=.04$, n=41). Thus the coupling of NO_3^-, DO, and DOC in these systems makes it difficult to decipher which factors are truly controlling the mechanisms of NO_3^- uptake.

To address the complex biogeochemical relationships observed within the streams of the Ipswich and Parker River watersheds this work employed a multi-factorial, whole-reach, experimental approach. We used short-term manipulations to determine the effects of NO_3^-, DO, and DOC on stream NO_3^- dynamics. Two types of experiments were employed: (1) NO_3^- additions in low NO_3^- streams of contrasting DO and DOC, and (2) manipulations of DO and DOC under ambient NO_3^- in these same streams. Along with the traditional method of NO_3^- enrichment to estimate gross NO_3^- uptake, this study investigated the impact of DO and DOC concentrations on net NO_3^- uptake, a metric for identifying dominant controls of nutrient export (Roberts and Mulholland 2007). The manipulations of both DOC and DO employed in this study represent a novel experimental approach to stream reach NO_3^- investigations. Manipulating NO_3^-, DO, and DOC in low NO_3^- streams affords perspectives on how these three parameters influence the dominant processes that ultimately determine the fate of NO_3^- retention and export. The following 4 hypotheses were tested:

Hypothesis 1: NO_3^- vertical velocity will be inversely related to NO_3^- concentration, because increasing concentrations of NO_3^- will decrease NO_3^- limitation.

Hypothesis 2: DO concentrations will be inversely related to net NO_3 uptake (ie. removal of NO_3^- from surface waters), because net NO_3^- uptake is influenced by rates of nitrification and denitrification, which is dependent on DO availability,

Hypothesis 3: DOC concentrations will be directly related to net NO_3^- uptake, because DOC will increase NO_3^- immobilization under aerobic conditions and fuel denitrification under anoxic conditions.

Hypothesis 4: DOC concentrations exert greater control over net NO_3^- uptake than DO concentrations; addition of DOC to surface waters will increase net NO_3^- uptake under all DO conditions by inhibiting nitrification and fueling immobilization and denitrification.

CHAPTER II

Methods

Site Description

Two 1st order streams, Cedar Swamp Creek and Cart Creek, were selected as the study sites for experimentation. These headwater streams are located in the Ipswich and Parker River watersheds, which drain to Plum Island estuary in northeastern Massachusetts (Figure 1). The Ipswich and Parker watersheds are typical of the low gradient, poorly drained, coastal landscapes found in much of New England (Baker et al. 1964). Shallow soils overlay the sand, gravel, and till of the local surficial geology and the igneous and sedimentary Paleozoic and Precambrian formations that comprise the bedrock geology (Baker et al. 1964). Average annual precipitation in the region is 115 cm (Wollheim et al. 2005).

Cedar Swamp Creek and Cart Creek were selected because they are relatively pristine watersheds, but differ in ambient water chemistry (Table 1). Due to abundant wetlands in the catchment (49 %), Cedar Swamp Creek has relatively high levels of DOC and dissolved organic nitrogen (DON), and low levels of NO_3^- and DO. In contrast, Cart Creek with 19 % wetlands has lower DOC, higher DO, and moderately higher NO_3^-. Experiments at these sites were performed in late summer of 2005 and 2006 during low, channelized stream flow and under full, deciduous canopy. The study reaches were 180 m and 175 m in

Cedar Swamp Creek and Cart Creek, respectively, with 6 to 8 sample stations distributed along the reach and one upstream of the addition site.

Nutrient Enrichments and Manipulations

Standard solute addition procedures summarized by Webster and Ehrman (1996) were followed for all enrichments and manipulations. Continuous additions of solutes and gasses were accompanied by a conservative tracer (NaCl) to determine dilution via lateral water inputs, hydrologic equilibrium (plateau), and transient storage in the study reach (Stream Solute Workshop 1990, Hart et al. 1995). All solutes were delivered using a peristaltic pump, which was monitored to ensure a constant delivery rate. Stationary YSI sondes-6920 and handheld YSI-85 meters (Yellow Springs Instruments, Yellow Springs, OH) were used to track conservative tracer movement and determine the time of hydrologic equilibrium for each addition. Discharge was quantified from in situ depth measurements using HOBO-U20 water level loggers (Onset Computer Corporation, Bourne, MA) in coordination with site-specific rating curves. Stream width was computed from measurements taken along the reaches at 10 m intervals.

All water samples were filtered in the field using ashed, 2.5 cm GF/F filters (0.7 μm). Samples were stored in acid washed HDPE plastic bottles, and kept on ice in the field. Upon returning from the field each day, samples were frozen until they could be analyzed. Wet chemistry included DOC (Shimadzu TOC-5000 with ASI-5000 autosampler), TDN (Antek 720C Chemiluminescent N detector coupled to TOC-5000) (Merriam et al. 1996), PO_4^{3-} and NH_4^+ (Westco

Smartchem Robotic Analyzer), and Anions (Cl^-, NO_3^-, SO_4^-) (Ion Chromatograph/HPLC System with autosampler). DON was derived as the difference between TDN and the sum of NH_4^+ and NO_3^-. All chemical analyses were performed by the Water Quality Analysis Laboratory in the New Hampshire Water Resources Research Center at the University of New Hampshire.

<u>NO_3^- Enrichments</u>

In the summer of 2005, multiple solute additions of $NaNO_3$ were conducted at Cedar Swamp Creek and Cart Creek to determine the influence of NO_3^- concentration on NO_3^- vertical velocity ($\square_f$). Both sites received 4 enrichments of $NaNO_3$, and each was successively greater in magnitude. Cedar Swamp Creek received additions of 0.02 (2x), 0.06 (5x), 0.3 (20x), and 1.7 (111x) mg N/L. Cart Creek received additions of 0.13 (1.3x), 0.45 (2x), 1.2 (4x), and 5.4 (13x) mg N/L. For each addition, lognormal NO_3^- concentrations (mg N/L) corrected for background concentration and dilution were plotted against distance downstream (Mulholland et al. 2002). The negative slope of this linear relationship provided the NO_3^- distance specific uptake rate (1/m). The inverse of the uptake rate is the NO_3^- uptake length (m). Vertical velocity (m/y) of NO_3^- was calculated for each addition according to the following equation:

$$V_f = \frac{Q}{wS_W} \qquad (1)$$

where Q is the discharge at the time of the addition (m^3/yr), w is average stream width (m), and S_W is uptake length (m). Ambient uptake length and vertical velocity were also quantified using the method of Payn et al. (2005).

DO & DOC Manipulations

In 2006, experimental manipulations of DOC and DO were conducted at Cedar Swamp Creek and Cart Creek. Cedar Swamp Creek received 3 experimental additions on 2 consecutive days: (1) a labile DOC addition using a glucose solution (August 16, 2006), (2) a DO enrichment (August 23, 2006), and (3) a simultaneous addition of DO and DOC (August 23, 2006). Cart Creek received 3 experimental solute additions on 3 dates: (1) a labile DOC enrichment using glucose (August 30, 2006), (2) a sodium sulfite addition to remove dissolved oxygen (September 1, 2006) (Gameson et al. 1955), and (3) concurrent sodium sulfite and glucose additions to simultaneously remove DO and add DOC (September 11, 2006). The concentrated glucose solutions added to Cedar Swamp Creek and Cart Creek targeted increases of 7 to 10 mg C/L in each stream, representing a carbon increase of 15 to 22 % and 125 to 178 % in Cedar Swamp Creek and Cart Creek respectively. Additions were started in the morning with plateaus generally reached within 4 hours.

During the DO additions in Cedar Swamp Creek, pressurized oxygen was added continuously through a diffusion stone placed on the stream bed, which raised DO levels at the upper most sampling station to 6.25 mg/L. Attaining this elevated concentration necessitated construction of a weir to channel the water directly over the diffusion stone. To enhance dissolution of DO into the water, a trolling motor (Minn Kota Endura) was placed upstream of the diffusion stone to aid channel mixing and inhibit the amended oxygen bubbles from quickly coalescing, rising, and degassing as they left the diffusion stone. A tarp was used to cover the stream bottom directly beneath and adjacent to the trolling motor to prevent sediments from being stirred up.

Oxygen was purged from Cart Creek using a concentrated solution of sodium sulfite, targeting a DO concentration in channel flow of 1-2 mg/L. Sodium sulfite was previously used to reduce stream oxygen for re-aeration studies (Gameson et al. 1955). The reaction required sodium sulfite concentrations to be roughly 8x greater than DO by weight. Due to the oxidizing capacity of this solution and its reactivity with atmospheric oxygen the solution of sodium sulfite was held in an airtight polyurethane container on the stream bank and sealed with petroleum jelly. Tubing from the peristaltic pump, used to deliver the solute, was inserted in the top of this container and sealed in place with caulk. To aid mixing of the solute with the water column, a weir was constructed at the point of solute release. Also, several baffles and an additional weir were installed within the first 20 m of the addition point to increase solute residence time and the dispersion necessary to allow the sulfite time to sufficiently react with the DO to achieve the target reduction prior to entering the study reach.

Nutrient Uptake

Analysis of the DOC and DO manipulations focused on the change in net NO_3^- uptake rate (mg N m^{-2} d^{-1}) during plateau of each experiment compared to that occurring under ambient conditions just prior to the experimental manipulation. The observed change between plateau and ambient conditions is referred to here as delta net NO_3^- uptake. Delta net NO_3^- uptake rate per unit area (mg N m^{-2} d^{-1}) was quantified using the equation:

$$U = \frac{-F}{w} \qquad (2)$$

where F is the slope of the difference between experiment and ambient flux versus distance (mg m^{-1} d^{-1}), and w is average stream width (m). Positive U represent net nutrient uptake, while negative U represents net nutrient production. Slopes and intercepts were determined for ambient and plateau NO_3^- flux, and for the change in flux through the reach. The slope of change in flux was used to assess the significance of the experimental manipulation with respect to nitrate fluxes. Two-tailed paired t-tests were also performed to identify whether the experiments had a significant effect on nitrate chemistry ($p<0.05$). DOC and DO uptake rates and decay deficits per unit distance, k (1/m), during the manipulations were calculated using the slope of background corrected, lognormal nutrient flux plotted against distance (Webster and Ehrman 1996). Positive k values for the oxygen removal experiments represent the decay of the oxygen deficit (i.e. re-oxygenation).

CHAPTER III

Results

NO_3^- Enrichments and Vertical Velocity

Uptake lengths increased and vertical velocities decreased with increasing NO_3^- concentrations at both Cedar Swamp Creek and Cart Creek (Table 2). Ambient estimates using the Payne et al. (2005) method resulted in S_W and υ_f of 15 m and 3202 m/y, respectively, at Cedar Swamp Creek and 517 m and 126 m/y, respectively, at Cart Creek. Cedar Swamp Creek had higher υ_f than Cart Creek, corresponding with lower nitrate concentrations. Combining the data from the two sites, uptake velocity declined as a power function of nitrate concentration (mg/L) ($105.35x^{-0.7607}$, $p=0.004$, $R^2 = 0.8406$). The relationship appears to apply across the two sites, despite their different characteristics (Figure 3).

DOC and DO conditions during carbon and oxygen manipulations

Cedar Swamp Creek and Cart Creek received DOC and DO manipulations to identify the independent and synergistic impacts of these parameters on NO_3^- dynamics. The experimentally altered characteristics at plateau (change at the first station, and k (1/m) through the reach) during the 3 manipulations for both Cedar Swamp Creek and Cart Creek are shown in Tables 3 and 4. At Cedar Swamp Creek the labile DOC (glucose) addition (August 16, 2006, Q = 2.935 L/s) achieved an upstream (site 1, 30m) DOC concentration 19

% (8.0 mg/L) higher than ambient values, and average transect concentrations rose 7.09 mg C/L. The DO addition at Cedar Swamp Creek (August 23, 2006, Q = 2.387 L/s) increased concentrations 90 % (2.74 mg/L) above ambient values at the most upstream sampling station resulting in an average transect concentration 1.93 mg/L higher than ambient values. The simultaneous DO and DOC enrichment (August 23, 2006, Q = 2.387 L/s) increased DO at the upstream site 93 % (2.84 mg/L), and the experimental transect experienced an average increase of 2.07 mg/L. However, although the target DOC elevation of 9 to10 mg C/L was successfully injected, the concentrations 30 m downstream were 35% lower than ambient levels, and the average transect concentration dropped 1.61 mg C/L.

In Cart Creek the initial glucose addition (August 30, 2006, Q = 2.595 L/s) raised the DOC level at the upstream station (25 m) to 11.9 mg C/L (+108 %), and average DOC concentrations increased by 3.79 (mg C/L) over the entire reach. The second experiment was DO removal (September 1, 2006, Q = 1.615 L/s) in which DO levels dropped at the upstream station by 88 % (-7.1 mg/L). Average transect concentrations in flowing water during this experiment were 5.7 mg/L below ambient values. The third manipulation at Cart Creek, the DO removal and simultaneous glucose addition (September 11, 2006, Q = 1.705 L/s), decreased DO concentrations at the upstream station from 7.94 to 1.08 mg/L (-86 %). Average transect DO concentrations during this removal were 5.42 mg/L below ambient values. The glucose solution of this third manipulation raised DOC concentrations at the upstream station 146 % to 11.8 mg/L, and the average reach concentration increased by 6.04 mg/L. Temporal profiles of dissolved oxygen from Cedar Swamp Creek and Cart Creek during the combined DO and DOC manipulations are shown in Figures 4 and 5, and oxygen transects (as concentration, mg/L) for all experiments are shown in Figure 6.

While the design and focus of all the experiments was the influence of DOC and DO concentrations on net NO_3^- dynamics, there was a surprising result involving the metabolism of organic matter that we point out here. The phenomenon was most prominent during the combined DOC and DO addition at Cedar Swamp Creek. As noted above, the plateau concentrations of DOC at the first sampling station during the combined DOC and DO addition were actually lower than ambient levels (-17.17 mg C/L). Downstream of this sampling station we observed DOC concentrations gradually returning to ambient levels with distance along the transect (Figure 7A). This suggests that there was immediate removal of both ambient and labile DOC between the point of addition and the first sampling station, with a DOC uptake velocity equivalent to 1074 m/y. This interpretation is corroborated by DON concentrations along the transect, which display a very similar pattern (Figure 7B). The concentration of DON removed from the water column corresponds to a vertical velocity value of 1809 m/y. Further, the decreasing levels of DON in the water column corresponded with elevated levels of NH_4^+ (Figure 7C). This increase in NH_4^+ concentration at the first sampling station may account for approximately 25 % of the observed DON removal. Over the distance of the entire transect, the rate of net NH_4^+ removal was 0.0006 (1/m). If completely nitrified, this amount of net NH_4^+ loss could result in an increase in NO_3^- of 0.075 mg N/L. Nitrate had a net increase of 0.047 mg N/L over this transect suggesting that a portion of the NH_4^+ removed from the water column was converted to NO_3^- via nitrification, and the remaining N unaccounted for is assumed to have been removed from the water column via biotic or abiotic processes untraceable by our methods. Less intense yet similar shifts in concentration of DON, NH_4^+, and NO_3^- were observed during the DOC addition at Cart Creek when average concentrations of DON in the reach dropped 0.013 mg N/L, and concentrations of NH_4^+ and NO_3^- rose 0.002 and 0.019 mg N/L respectively.

NO_3^- Response to DOC and DO Manipulations

The DOC and DO manipulations induced either increases or decreases in net NO_3^- uptake. Paired t-tests comparing NO_3^- concentrations at all stations along the transects collected during experimental plateau versus their ambient counterparts showed that all manipulations significantly altered mean NO_3^- concentrations ($p<0.05$).

The addition of DOC had inconsistent effects on NO_3^- dynamics at Cedar Swamp Creek and Cart Creek. Under ambient conditions at Cedar Swamp Creek, slopes of NO_3^- flux increased through the study reach. Addition of DOC to Cedar Swamp Creek (low DO stream) created a marginally significant change ($p=0.051$) as the slope of NO_3^- flux became less positive (Table 5), and net NO_3^- uptake increased (Figure 8A). At Cart Creek (high DO stream), where ambient slopes of NO_3^- flux decreased with distance, the addition of DOC positively increased the slope of NO_3^- flux and resulted in a positive delta NO_3^- flux. Thus, addition of DOC at Cart Creek decreased net NO_3^- uptake (Figure 8B).

The DO manipulations resulted in changes in net NO_3^- uptake through each stream reach, but the effects were relatively small. The addition of DO to DOC-rich Cedar Swamp Creek caused the slope of NO_3^- flux versus distance to increase positively (Table 5), and resulted in a positive delta NO_3^- flux and a decline in net NO_3^- uptake (Figure 8A). This result is consistent with Cart Creek's DOC addition where high DOC and high DO were paired. The DO removal at Cart Creek had little effect on net NO_3^- uptake, indicating a small increase in delta NO_3^- flux and a decrease in net NO_3^- uptake (Figure 8B). Note however that nitrate fluxes declined with distance through the reach in this experiment, with most of the change having occurred prior to the first sample station (negative intercept for delta, Table 5). As stated above, a pool was artificially created to ensure sufficient residence time to ensure DO was removed from the water column.

Concurrent manipulations of DOC and DO produced the strongest changes in net NO_3^- uptake in Cedar Swamp Creek and Cart Creek (Figures 8A and 8B). Furthermore, the changes observed during these manipulations were exact opposites. The concurrent addition of DOC and DO in Cedar Swamp increased delta NO_3^- flux. This change in flux was marginally significant ($p = 0.052$), and resulted in a stronger decline in delta net NO_3^- uptake than the independent DO addition at Cedar Swamp Creek. At Cart Creek the simultaneous removal of DO and addition of DOC decreased NO_3^- flux below ambient conditions, and resulted in a marginally significant ($p = 0.057$), negative delta net NO_3^- flux. This concurrent DO removal and DOC addition at Cart Creek led to an increase in delta net NO_3^- uptake (Figure 8B).

CHAPTER IV

Discussion

NO_3^- Enrichments

Compared with NO_3^- vertical velocity values determined from 52 studies in other 1st order streams (Ensign and Doyle 2006) Cedar Swamp Creek and Cart Creek were found to be true end-member sites with all experimentally derived υ_f values falling outside the interquartile range of those data (420 – 2208 m/yr). Cedar Swamp Creek demonstrated high υ_f during the lowest NO_3^- enrichment, suggesting Cedar Swamp Creek is severely NO_3^- limited. However, the decline in υ_f as NO_3^- concentrations increased (20 -110 % above ambient concentration) at Cedar Swamp Creek suggests that NO_3^- limitation at this site is removed at moderate NO_3^- concentrations, and that uptake efficiency of the bacterial community within Cedar Swamp Creek quickly declines with increasing NO_3^- concentrations during short-term additions. At Cart Creek, the υ_f values quantified from NO_3^- enrichments and the estimated ambient υ_f are an order of magnitude lower than the mean value (1472 m/yr) found in the literature (Ensign and Doyle 2006). However, estimated ambient NO_3^- vertical velocity at Cart Creek (126 m/yr) is similar to that estimated during the Lotic Intersite Nitrogen Experiment II (LINX II) using tracer ^{15}N additions (172 m/y, Peterson, unpublished). While υ_f at Cart Creek did decline with increasing NO_3^- concentration, the change observed was not as extreme as at Cedar Swamp

Creek. These data signify that among study streams Cart Creek has less efficient NO_3^- uptake, but that uptake efficiency within Cart Creek is also less sensitive to changes in concentration.

The results from the multiple enrichments at the two sites show a consistent inverse relationship between NO_3^- concentration and NO_3^- υ_f. The consistent trend both within and across sites in this study suggests NO_3^- concentration is truly a dominant control on NO_3^- dynamics in these streams. Furthermore, LINX II results of total NO_3^- uptake from isotope tracer additions in a nationwide study of stream N cycling also exhibit inverse relationships between NO_3^- υ_f and NO_3^- concentration (Mulholland et al.2008) (Figure 9). The υ_f data from this study are elevated compared to the overall results of LINX II. Typically ^{15}N tracer additions would have higher υ_f than a study using short-term increases in NO_3^-, because isotope data represent ambient NO_3^- metrics in systems with naturally higher NO_3^- concentrations where microbial communities should have had time to adapt to chronically high N levels (Mulholland et al. 2002). In this instance, our study may have higher υ_f despite being based on short-term solute additions due to other pollutants in the high N LINX II streams that result in less effective microbial communities, or perhaps due to other limiting nutrients in the LINX streams. Regardless of this discrepancy, NO_3^- concentrations appear to have an inverse relationship with NO_3^- υ_f in Cedar Swamp Creek and Cart Creek, and this trend is consistent with other research.

The power law relationship of NO_3^- υ_f versus NO_3^- concentration shown in Figure 3 has a steeper decline in uptake efficiency than that found by Mulholland et al. (2008) and LINX II. Again this finding may be attributed to our study involving short term additions compared to the other studies, which included streams with chronically high NO_3^- concentrations and used isotopic tracers. Our experimental results are based solely upon NO_3^- availability, while υ_f values from isotopic studies may reflect the influence of other limiting nutrients and site characteristics. Furthermore, the unique site conditions at Cedar Swamp Creek (high DOC, low DO, low NO_3^-) may have caused the steep slope by exhibiting extreme nitrate limitation and uptake during the lowest NO_3^- addition and a quickly declining uptake efficiency with the subsequently higher additions. This result may be the manifestation of a microbial community that is chronically NO_3^- limited and not adapted to receiving higher doses of NO_3^-.

<u>Effect of DO and DOC Concentrations on Dissolved Organic Matter</u>

DOC was removed from the water column more rapidly under higher DO conditions in both streams (Table 4). This result is consistent with the literature, which suggests that under aerobic conditions the addition of DOC can increase metabolism in streams (Weigner et al. 2005). However, the loss of DON and the liberation of NH_4^+ which occurred in both Cart Creek and Cedar Swamp Creek during DOC additions is inconsistent with other studies (Strauss and Lamberti 2000, Bernhardt and Likens 2002), which have found the addition of DOC increases NH_4^+ retention by heterotrophs due to nutrient immobilization necessary to meet demand for cellular growth.

The loss of dissolved organic matter from stream water at Cedar Swamp Creek during the concurrent addition of DOC and DO is particularly striking, as the estimated value of DOC υ_f within the first 30 meters reached levels 5 times higher than average levels recorded in the literature (Weigner et al. 2005). This mass removal of organic matter may in part be explained by the flocculation of dissolved organic matter into particulate organic matter (POC) (Lush & Hynes 1973), and by abiotic adsorption of dissolved organic matter to sediments (McDowell 1985). However, the concurrent rise in NH_4^+ during the addition of DOC and DO at Cedar Swamp Creek strongly suggests biotic processes, and that not only was the added, labile DOC quickly metabolized by the first sampling station, but that naturally occurring DON declined in this system due to remineralization of ambient organic matter (Scott and Binkley 1997). This phenomenon of labile DOC increasing the metabolism of ambient organic matter has not previously been reported in stream ecosystems, but is known in terrestrial ecosystems as a "priming effect" (Kuzyakov et al. 2000). Priming effects are possible in Cedar Swamp Creek because this is a heterotrophic system that contains high levels of organic matter compared to other studies involving DOC additions (Bernhardt and Likens 2002, Wiegner et al. 2005), and because Cedar Swamp Creek was simultaneously supplemented with DO.

Downstream of the priming effects, we suggest that concentrations of DOC and DON were reestablished and maintained near an equilibrium by leaching from benthic organic matter. Although the increase in concentration of DOC over this 150m reach is large (20 mg/L, or 65% of initial influx), previous reports suggest that the source of these concentrations may be attributed to in-channel leaching of stored benthic organic matter (Meyer et al. 1998, Wiegner et al. 2005). In this instance we believe that downstream of the oxygen addition (> 60 m) where oxygen concentrations were only modestly elevated and where the added, highly labile DOC was absent, the microbial community was unable to metabolize the ambient, more recalcitrant organic matter within the benthos. Diffusion/exchange of sediment dissolved organic matter reintroduced DOC and DON to the water column and maintained equilibrium concentrations (McDowell 1985) similar to that found under ambient conditions.

Effect of DO and DOC Concentration on Net NO_3^- Uptake

Results from the manipulations of DOC and DO suggest that DOC by itself does not lead to increased net nitrate uptake, but magnifies the dominant processes as determined by oxygen levels in the stream. Our results indicate that low DO/high DOC streams have higher net nitrate uptake than high DO/high DOC streams. Although Goodale et al. (2005) indicate that higher DOC concentrations aid NO_3^- retention, our experiments suggest that increased DOC concentrations only aid NO_3^- retention under depressed oxygen conditions, and that the results of Goodale et al. (2005) may in part be influenced by the covariation of DOC and DO in natural systems. From our results (Figure 8) we discern that the DO concentrations in these stream ecosystems determined the dominant processes that influence net NO_3^- uptake, and that the addition of DOC served mainly to enhance the dominant metabolic activity in each stream system.

High DO systems consistently resulted in decreased net NO_3^- uptake (net production), and disproved our hypothesis that DOC would increase net NO_3^- under all circumstances. In Cedar Swamp Creek the addition of DO decreased net NO_3^- uptake. In this DO deficient system, the addition of DO likely spurred nitrification (Kemp and Dodds 2001), thus increasing NO_3^- concentrations while at the same time making conditions for denitrification less favorable. Net NO_3^- uptake therefore declined. In both Cedar Swamp Creek and Cart Creek the addition of DOC under aerated conditions (Cedar Swamp Creek concurrent DOC and DO addition, Cart Creek DOC addition) led to a decrease in net NO_3^- uptake. The decrease in net NO_3^- uptake observed during these manipulations is inconsistent with the literature, which suggests that addition of DOC should increase the immobilization of dissolved inorganic nitrogen by heterotrophs (Bernhardt and Likens 2002). However, both Cedar Swamp Creek and Cart Creek experienced average plateau levels of NO_3^- and NH_4^+ that were higher and DON levels that were lower than ambient levels during these experiments, suggesting similar mechanisms were at play across these sites. We believe the high oxygen levels and aerobic metabolism ultimately determined the fate of NO_3^- in these reaches. The extreme "priming effect" of labile DOC in Cedar Swamp is a key example of this potential. In Cedar Swamp the "priming effect" was realized when sufficient oxygen was coupled with labile DOC, and it resulted in the heterotrophic metabolism of the labile, added DOC as well as the more recalcitrant, naturally occurring organic matter in this system (Kuzyakov et al. 2000). The breakdown of this organic matter led to accelerated rates of ammonification, leading to increased NH_4^+ in Cedar Swamp Creek (Scott and Binkley 1997). Increases in net NO_3^- production were likely the result of increased rates of nitrification, as the metabolic rate of nitrifying bacteria increased positively with both ammonification (Ollinger et al. 2002) and levels of dissolved oxygen (Kemp and Dodds 2001). Thus, despite obvious signs of DOC uptake and intense levels of heterotrophic metabolism, the addition of DOC and DO in this system ultimately increased levels of DO and NH_4^+, which favored nitrifying bacteria and led to a decrease in net NO_3^- uptake. This suggests that addition of DOC under aerated conditions may in some instances promote net NO_3^- production via remineralization and nitrification.

Experiments in Cedar Swamp Creek and Cart Creek carried out under low oxygen conditions support the hypothesis that DOC increases NO_3^- uptake (Goodale et al. 2005). At Cedar Swamp Creek where oxygen is naturally limited, the observed increase in net NO_3^- uptake during the DOC only addition is consistent with increased heterotrophic metabolism of DOC with immobilzation of NO_3^- (Bernhardt and Likens 2002), and/or increased rates of denitrification (Inwood et al. 2005). Removing DO from Cart Creek created virtually no change in net NO_3^- uptake, and actually the data show net NO_3^- uptake decreased slightly. The literature suggests that the expansion of anoxia is likely to inhibit nitrification (Kemp and Dodds 2001) and increase the prevalence of denitrification in the benthos (Seitzinger et al. 2006). Therefore, by inhibiting a NO_3^- producing process and promoting a NO_3^- reducing process, low DO levels in the water column should have contributed to an increase in net NO_3^- uptake. The minute reaction in net NO_3^- uptake found in the DO removal experiment in this study appears to be due to a lack of DOC necessary to fuel denitrification and/or the low DO leading to a reduction of coupled nitrification/denitrification

(Tomaszek and Czerwieniec 2003). Supporting this idea that reduced nitrification limited the response of dentirification, average NH_4^+ concentrations were higher during the low DO manipulaitons (data not shown). LINX II results had undetectable denitrification using tracer additions in Cart Creek (Peterson unpublished), and therefore suggest denitrification in this system may be DOC limited. In fact, when DOC was added to Cart Creek under reduced DO conditions in this study it created an environment favorable for positive net NO_3^- uptake. The increased intensity of net NO_3^- uptake during the concurrent DO removal and DOC addition experiment compared to the independent DO removal suggests that the added DOC was fueling benthic denitrification. This is consistent with recent findings by Inwood et al. (2005) where water column DOC shares a significant positive relationship with rates of denitrification. Furthermore, these results are consistent with Goodale et al. (2005) who suggest DOC increases NO_3^- uptake. Thus under low oxygen conditions, when NO_3^- production via nitrification is limited and the potential for denitrification is optimized, the addition of DOC can greatly increase net NO_3^- uptake.

CHAPTER V

Summary and Conclusions

Headwater streams have the potential to retain significant amounts of N introduced from the landscape (Peterson et al. 2001), and they serve as an important transition zone preventing terrestrial N from reaching marine ecosystems. A recent review of NO_3^- dynamics in streams (Goodale et al. 2005) shows that NO_3^- levels are inversely related to DOC concentrations, suggesting that DOC increases stream NO_3^- retention. Analysis of stream chemistry from the watersheds of the Ipswich and Parker Rivers draining to Plum Island Sound in northeastern Massachusetts show trends similar to that of Goodale et al (2005). However these data from the Ipswich and Parker River watersheds also show that concentrations of NO_3^-, DO, and DOC are all significantly interrelated and the control on net NO_3^- uptake is a more complex relationship among NO_3^- concentrations, DO, and DOC.

The results from our manipulations have important implications for the biogeochemistry and water quality management of the Ipswich and Parker River watersheds. The results of the NO_3^- enrichments suggest that NO_3^- uptake efficiency decreases with increasing concentration in local headwater streams, and that it is possible to overwhelm the NO_3^- buffering capacity of these systems. Results from the DOC and DO manipulations suggests that within headwater streams it is the level of DO that most significantly influences net NO_3^- uptake, but effects are magnified by the level of DOC. The proliferation or absence of DO in our study streams determines the dominant respiratory pathway of the stream ecosystems and consequently creates an environment that is either (a) a predominantly aerobic system that exceeds in organic matter metabolism and net NO_3^- production or (b) a predominantly anaerobic system with low DOC uptake rates and high net NO_3^- uptake. Our results also suggest that short-term increases in the availability of labile DOC within both low and high DO streams appear to increase metabolic activity and accentuate any existing, DO dependent processes that determine net NO_3^- uptake and production. Wetland streams with characteristically low DO and high DOC are therefore excellent NO_3^- sinks. Furthermore, within the Ipswich and Parker River watersheds where wetland streams are abundant, these natural NO_3^- sinks should serve to maintain low water column NO_3^- concentrations, thereby promoting high NO_3^- uptake velocity and creating a positive feedback system wherein environmental conditions conducive to net NO_3^- uptake are reinforced. On the other hand, our results suggest that stream reaches with accelerated reaeartion rates, such as those dominated by riffles, may serve as sources of net NO_3^- production via remineralization and nitrification. Moving beyond the scope of this study, the coupling of environments which link net NO_3^- sources and NO_3^- sinks, such as the natural riffle and pool sequences inherent in stream ecosystems (Dunne and Leopold 1978), may serve as a critical component in the longitudinal removal of N within streams as DON and NH_4^+ are converted to NO_3^- and then NO_3^- is subsequently transported downstream to an area more optimized for NO_3^-

removal. Quantifying the abundance and linkages of different stream types at river network scales is necessary to further understand how river systems influence the export of NO_3^- from basins with high nitrogen inputs.

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TABLES

Table 1: Characteristics of Cedar Swamp Creek and Cart Creek. Data represent average of all ambient transect values measured prior to each manipulation in summer 2006.

Parameter / Variable	Cedar S.	Cart C.
[a]Basin characteristics		
Area (Km^2)	1.4	3.96
- Agriculture (%)	6	8
- Forest (%)	36	57
- Wetland (%)	49	19
- Industrial (%)	0	5
- Residential (%)	9	11
Water chemistry		
NO_3^- (mg N/L)	0.08 $\pm$ .01	0.25 $\pm$ .03
DOC (mg C/L)	45.29 $\pm$ 3.83	5.60 $\pm$ .58
DO (mg DO/L)	3.57 $\pm$ .16	8.46 $\pm$ .20
DON (mg N/L)	0.64 $\pm$ .059	0.21 $\pm$ .03
NH_4^+ (mg N/L)	1.61 $\pm$ .05	0.019 $\pm$ .007
[b]PO_4^{-3} (mg P/L)*	1.01 $\pm$ .095	0.004 $\pm$ .004
Temp (°C) (during summer sampling 2006)	18.33 $\pm$ 0.17	14.2 $\pm$ 1.32
Channel characteristics and hydrology		
Q (L/s)	2.57 $\pm$ 0.04	2.08 $\pm$ 0.54
Study reach length (m)	180	175
Width (m)	1.81	1.70
As/A, Ratio of storage zone to water column	0.18	0.17
Water exchange rate coefficients (1/min)		
Flowing water column to the storage zone	$2.03*10^{-3}$	$2.44*10^{-3}$
Storage zone to the flowing water column	$1.47*10^{-2}$	$1.47*10^{-2}$
Lateral Inputs (%)	4.5	16.8
Oxygen exchange rate coefficient (1/min)	0.013	0.035

[a] Land cover data from MassGIS

[b] Phosphorus values are from summer 2005.

Table 2: Uptake length and vertical velocity from NO_3^- additions at Cedar Swamp Creek and Cart Creek.

Site	Addition	Added NO_3^- (mg N/L)	Uptake length (m)	υ_f (m/y)
Cedar Swamp Creek				
	[a]Ambient	0	15	3202
	1	0.02 (2.1 x N_{AMB})	12	3981
	2	0.06 (5.0 x N_{AMB})	[c]94	[c]311
	3	0.29 (19.6 x N_{AMB})	[c]357	[c]132
	4	1.74 (110.6 x N_{AMB})	714	66
Cart Creek				
	Ambient	0	517	126
	[b]1	0.13 (1.3 x N_{AMB})	N/A	N/A
	2	0.45 (2.0 x N_{AMB})	[c]556	[c]117
	3	1.24 (3.8 x N_{AMB})	909	72
	4	5.40 (13.2 x N_{AMB})	1429	46

[a]Ambient calculated using Payn et al method. Addition 4 from Cedar Swamp Creek was excluded to meet the assumption of linearity

[b] The lowest NO_3^- enrichment at Cart Creek was too dilute to be detected

[c] Regression is statistically significant ($p < 0.05$)

Table 3: Change in DOC and DO concentrations at plateau at the first sampling station relative to ambient concentrations at Cedar Swamp Creek (30 m) and Cart Creek (25 m) during each of the three manipulations at these sites.

Experiment	Cedar Swamp Creek		Cart Creek	
	DOC (mg C/L)	DO (mg/L)	DOC (mg C/L)	DO (mg/L)
DOC Added	+8.0	-	+6.2	-
DO Added	-	+2.74	-	-
DOC Added, DO Added	-17.17	+2.84	-	-
DO Removed	-	-	-	-7.1
DOC Added, DO Removed	-	-	+7.0	-6.9

Table 4: Distance specific uptake rates (k, 1/m) for dissolved organic carbon (DOC) and dissolved oxygen (DO) derived from Ln transformed, background corrected fluxes along longitudinal transects in Cedar Swamp Creek and Cart Creek. Positive values for DO reflect rates of reoxygentation, and negative values reflect rates of uptake.

Experiment	Cedar Swamp Creek		Cart Creek	
	DOC	DO	DOC	DO
DOC Added	-0.003437	-	-0.005572	-
DO Added	-	-0.003197	-	-
DOC Added, DO Added	[b]<30 m, -0.02	[a]-0.003956	-	-
DO Removed	-	-	-	[a]0.003078
DOC Added, DO Removed	-	-	[a]-0.001375	[a]0.003017

[a] Slope is statistically significant different from 0 ($p < 0.05$)

[b] Estimated k based on total DOC removed between the point of solute addition and the first sampling station at 30 m

Table 5: Linear slope (m) and intercept (b) values of NO_3^- flux (mg/s) from ambient transects, plateau transects, and the delta (determined from the difference between experiment and ambient fluxes though the reach). P-values for slope and intercepts of delta flux are also shown.

Experiment	Ambient		Plateau		Delta	
	m	b	m	b	m (p-value)	b (p-value)
Cedar Swamp Creek						
DOC Added	[a]0.00058	[a]0.16274	[a]0.00044	[a]0.15504	-0.00014 (0.0508)	-0.00770 (0.2648)
DO Added	[a]0.00048	[a]0.14560	[a]0.00061	[a]0.15832	0.00012 (0.2502)	0.01272 (0.2852)
DOC Added, DO Added	[a]0.00048	[a]0.14560	[a]0.00071	[a]0.1582	0.00023 (0.0517)	0.01260 (0.2714)
Cart Creek						
DOC Added	-0.00031	[a]0.72831	-0.00009	[a]0.75898	0.00022 (0.3655)	0.03070 (0.2665)
DO Removed	-0.00007	[a]0.45061	-0.00006	[a]0.41783	0.00001 (0.9506)	-0.03280 (0.1496)
DOC Added, DO Removed	-0.00010	[a]0.43436	[a]-0.00066	[a]0.39612	-0.00055 (0.0574)	-0.03824 (0.1687)

[a] Slope is statistically significant different from 0 ($p < 0.05$)

FIGURES

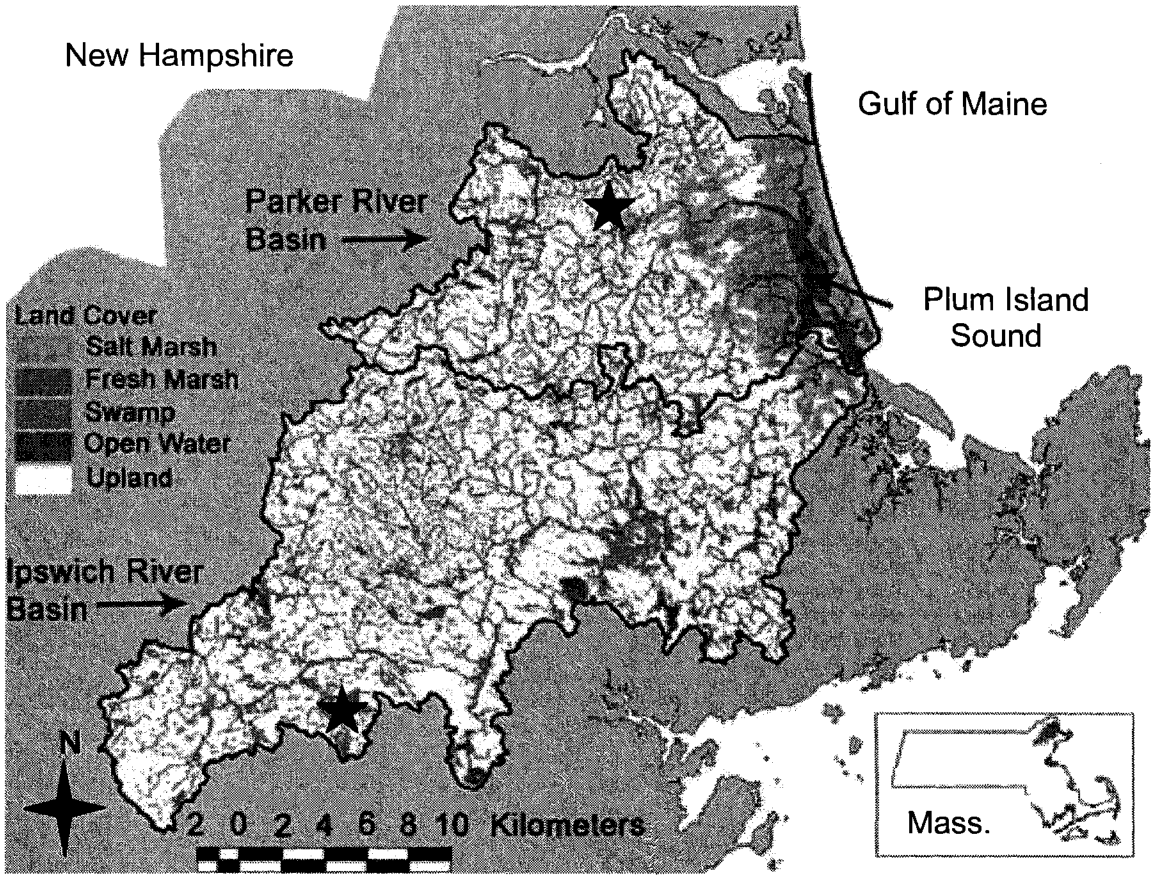


Figure 1: Stream study sites Cart Creek (northern star) and Cedar Swamp Creek (southern star) within the Ipswich and Parker River Watersheds of Massachusetts. Map courtesy of Plum Island LTER (http://ecosystems.mbl.edu/PIE/PlumIslandBrochure.pdf)

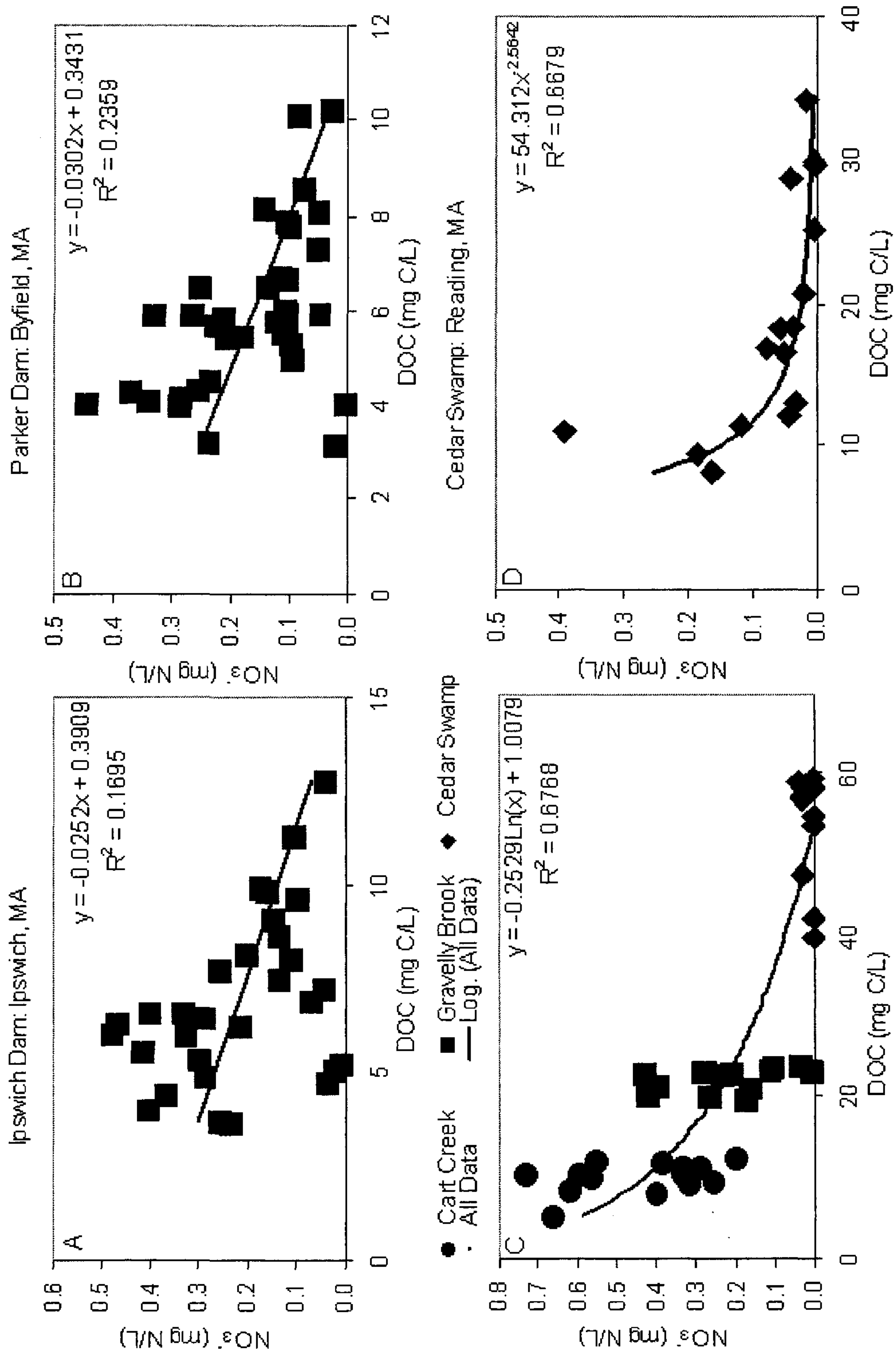


Figure 2: Inverse relationship between DOC and NO_3^- concentrations in monthly grab samples at the two main rivers flowing to Plum Island Sound (A, p=0.017 and B, p=0.0027), among headwater sites in summer 2005 (C, p<.001)), and in monthly grab samples at a single headwater site throughout 2005 and 2006 (D, p=0.011).

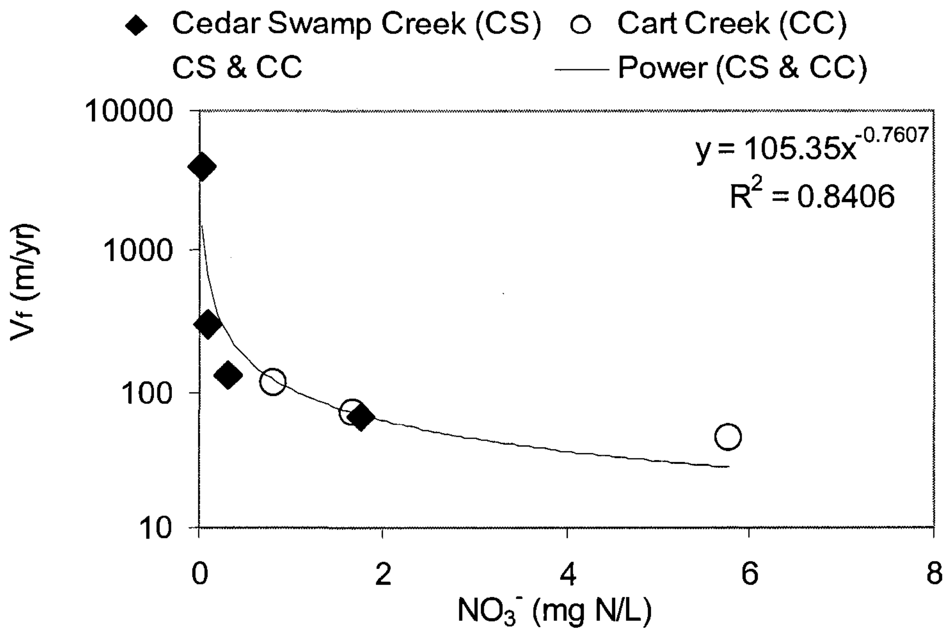


Figure 3: Average reach NO_3^- concentration is inversely related to measurements of NO_3^- vertical velocity at Cedar Swamp Creek and Cart Creek. These data show a continuum of uptake efficiency between sites as displayed by the power regression through the points at Cedar Swamp Creek and Cart Creek (CS & CC).

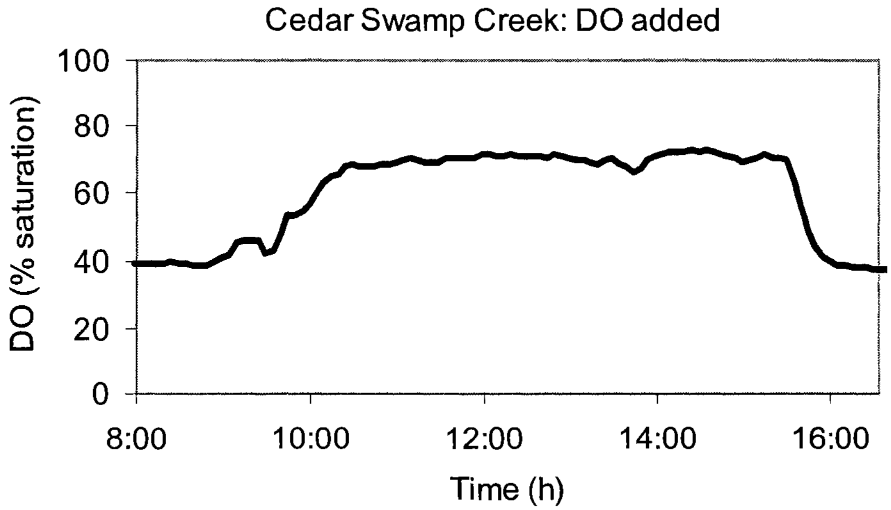


Figure 4: Time series of DO in Cedar Swamp Creek at 60 m downstream of the DO addition site during the DO addition experiments. Oxygen was added from 9:50 to 15:15 hours.

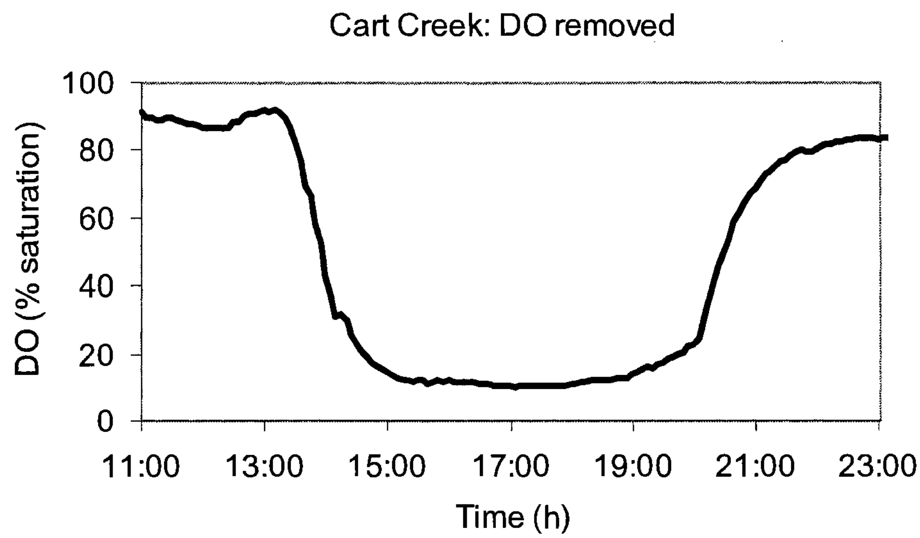
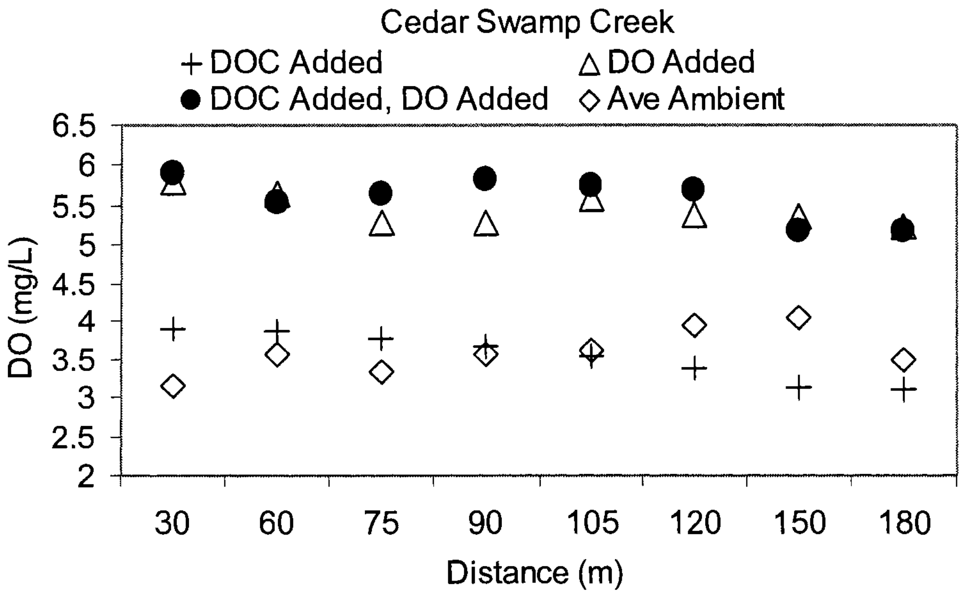


Figure 5: Time series of DO in Cart Creek at 60 m downstream of the DO removal site during the combined DOC addition and DO removal experiment. Sulfite, used to remove DO, was added between 11:45 and 18:15 hours.



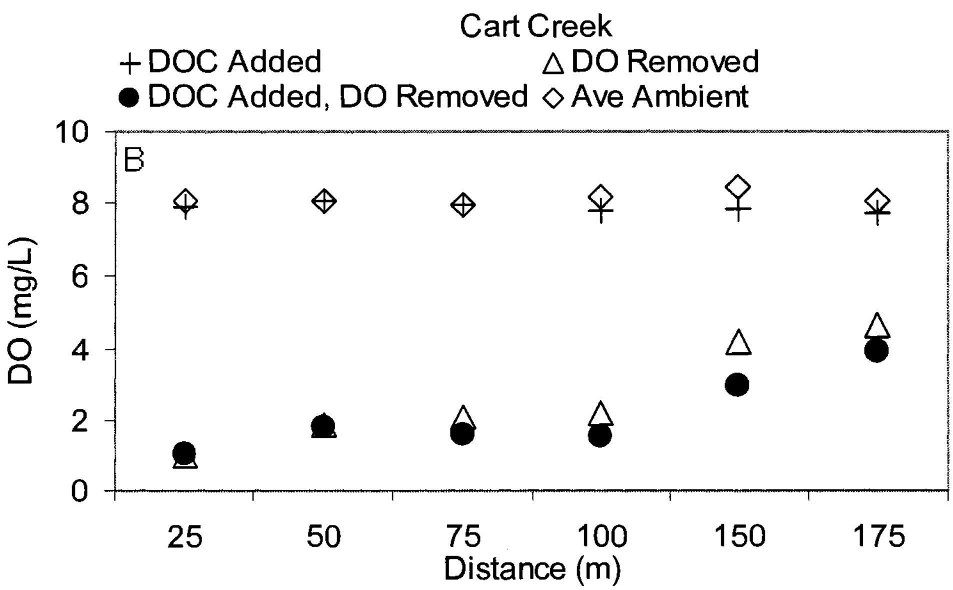


Figure 6: DO concentrations along experimental transects during plateau of experiments at Cedar Swamp Creek (A) and Cart Creek (B) including average ambient concentrations.

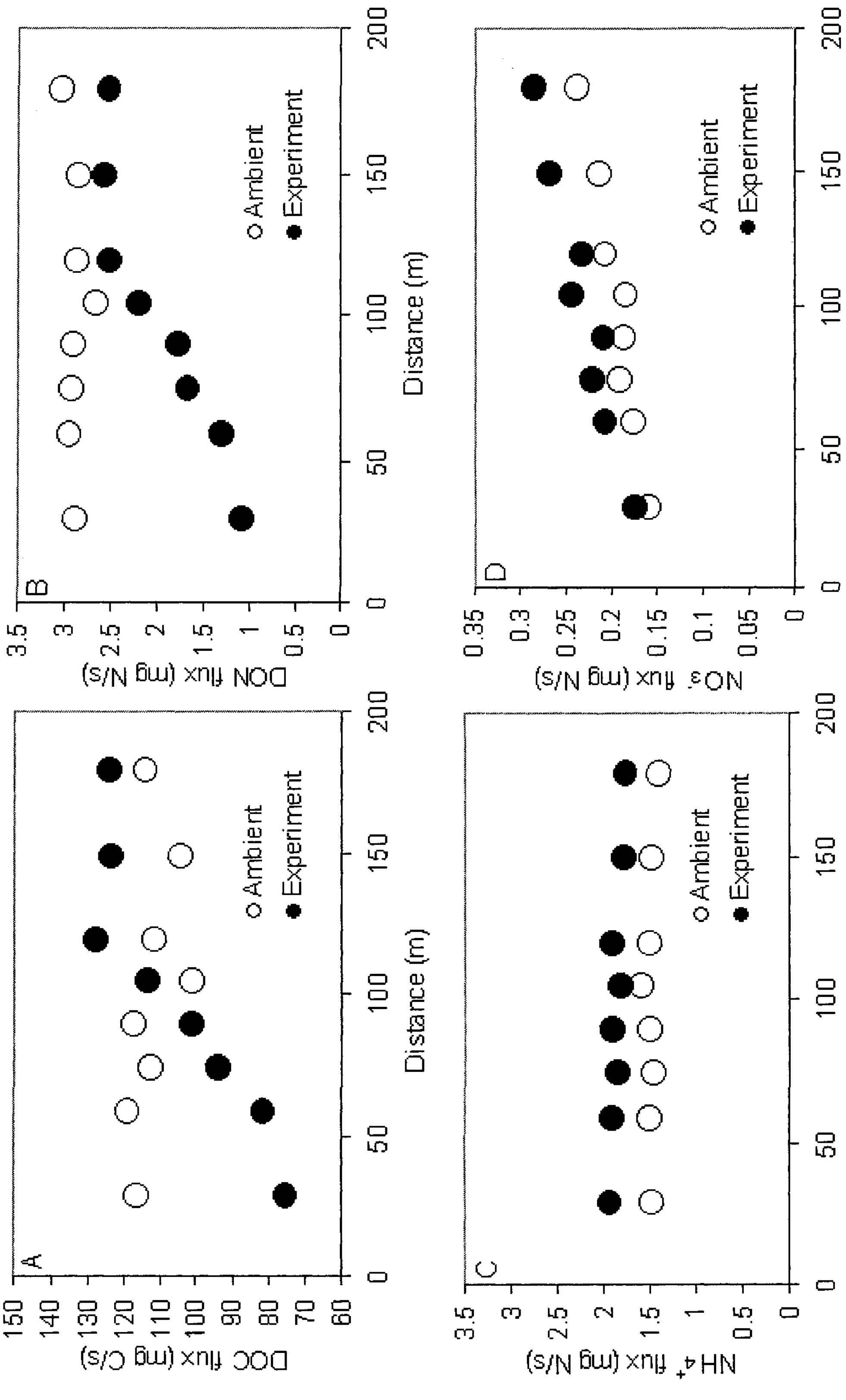


Figure 7: Ambient and plateau chemistry of (A) DOC, (B) DON, (C) NH_4^+, and (D) NO_3^- at Cedar Swamp Creek from the concurrent addition of DOC and DO.

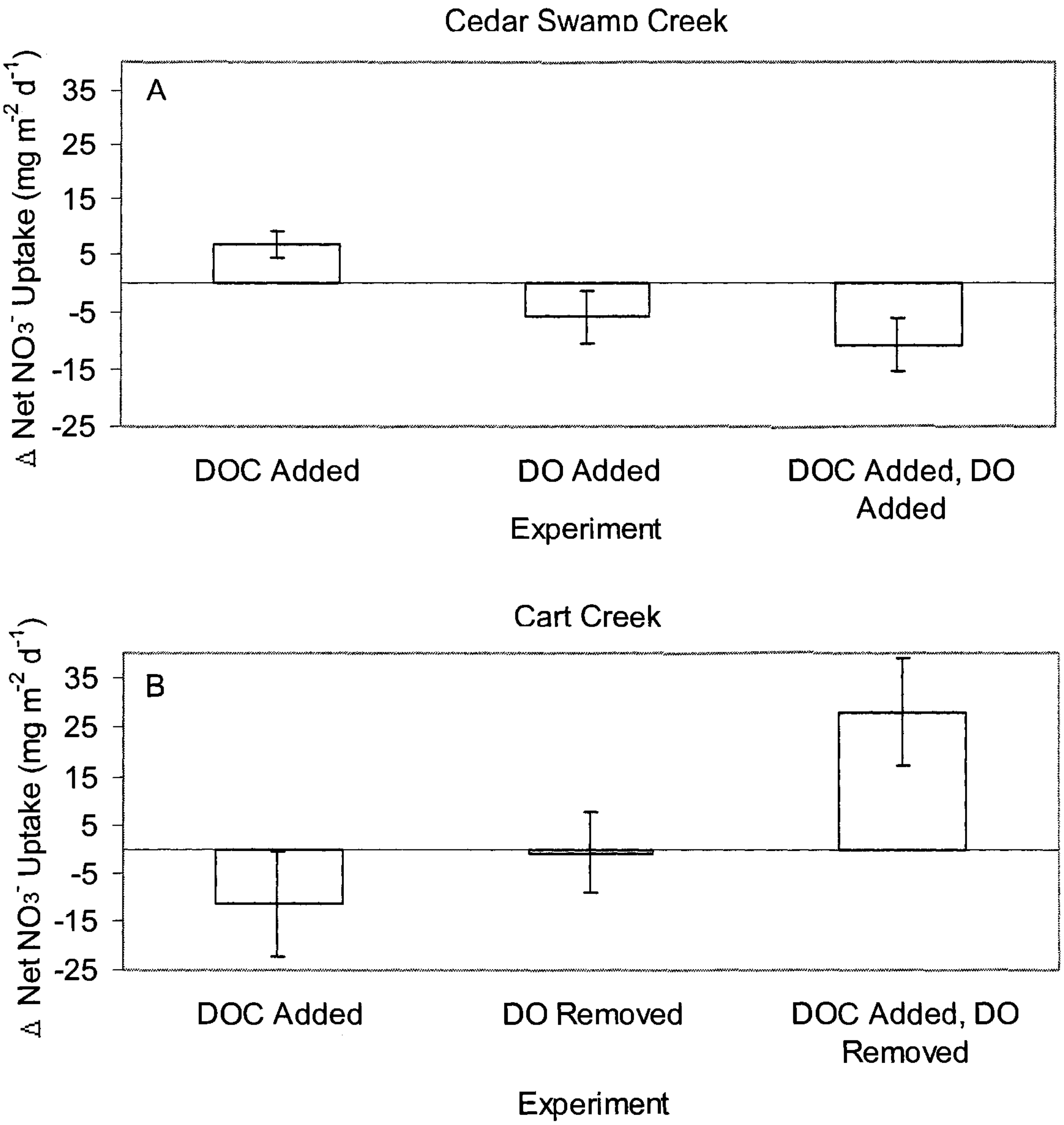


Figure 8: Change in net NO_3^- uptake during manipulations at Cedar Swamp Creek (Figure A) and Cart Creek (Figure B). Positive values reflect net NO_3^- uptake while negative values reflect net nitrate production. Error bars refer to the standard error of the slope in delta nitrate flux through the reach.

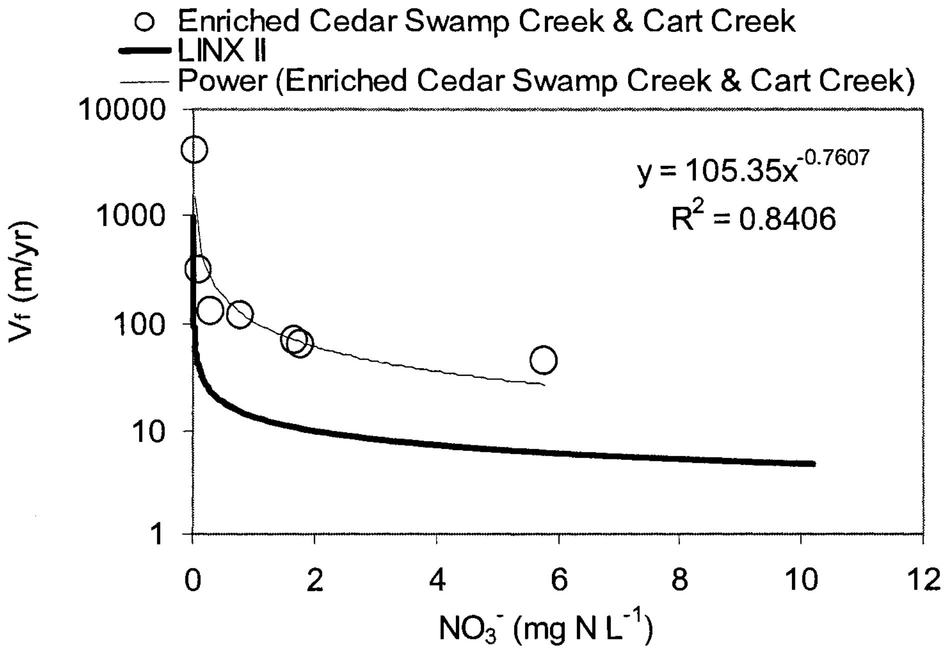


Figure 9: NO_3^- vertical velocity versus NO_3^- concentration determined from $^{15}NO_3^-$ additions by LINX II (Mulholland et al. 2008) and from NO_3^- enrichments to Cedar Swamp Creek and Cart Creek during this study.

APPENDIX

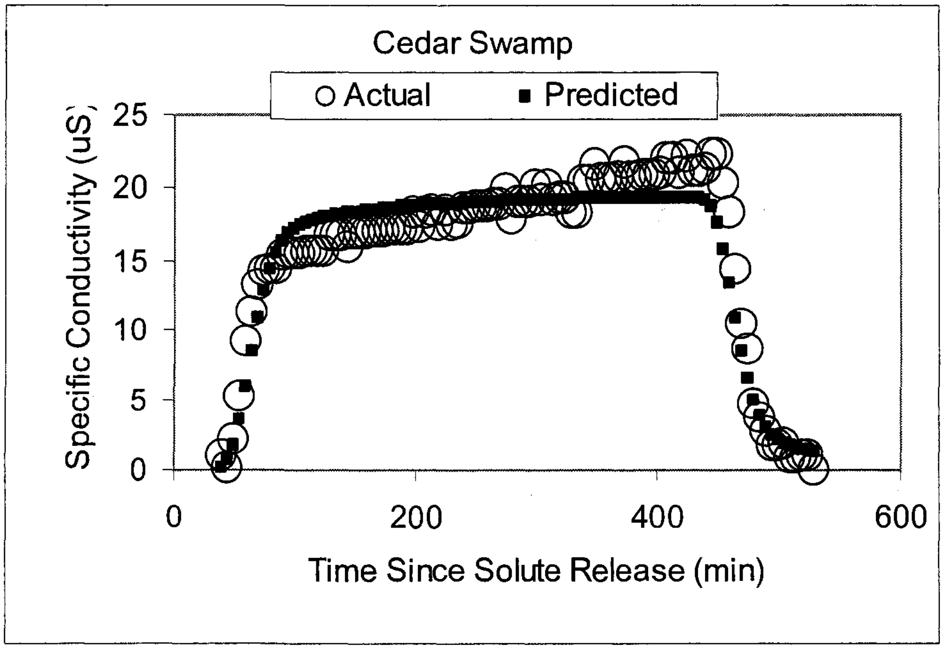


Figure A1: The Fit32 model (Hart et al. 1995) was used to estimate transient storage values in Cedar Swamp and Cart Creek. The modeled data, used to estimate transient storage, matched up well with the actual data. This is a graph of actual versus predicted values of conductivity in Cedar Swamp.

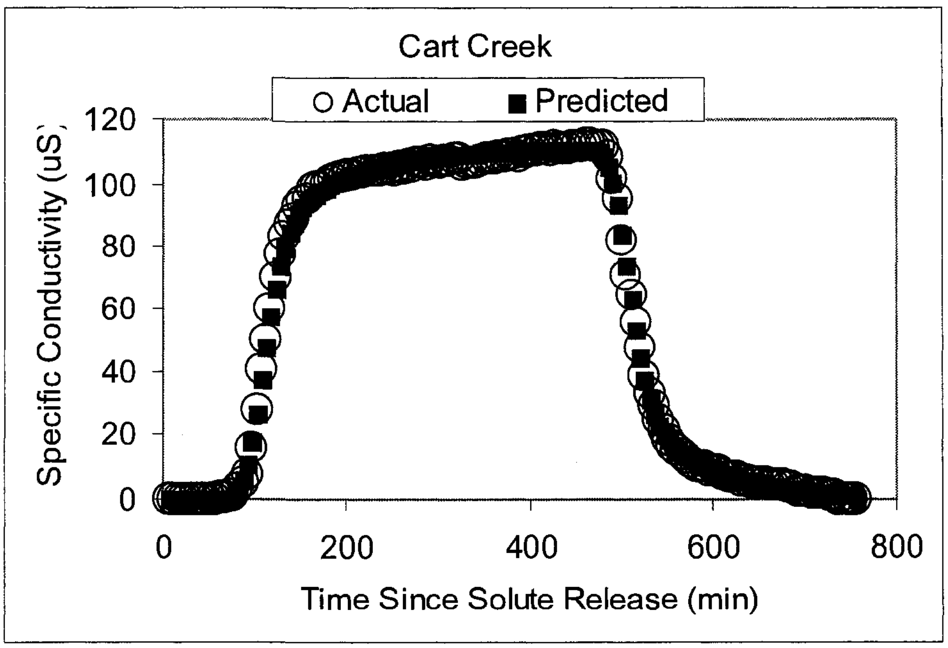


Figure A2: The Fit32 model (Hart et al. 1995) was used to estimate transient storage values in Cedar Swamp and Cart Creek. The modeled data, used to estimate transient storage, matched up well with the actual data. This is a graph of actual versus predicted values of conductivity in Cart Creek.

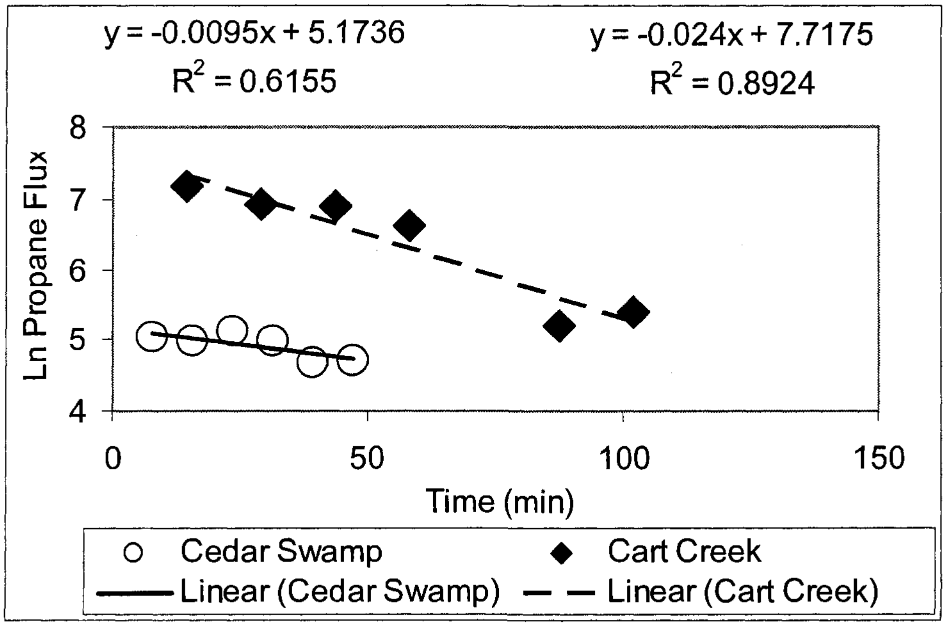


Figure A3: Natural oxygen reaeration rates were estimated using additions of propane. Dilution corrected, Ln transformed propane declined linearly with time at Cedar Swamp ($p=0.065$) and Cart Creek ($p=0.0045$). The rate of propane loss through time was multiplied by 1.39 to simulate natural oxygen reaeration (Rathbun et al. 1978).

Table A1: Distance specific water quality data from the 0.02 mg N L^{-1} NO_3^- enrichment at Cedar Swamp

Cedar Swamp, NO3 Addition 1		
Distance	NO3	Chloride
(m)	(mg L^{-1})	(mg L^{-1})
Ambient		
-5	0.000	43.65
30	0.000	65.71
60	0.000	49.19
90	0.015	47.57
120	0.029	45.94
150	0.041	71.68
180	0.035	
Plateau		
-5	0.000	49.68
30	0.044	66.88
60	0.030	73.96
90	0.018	61.77
120	0.014	64.02
150	0.017	71.29
180	0.024	91.12

Table A2: Distance specific water quality data from the 0.06 mg N L^{-1} NO_3^- enrichment at Cedar Swamp

Cedar Swamp, NO3 Addition 2		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.000	186.80
30	0.000	179.10
60	0.000	184.50
90	0.015	185.10
120	0.021	185.30
150	0.014	185.80
180	0.015	186.80
Plateau		
-5	0.000	175.50
30	0.139	380.20
60	0.089	368.80
90	0.075	363.00
120	0.066	354.10
150	0.059	352.40
180	0.055	344.00

Table A3: Distance specific water quality data from the 0.29 mg N L^{-1} NO_3^- enrichment at Cedar Swamp

Cedar Swamp, NO3 Addition 3		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.000	181.20
30	0.000	179.10
60	0.003	184.50
90	0.000	185.10
120	0.000	185.30
150	0.014	185.80
180	0.015	186.80
Plateau		
-5	0.000	175.50
30	0.437	380.20
60	0.344	368.80
90	0.293	363.00
120	0.279	354.10
150	0.250	352.40
180	0.239	344.00

Table A4: Distance specific water quality data from the 1.74 mg N L^{-1} NO_3^- enrichment at Cedar Swamp

Cedar Swamp, NO3 Addition 4		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.000	186.80
30	0.000	179.10
60	0.003	184.50
90	0.000	185.10
120	0.000	185.30
150	0.014	185.80
180	0.015	186.80
Plateau		
-5	0.000	175.50
30	2.256	380.20
60	1.897	368.80
90	1.873	363.00
120	1.630	354.10
150	1.413	352.40
180	1.515	344.00

Table A5: Distance specific water quality data from the 0.13 mg N L^{-1} NO_3^- enrichment at Cart Creek.

Cart Creek, NO3 Addition 1		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.397	581.0
25	0.615	579.0
50	0.561	577.0
75	0.552	576.0
100	0.660	572.0
150	0.329	573.0
200	0.332	570.0
Plateau		
-5	0.344	591.0
25	0.644	707.0
50	0.530	701.0
75	0.679	700.0
100	0.717	696.0
150	2.877	682.0
200	1.501	670.0

Table A6: Distance specific water quality data from the 0.45 mg N L^{-1} NO_3^- enrichment at Cart Creek.

Cart Creek, NO3 Addition 2		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.340	0.0
25	0.340	577.0
50	0.340	577.0
75	0.340	577.0
100	0.340	577.0
150	0.340	577.0
200	0.340	577.0
Plateau		
-5	0.340	577.0
25	0.912	730.0
50	0.851	723.0
75	0.872	721.0
100	0.851	719.0
150	0.774	706.0
200	0.696	698.0

Table A7: Distance specific water quality data from the 1.24 mg N L^{-1} NO_3^- enrichment at Cart Creek.

Cart Creek, NO3 Addition 3		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.430	0.0
25	0.430	556.0
50	0.430	556.0
75	0.430	556.0
100	0.430	556.0
150	0.430	556.0
200	0.430	556.0
Plateau		
-5	0.427	556.0
25	1.714	728.0
50	1.640	727.0
75	1.852	721.0
100	1.763	718.0
150	1.678	703.0
200	1.438	693.0

Table A8: Distance specific water quality data from the 5.40 mg N L^{-1} NO_3^- enrichment at Cart Creek.

Cart Creek, NO3 Addition 4		
Distance	NO3	Cond
(m)	(mg L^{-1})	(uS cm^{-1})
Ambient		
-5	0.450	541.0
25	0.450	541.0
50	0.450	541.0
75	0.450	541.0
100	0.450	541.0
150	0.450	541.0
200	0.450	541.0
Plateau		
-5	0.448	541.0
25	4.837	751.0
50	6.242	717.0
75	6.105	738.0
100	6.505	732.0
150	5.550	719.0
200	4.976	707.0

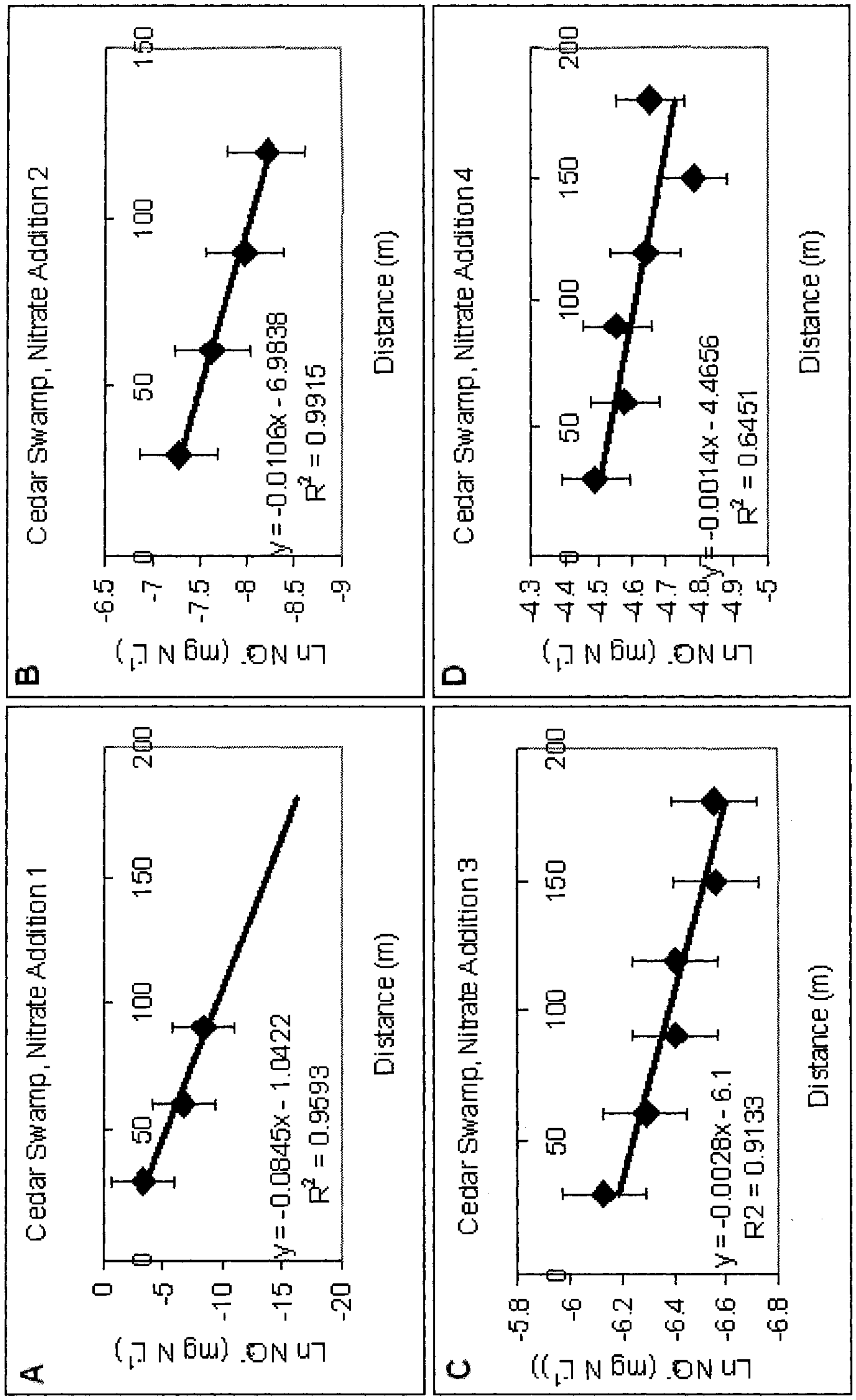


Figure A4: Results from four nitrate additions at Cedar Swamp: (A) 0.02 mg N L^{-1} (p=0.129), (B) 0.06 mg N L^{-1} (0.004), (C) 0.29 mg N L^{-1} (p=0.003), (D) 1.74 mg N L^{-1} (p=0.054)

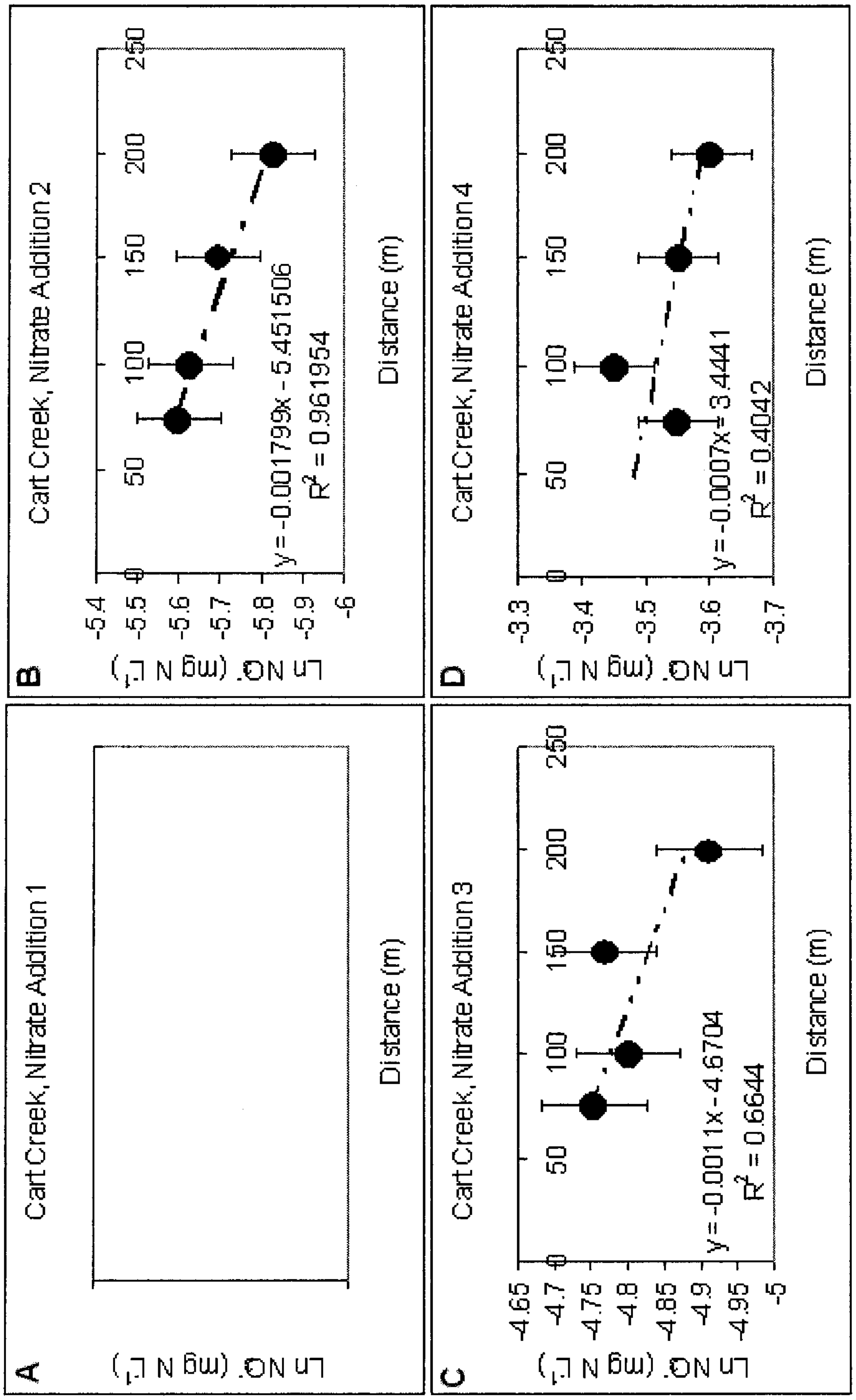


Figure A5: Results from four nitrate additions at Cart Creek: (A) 0.13 mg N L^{-1}, (B) 0.45 mg N L^{-1} (p=0.019), (C) 1.24 mg N L^{-1} (p=0.185), (D) 5.40 mg N L^{-1} (p=0.364). Note, Addition 1 at Cart Creek is not represented because the addition was undetectable.

Table A9: Distance specific water quality data from the DOC addition at Cedar Swamp.

Cedar Swamp, DOC Addition											
Distance (m)	NH4 (mg L^{-1})	DOC (mg L^{-1})	TDN (mg L^{-1})	DON (mg L^{-1})	Cl (mg L^{-1})	NO3 (mg L^{-1})	SO4 (mg L^{-1})	DO (mg L^{-1})	Temp (C)	Cond (uS cm^{-1})	Q (L s^{-1})
Ambient											
0	0.73	39.57	1.79	0.99	37.90	0.08	1.01	3.10	18.30	168.20	2.94
30	0.67	42.57	1.80	0.95	37.48	0.06	0.91	3.35	18.40	166.60	2.94
60	0.67	44.31	1.84	0.94	37.56	0.07	0.82	3.68	18.40	166.70	2.94
75											
90	0.67	45.54	1.87	1.13	37.67	0.07	0.83	3.90	18.40	166.40	2.94
105											
120	0.66	43.57	1.78	1.05	37.71	0.08	0.84	3.92	18.50	167.50	2.94
150	0.66	46.60	1.90	1.17	37.67	0.09	0.83	4.20	18.50	167.70	2.94
180	0.65	44.16	1.83	1.09	37.53	0.09	0.85	3.74	18.40	169.20	2.94
Plateau											
0	0.62	40.32	1.72	1.04	27.50	0.06	0.46		22.20	166.90	2.94
30	0.67	51.33	1.93	1.21	42.69	0.06	0.51	3.91	21.70	183.00	2.94
60	0.66	52.51	1.97	1.24	43.91	0.06	0.52	3.88	21.70	183.50	2.94
75	0.65	52.10	2.01	1.29	43.30	0.06	0.53	3.78	21.70	183.30	2.94
90	0.64	51.69	2.05	1.34	42.69	0.06	0.53	3.67	21.70	183.10	2.94
105	0.64	52.10	2.01	1.30	43.42	0.07	0.55	3.54	21.70	183.95	2.94
120	0.64	52.52	1.97	1.26	44.16	0.07	0.57	3.40	21.70	184.80	2.94
150	0.63	52.03	1.98	1.27	44.84	0.08	0.59	3.12	21.70	184.60	2.94
180	0.63	49.22	1.53	0.83	42.52	0.08	0.58	3.11	21.80	190.00	2.94

Table A10: Distance specific water quality data from the DO addition at Cedar Swamp.

Cedar Swamp, DO Addition											
Distance (m)	NH4 (mg L^{-1})	DOC (mg L^{-1})	TDN (mg L^{-1})	DON (mg L^{-1})	Cl (mg L^{-1})	NO3 (mg L^{-1})	SO4 (mg L^{-1})	DO (mg L^{-1})	Temp (C)	Cond (uS cm^{-1})	Q (L s^{-1})
Ambient											
0	0.69	46.80	2.05	1.27	33.49	0.09	0.52	3.40	18.10	160.50	2.39
30	0.62	48.70	1.89	1.21	34.30	0.07	0.43	3.06	18.00	155.50	2.39
60	0.63	49.81	1.94	1.24	34.47	0.07	0.43	3.50	18.00	154.50	2.39
75	0.64	47.14	2.06	1.22	34.47	0.08	0.44	3.35	18.10	156.10	2.39
90	0.62	49.17	1.91	1.21	34.29	0.08	0.44	3.40	18.00	155.80	2.39
105	0.67	42.32	1.86	1.11	38.65	0.08	0.55	3.62	18.00	156.80	2.39
120	0.62	46.71	1.91	1.20	34.56	0.09	0.44	3.97	18.00	157.20	2.39
150	0.61	43.88	1.90	1.20	34.60	0.09	0.45	4.00	18.00	156.80	2.39
180	0.58	47.87	1.96	1.27	34.78	0.10	0.47	3.35	18.10	158.80	2.39
Plateau											
0	0.69	36.23	1.73	0.93	33.39	0.11	0.57	2.77	19.70	155.70	2.39
30	0.64	37.26	1.63	0.92	43.56	0.07	0.42	5.80	19.50	174.40	2.39
60	0.61	46.43	1.89	1.20	40.34	0.08	0.44	5.65	19.50	174.10	2.39
75	0.61	36.32	1.59	0.90	40.11	0.08	0.45	5.30	19.50	174.30	2.39
90	0.61	36.81	1.58	0.88	40.17	0.09	0.45	5.28	19.50	174.50	2.39
105	0.79	34.96	1.51	0.62	40.88	0.10	0.44	5.60	19.50	173.90	2.39
120	0.60	46.49	1.88	1.18	40.29	0.10	0.44	5.40	19.50	174.10	2.39
150	0.61	40.12	1.72	1.01	40.15	0.10	0.45	5.37	19.60	174.40	2.39
180	0.60	40.14	1.69	0.98	40.08	0.11	0.46	5.25	19.60	174.90	2.39

Table A11: Distance specific water quality data from the concurrent DOC and DO addition at Cedar Swamp.

Cedar Swamp, Concurrent DOC Addition and DO Addition											
Distance	NH4	DOC	TDN	DON	Cl	NO3	SO4	DO	Temp	Cond	Q
(m)	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(C)	(uS cm^{-1})	(L s^{-1})
Ambient											
0	0.69	46.80	2.05	1.27	33.49	0.09	0.52	3.40	18.10	160.50	2.39
30	0.62	48.70	1.89	1.21	34.30	0.07	0.43	3.06	18.00	155.50	2.39
60	0.63	49.81	1.94	1.24	34.47	0.07	0.43	3.50	18.00	154.50	2.39
75	0.61	47.14	1.59	1.22	34.47	0.08	0.44	3.35	18.10	156.10	2.39
90	0.62	49.17	1.91	1.21	34.29	0.08	0.44	3.40	18.00	155.80	2.39
105	0.67	42.32	1.86	1.11	38.65	0.08	0.55	3.62	18.00	156.80	2.39
120	0.62	46.71	1.91	1.20	34.56	0.09	0.44	3.97	18.00	157.20	2.39
150	0.61	43.88	1.90	1.20	34.60	0.09	0.45	4.00	18.00	156.80	2.39
180	0.58	47.87	1.96	1.27	34.78	0.10	0.47	3.35	18.10	158.80	2.39
Plateau											
0	0.79	46.58	1.83	0.98	36.65	0.07	0.39	2.70	20.30	156.00	2.39
30	0.81	31.53	1.33	0.45	46.38	0.07	0.40	5.90	20.70	194.00	2.39
60	0.79	34.03	1.43	0.55	45.79	0.09	0.42	5.56	20.50	190.80	2.39
75	0.78	39.46	1.57	0.70	45.69	0.09	0.42	5.64	20.50	192.90	2.39
90	0.79	42.40	1.62	0.74	45.93	0.09	0.42	5.82	20.60	191.80	2.39
105	0.76	47.44	1.78	0.92	45.63	0.10	0.43	5.75	20.50	193.30	2.39
120	0.80	53.47	1.95	1.05	45.46	0.10	0.43	5.70	20.50	192.70	2.39
150	0.74	51.67	1.93	1.08	47.23	0.11	0.45	5.20	20.50	193.10	2.39
180	0.74	51.92	1.91	1.06	45.64	0.12	0.45	5.20	20.50	192.30	2.39

Table A12: Distance specific water quality data from the DOC addition at Cart Creek.

Cart Creek, DOC Addition											
Distance	NH4	DOC	TDN	DON	Cl	NO3	SO4	DO	Temp	Cond	Q
(m)	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(C)	(uS cm^{-1})	(L s^{-1})
Ambient											
0	13.69	6.64	0.58	0.28	81.97	0.27	1.88	8.10	15.60	370.00	
25	13.20	5.73	0.52	0.21	81.79	0.27	1.89	8.10	15.50	367.50	2.60
50	15.16	6.44	0.55	0.21	84.73	0.27	2.01	8.20	15.60	364.10	2.63
75	12.70	5.79	0.52	0.21	80.37	0.28	1.91	8.30	15.60	365.50	2.67
100	16.42	6.39	0.50	0.19	80.03	0.25	1.93	8.40	15.80	361.30	2.70
150	16.31	5.35	0.41	0.20	59.98	0.25	1.45	8.90	15.60	356.30	2.77
175	13.46	4.82	0.44	0.22	63.55	0.24	1.50	8.40	15.50	359.00	2.81
Plateau											
0	11.86	4.46	0.35	0.19	48.13	0.15	0.96	7.73	17.20	390.10	
25	15.49	11.90	0.56	0.25	114.34	0.30	1.79	7.91	17.40	510.00	2.60
50	14.58	12.01	0.58	0.28	113.85	0.28	1.80	8.05	17.40	509.00	2.63
75	16.21	11.02	0.42	0.12	112.77	0.29	1.83	7.93	17.40	504.00	2.67
100	19.34	10.02	0.53	0.23	111.88	0.28	1.84	7.76	17.30	454.50	2.70
150	17.00	9.96	0.48	0.19	110.58	0.27	2.34	7.81	17.40	485.10	2.77
175	14.50	6.74	0.38	0.10	109.29	0.26	1.83	7.75	17.50	489.00	2.81

Table A13: Distance specific water quality data from the DO removal at Cart Creek.

Cart Creek, DO Removal											
Distance (m)	NH4 (mg L^{-1})	DOC (mg L^{-1})	TDN (mg L^{-1})	DON (mg L^{-1})	Cl (mg L^{-1})	NO3 (mg L^{-1})	SO4 (mg L^{-1})	DO (mg L^{-1})	Temp (C)	Cond (uS cm^{-1})	Q (L s^{-1})
Ambient											
0	14.19	6.22	0.51	0.23	83.23	0.27	1.69	8.10	14.00	360.20	
25	13.13	5.90	0.56	0.25	84.00	0.27	1.70	8.10	14.00	360.10	1.62
50	14.76	5.80	0.55	0.25	84.98	0.27	1.71	8.20	14.00	375.10	1.65
75	15.78	6.21	0.52	0.22	85.12	0.28	1.74	8.30	13.90	377.20	1.69
100	19.17	6.14	0.50	0.23	84.74	0.25	1.72	8.40	14.40	375.20	1.72
150	19.62	6.14	0.54	0.27	85.31	0.25	1.69	8.90	13.90	380.20	1.79
175	24.60	6.13	0.50	0.23	85.43	0.24	1.68	8.40	13.90	385.60	1.83
Plateau											
0	12.44	5.98	0.51	0.22	76.11	0.28	1.73	7.70	15.90	349.50	
25	22.29	4.82	0.42	0.13	106.88	0.26	25.91	0.99	16.40	620.00	1.62
50	22.69	3.98	0.38	0.10	107.07	0.25	25.58	1.89	16.50	640.00	1.65
75	22.35	5.43	0.47	0.21	106.54	0.24	25.46	2.12	16.60	633.00	1.69
100	18.72	4.57	0.39	0.14	106.14	0.24	25.15	2.24	16.60	625.00	1.72
150	23.25	5.17	0.50	0.25	104.90	0.23	24.60	4.20	17.10	620.00	1.79
175	23.70	2.49	0.29	0.04	104.44	0.23	23.95	4.65	17.20	609.00	1.83

Table A14: Distance specific water quality data from the concurrent DOC addition and DO removal at Cart Creek.

Cart Creek, Concurrent DOC Addition and DO Removal											
Distance (m)	NH4 (mg L^{-1})	DOC (mg L^{-1})	TDN (mg L^{-1})	DON (mg L^{-1})	Cl (mg L^{-1})	NO3 (mg L^{-1})	SO4 (mg L^{-1})	DO (mg L^{-1})	Temp (C)	Cond (uS cm^{-1})	Q (L s^{-1})
Ambient											
0	17.17	4.53	0.42	0.14	71.29	0.26	1.84	6.78	13.10	252.30	
25	10.02	4.81	0.46	0.20	69.97	0.25	1.86	7.94	12.70	248.70	1.71
50	10.97	4.97	0.43	0.17	69.85	0.25	1.82	7.78	12.90	249.30	1.75
75	19.32	4.98	0.44	0.18	69.28	0.24	1.86	7.22	12.90	246.80	1.80
100	24.80	4.96	0.43	0.17	69.02	0.23	1.84	7.68	13.10	250.00	1.84
150	20.98	5.04	0.43	0.19	69.26	0.22	1.83	7.51	13.20	249.30	1.93
175	22.89	5.11	0.44	0.21	68.99	0.21	1.83	7.41	13.10	235.50	1.98
Plateau											
0	9.78	5.08	0.45	0.19	70.76	0.25	1.84	5.90	14.00	258.50	
25	17.17	11.81	0.49	0.24	113.09	0.22	31.10	1.08	14.10	555.00	1.71
50	21.46	11.50	0.47	0.25	112.75	0.20	30.83	1.81	14.00	542.00	1.75
75	25.75	11.29	0.50	0.29	111.39	0.19	30.05	1.62	14.10	551.00	1.80
100	17.17	11.21	0.46	0.25	110.49	0.20	30.03	1.55	14.30	551.00	1.84
150	22.65	10.46	0.46	0.29	107.08	0.14	28.96	2.98	14.70	531.00	1.93
175	24.32	9.87	0.44	0.27	103.84	0.15	27.78	3.97	14.60	516.00	1.98