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The biogeochemical influences of NO_3^- , dissolved O_2 , and dissolved organic C on stream NO_3^- uptake

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Abstract. Streams are potential hotspots for retention and removal of NO_3^- , and understanding the mechanisms that enhance NO_3^- reactivity in stream systems is critical for predicting and preventing eutrophication. Both dissolved organic C (DOC) and dissolved O_2 (DO) influence NO_3^- removal processes. Assessing the individual impacts of NO_3^- , DO, and DOC concentrations on stream NO_3^- removal is difficult because these factors covary and are coupled through the C and N cycles. We used an experimental approach to quantify the influences of NO_3^- , DOC, and DO on NO_3^- transport in headwater streams of the Ipswich and Parker River watersheds (Massachusetts, USA) with contrasting levels of DOC and DO. In a 1st set of experiments, we added NO_3^- to address how uptake kinetics differed between a low-DO/high-DOC stream (Cedar Swamp Creek) and a high-DO/low-DOC stream (Cart Creek). In a 2nd 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 O_2 and was removed from the high-DO stream by adding sodium sulfite. DOC was added both alone and in combination with the DO manipulations. NO_3^- concentration was an important control of NO_3^- uptake velocity in our study streams, consistent with previous findings. The results of the DOC and DO manipulations suggested that DO determines whether a stream has net NO_3^- uptake or production and that the presence of DOC magnifies the DO response processes. Addition of DOC by itself did not lead to increased NO_3^- uptake. In addition, we observed organic matter priming effects, wherein the addition of labile organic matter resulted in accelerated metabolism of naturally occurring DOC in the water column. Priming effects have not been reported previously in stream systems. Results from our experiments suggest that NO_3^- uptake in streams might arise from complex interactions among DOC, DO, and NO_3^- , and ultimately, from the influence of DO on dominant stream processes.

Key words: nitrate, nitrate uptake, dissolved oxygen, dissolved organic carbon, net nutrient uptake, solute addition, priming effect.

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N is a naturally occurring element that is essential to life on Earth and often controls productivity in terrestrial, freshwater, and marine ecosystems (Grimm and Fisher 1986, Vitousek and Howarth 1991). Excessive anthropogenic N inputs from sources, such as atmospheric deposition, fertilizer use, and septic systems, are exceeding terrestrial demand in many parts of the world and are causing N concentrations to increase in river systems (Aber et al. 1989, Boyer et al. 2002, Driscoll et al. 2003). Once in river systems, inland N pollution has the potential to

be translocated to coastal zones with deleterious effects (Howarth et al. 2002, Rabalais 2002). NO_3^- is the predominant form of dissolved inorganic N that reaches the coastal zone (Howarth et al. 1996), and thus, plays a significant role in coastal eutrophication. To mitigate the negative effects of N entering the coastal zone, we must first understand how NO_3^- is loaded into and then processed and transported within river systems.

Rivers are an important transport route for nutrients originating in terrestrial ecosystems, but they are not passive conduits (Alexander et al. 2000, Cole et al. 2007). Streams and rivers can retain or remove anthropogenic N inputs through abiotic and biotic instream 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 respiration by bacteria, i.e., denitrification (Bernot and Dodds 2005, Seitzinger et al. 2006). Peterson et al. (2001) found that N uptake in headwater streams can at times reduce up to $\frac{1}{2}$ of the N that is introduced from the adjoining terrestrial ecosystem. Total river length in most watersheds is dominated by small streams (Leopold and Maddock 1953), so headwater systems have the potential to play an integral role in buffering N exports to coastal waters.

The effects of variable biotic and abiotic conditions on stream N uptake have been quantified via standard solute-addition methods (Stream Solute Workshop 1990). Stream spiraling techniques have been used to determine N spiraling metrics, such as areal uptake (mass removal of a nutrient per unit area of the streambed per time) and uptake velocity (V_f ; the speed at which a nutrient is removed from the water column) (Stream Solute Workshop 1990) under N-enriched conditions (with solute additions; Dodds et al. 2002, Payn et al. 2005) and under ambient conditions (with isotopic tracer techniques; Webster et al. 2003, Mulholland et al. 2004, 2008). These methods have been used to compare N retention and removal across sites (Wollheim et al. 2001, Mulholland et al. 2002, 2008, Webster et al. 2003). Fewer studies have determined the influence of hydrologic and biogeochemical factors on N uptake by manipulating physical and chemical conditions in individual stream systems (Dodds et al. 2002, Ensign and Doyle 2005).

Intersite comparisons enable formulation of general relationships linking watershed characteristics and stream biogeochemistry, but short-term stream-reach manipulations offer the opportunity to gain better insight into the causal mechanisms responsible for observed variability. This opportunity is important

because streams are prone to variable conditions over both spatial and temporal domains that, together, significantly influence N retention and removal (Simon et al. 2005). NO_3^- concentration (Dodds et al. 2002), dissolved O_2 (DO) concentration (Kemp and Dodds 2001), and dissolved organic C (DOC) concentration (Webster et al. 2000) are among the spatially and temporally heterogeneous biogeochemical controls that can significantly alter demand for NO_3^- .

NO_3^- concentrations are a primary influence on NO_3^- uptake rates. Dodds et al. (2002) suggested that biotic uptake is directly related to NO_3^- concentration, and as such, NO_3^- uptake will increase with increasing NO_3^- concentration. However, recent findings indicate that NO_3^- removal rates do not increase linearly with increasing concentrations across sites (O'Brien et al. 2007, 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 are partly determined by biotic processes, such as nitrification and denitrification, that are dependent on DO. DO is positively correlated with nitrification (Kemp and Dodds 2001), and high DO can lead to increased NO_3^- in the water column. DO also provides an electron acceptor for C respiration, which can lead to remineralization of organic N as NH_4^+ via ammonification (Scott and Binkley 1997). Increased NH_4^+ can elevate rates of nitrification (Ollinger et al. 2002) and produce higher levels of NO_3^- . Low DO concentrations tend to decrease NO_3^- concentrations by inhibiting nitrification and by providing conditions favorable for denitrification (Seitzinger et al. 2006), which removes NO_3^- from streams.

In a recent review article, focused on data from streams of the northeastern US, Goodale et al. (2005) showed that water-column DOC levels are inversely related to NO_3^- concentrations and suggested that high DOC might 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 N cycle through its use by heterotrophic bacteria (Meyer et al. 1988). Strong coupling of C and N has been demonstrated in empirical studies of soils (Swerts et al. 1996, Ollinger et al. 2002) and streams (Bernhardt and Likens 2002, Starry and Valett 2005). DOC in streams might augment NO_3^- uptake (and hence, loss from the water column) by increasing heterotrophic immobilization (Bernhardt and Likens 2002) and denitrification (Inwood et al. 2005). Heterotrophs can out-compete

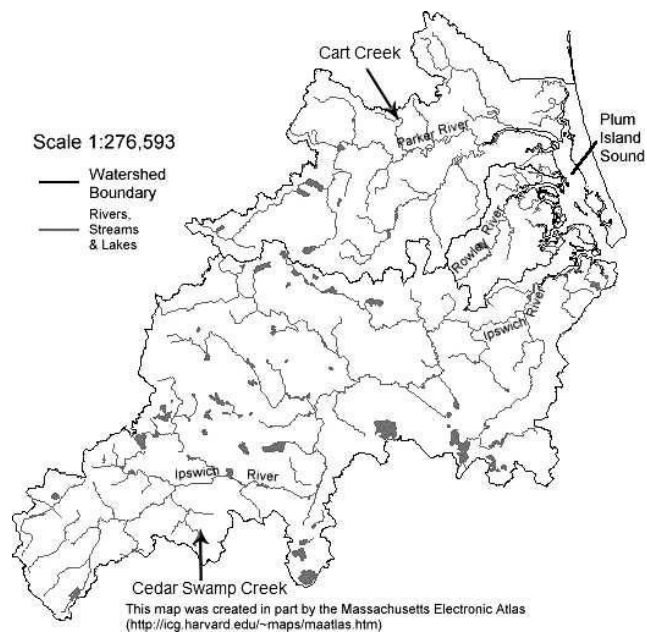


FIG. 1. Stream study sites Cedar Swamp Creek and Cart Creek within the Ipswich and Parker River watersheds (Massachusetts, USA).

nitrifiers for NH_4^+ . Thus, DOC inhibits nitrification (Strauss and Lamberti 2000), which would have the net effect of reducing NO_3^- in the water column. The biological O_2 demand associated with aerobic DOC metabolism also can affect DO levels (Sand-Jensen and Pedersen 2005), and thus, indirectly influence nitrification and denitrification.

The overall goal of our study was to better understand how NO_3^- dynamics in headwater streams of the Ipswich and Parker River watersheds in Massachusetts (USA; Fig. 1) are controlled by concentrations of NO_3^- , DO, and DOC in the water column. These watersheds drain to the Plum Island Sound ecosystem in northeastern Massachusetts. They are urbanizing rapidly and have elevated N 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) that lead to relatively low DO in many reaches.

We used a multifactorial, whole-reach experimental approach to help us better understand the complex biogeochemical relationships in the streams of the Ipswich and Parker River watersheds. We used short-term manipulations to determine the effects of NO_3^- , DO, and DOC on stream NO_3^- dynamics. We used 2 types of experiments: 1) NO_3^- additions in low NO_3^- streams of contrasting DO and DOC and 2) manipulations

TABLE 1. Landuse data (from MassGIS; <http://www.mass.gov/mgis/>) for Cedar Swamp Creek and Cart Creek, Massachusetts.

| Variable | Cedar Swamp Creek | Cart Creek |
|------------------------|-------------------|------------|
| Area (km^2) | 1.4 | 3.96 |
| Agriculture (%) | 6 | 8 |
| Forest (%) | 36 | 57 |
| Wetland (%) | 49 | 19 |
| Industrial (%) | 0 | 5 |
| Residential (%) | 9 | 11 |

ulations of DO and DOC under ambient NO_3^- in these same streams. We used the traditional method of NO_3^- addition to estimate gross NO_3^- uptake, and we investigated the effects of DO and DOC concentrations on net NO_3^- uptake, a metric for identifying dominant controls of nutrient export (Roberts and Mulholland 2007). Simultaneous manipulation of DOC and DO is a novel experimental approach to investigation of stream-reach NO_3^- .

Methods

Site description

We selected two 1st-order streams, Cedar Swamp Creek and Cart Creek, as study sites. These headwater streams are in the Ipswich and Parker River watersheds, which drain to Plum Island estuary (PIE) in northeastern Massachusetts (Fig. 1). The Ipswich and Parker watersheds are typical of the low gradient, poorly drained, coastal landscapes in New England (Baker et al. 1964). Shallow soils overlie the sand, gravel, and till of the local surficial geology and the igneous and sedimentary Paleozoic and Precambrian formations of the bedrock geology (Baker et al. 1964). Average annual precipitation in the region is 115 cm (Wollheim et al. 2005). Because of shallow slopes, wetlands are abundant throughout the PIE watersheds. Watersheds draining wetland areas have elevated DOC, low DO, and low NO_3^- concentrations (Raymond and Hopkinson 2003, PIE Long-Term Ecological Research [LTER] site, unpublished data).

We worked in Cedar Swamp Creek and Cart Creek because they are in watersheds with relatively pristine land use (Table 1). The watershed draining to Cedar Swamp Creek has significantly more wetlands (49% of the watershed) than does the watershed draining to Cart Creek (19%), and this difference provided a natural contrast in biogeochemical characteristics. We conducted experiments at these 2 sites in late summer 2005 and 2006 during low, channelized stream flow and under full, decid-

uous canopy. The study reaches were 180 m and 175 m in Cedar Swamp Creek and Cart Creek, respectively. We established 6 to 8 sample stations distributed along the reach and 1 upstream of the addition site in each reach.

Nutrient additions and manipulations

We followed standard solute-addition procedures (summarized by Webster and Ehrman 1996) for all additions 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 1995). We delivered all solutes with a peristaltic pump, which was monitored to ensure a constant delivery rate. We used stationary YSI sondes-6920 and handheld YSI-85 meters (Yellow Springs Instruments, Yellow Springs, Ohio) to track conservative tracer movement and to determine the time of hydrologic equilibrium for each addition. We quantified discharge from in situ depth measurements with HOBO-U20 water-level loggers (Onset Computer Corporation, Bourne, Massachusetts) in coordination with site-specific rating curves. We computed stream width from measurements taken along the reaches at 10-m intervals.

We filtered all water samples in the field through precombusted, 2.5-cm GF/F filters (0.7 μm ; Whatman Inc., Piscataway, New Jersey). We stored samples in acid-washed high-density polyethylene bottles, and kept them on ice in the field. We stored samples frozen until they could be analyzed. All chemical analyses were done by the Water Quality Analysis Laboratory in the New Hampshire Water Resources Research Center at the University of New Hampshire. DOC (detection limit [DL] = 0.05 mg C/L) and total dissolved N (TDN; DL = 0.09 mg N/L) were measured with a Shimadzu TOC-5000 (Shimadzu Scientific Instruments, Columbia, Maryland) with chemiluminescent detector for TDN (Antek Instruments Inc., Houston, Texas). PO_4^{3-} (DL = 0.005 mg P/L) and NH_4^+ (DL = 0.005 mg N/L) were measured with a Westco Smartchem Robotic Analyzer (Westco Scientific Instruments, Inc., Brookfield, Connecticut). Anions (Cl^- : DL = 0.02 mg Cl/L, NO_3^- : DL = 0.002 mg N/L, and SO_4^{2-} : DL = 0.04 mg S/L) were measured with an ion chromatograph/high performance liquid chromatography system (Dionex Corporation, Sunnyvale, California). We derived dissolved organic N (DON) as the difference between TDN and the sum of NH_4^+ and NO_3^- .

NO_3^- additions

In summer 2005, we conducted multiple solute additions (NaNO_3) at Cedar Swamp Creek and Cart Creek to determine the influence of NO_3^- concentration on $\text{NO}_3^- V_f$. Both sites received 4 additions of NaNO_3 , and each was successively greater in magnitude. Cedar Swamp Creek received additions of 0.02 (2 \times), 0.06 (5 \times), 0.3 (20 \times), and 1.7 (111 \times) mg N/L. Cart Creek received additions of 0.13 (1.3 \times), 0.45 (2 \times), 1.2 (4 \times), and 5.4 (13 \times) mg N/L. For each addition, we plotted log-normal NO_3^- concentrations (mg N/L) corrected for background concentration and dilution against distance downstream of the point of addition (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). V_f (m/s) of NO_3^- was calculated for each addition as:

$$V_f = \frac{Q}{wS_W} \quad [1]$$

where Q is discharge at the time of the addition (m^3/s), w is average stream width (m), and S_W is uptake length (m). Ambient S_W and V_f also were quantified with the method of Payn et al. (2005). This method requires a linear relationship between added N concentration and S_W . To meet this assumption of linearity, we excluded the 4th addition at Cedar Swamp Creek (1.7 mg N/L) from the data used to quantify ambient S_W and V_f for this site.

DO and DOC manipulations

In 2006, we conducted experimental manipulations of DOC and DO at Cedar Swamp Creek and Cart Creek. At Cedar Swamp Creek, we did 3 experimental additions on 2 consecutive days: 1) labile DOC (glucose) addition (16 August 2006), 2) DO addition (23 August 2006), and 3) a simultaneous addition of DO and DOC (23 August 2006). At Cart Creek, we did 3 experimental additions on 3 days: 1) labile DOC (glucose) addition (30 August 2006), 2) sodium sulfite addition to remove DO (1 September 2006) (Gameson et al. 1955), and 3) concurrent sodium sulfite and glucose additions to simultaneously remove DO and add DOC (11 September 2006). We targeted the concentrated glucose solutions added to Cedar Swamp Creek and Cart Creek to 7 to 10 mg C/L in each stream, representing C increases of 15 to 22% and 125 to 178% in Cedar Swamp Creek and Cart Creek, respectively. We began additions in the morning (0900–1000 h), and plateaus generally were reached within 4 h. We began the simultaneous DO

and DOC experiment in Cedar Swamp Creek in the early afternoon. Observed diurnal DO concentrations at these sites showed DO peaks between 0900 and 1000 h and varied with temperature, a pattern suggesting that gross primary production was not large in these systems.

Our goal for the DO additions at Cedar Swamp Creek was to raise the DO concentration to the greatest extent possible using pressurized O₂ that was fed continuously to the stream through a diffusion stone placed on the stream bed. Attaining elevated DO concentrations required that we construct a weir to channel the water directly over the diffusion stone. To enhance dissolution of DO into the water, we placed a trolling motor (Minn Kota Endura; Johnson Outdoors Inc., Racine, Wisconsin) upstream of the diffusion stone to aid channel mixing and to inhibit the amended O₂ bubbles from quickly coalescing, rising, and degassing as they left the diffusion stone. We used a tarp to cover the stream bottom directly beneath and adjacent to the trolling motor to prevent resuspension of sediments.

We purged O₂ from Cart Creek with a concentrated solution of sodium sulfite and targeted a DO concentration in channel flow of 1 to 2 mg/L. Sodium sulfite has been used to reduce stream O₂ for reaeration studies (Gameson et al. 1955). The reaction requires sodium sulfite concentrations that are ~8× greater than DO by mass. Because of the oxidizing capacity of this solution and its reactivity with atmospheric O₂, we held the solution of sodium sulfite on the stream bank in an airtight polyurethane container 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. We constructed a weir at the point of solute release to aid mixing of the solute in the water column. We also installed several baffles and an additional weir within the first 20 m of the addition point to increase sodium sulfite residence time and the dispersion necessary for the sulfite to react sufficiently with DO to achieve our target reduction before the water entered the study reach.

Nutrient uptake

Analysis of the DOC and DO manipulations focused on the change in net NO₃⁻ uptake rate (mg N m⁻² d⁻¹) during plateau of each experiment compared to net NO₃⁻ uptake rate occurring under ambient conditions just before the experimental manipulation. We refer to the observed change between plateau and ambient conditions as Δ net NO₃⁻ uptake. We quantified Δ net NO₃⁻ uptake rate

per unit area (Δ*U*; mg N m⁻² d⁻¹) with the equation:

$$\Delta U = \frac{-\Delta F_S}{w} \quad [2]$$

where Δ*F*_{*S*} is the slope of the difference between experimental and ambient flux vs distance (mg m⁻¹ d⁻¹), and *w* is average stream width (m). Positive Δ*U* represents an increase in net nutrient uptake caused by the experimental manipulation, whereas negative Δ*U* represents an increase in net nutrient production. We used regression analysis to evaluate if Δ*F*_{*S*} was different from 0 to help determine if the experiments significantly altered NO₃⁻ fluxes through the reach. Two-tailed paired *t*-tests also were done with NO₃⁻ concentration from each site to identify whether the experiments had a significant effect on NO₃⁻ chemistry (*p* < 0.05). DOC and DO uptake rates and decay rates per unit distance, *k* (1/m), during the manipulations were calculated from the slope of background-corrected, log-normal nutrient flux plotted against distance (Webster and Ehrman 1996). Positive *k* values for the O₂ removal experiments represent the decay of the O₂ deficit (i.e., reoxygenation).

Results

Study-reach biogeochemical trends

Q was similar for Cedar Swamp Creek and Cart Creek, but the streams had drastically different background chemistry (Table 2). High DOC is common during summer baseflow periods in the PIE watersheds. DOC levels in Cart Creek were relatively high, but concentrations in Cedar Swamp were 10× higher. NH₄⁺ and PO₄³⁻ concentrations at Cedar Swamp Creek were significantly greater than those found at Cart Creek and all other known stream baseflow concentrations from within the Ipswich and Parker River watersheds. Concentrations of DO and NO₃⁻ at Cart Creek were >2× those recorded at Cedar Swamp Creek.

NO₃⁻ additions and *V_f*

NO₃⁻ *S_W* increased and *V_f* decreased with increasing NO₃⁻ concentrations at both Cedar Swamp Creek and Cart Creek (Table 3). Ambient estimates based on the Payn et al. (2005) method resulted in *S_W* and *V_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 *V_f* than Cart Creek, a result corresponding with lower NO₃⁻ concentrations. Combining the data from the 2 sites,

TABLE 2. Mean (± 1 SD; $n = 3$) values for physicochemical and hydrological variables in Cedar Swamp Creek and Cart Creek measured at the monitoring stations of the study reaches before all manipulations in summer 2006. PO_4^{3-} was measured in summer 2005. DOC = dissolved organic C, DON = dissolved organic N, DO = dissolved O_2 , Q = discharge, A_s/A = ratio of storage zone to water column.

| Variable | Cedar Swamp Creek | Cart Creek |
|---|-----------------------|-----------------------|
| Physicochemical | | |
| NO_3^- (mg N/L) | 0.08 ± 0.01 | 0.25 ± 0.03 |
| DOC (mg C/L) | 45.29 ± 3.83 | 5.60 ± 0.58 |
| DO (mg O_2 /L) | 3.57 ± 0.16 | 8.46 ± 0.20 |
| DON (mg N/L) | 0.64 ± 0.059 | 0.21 ± 0.03 |
| NH_4^+ (mg N/L) | 1.61 ± 0.05 | 0.019 ± 0.007 |
| PO_4^{3-} (mg P/L) | 1.01 ± 0.095 | 0.004 ± 0.004 |
| Temperature ($^\circ\text{C}$) | 18.33 ± 0.17 | 14.2 ± 1.32 |
| Hydrological | | |
| Q (L/s) | 2.57 ± 0.04 | 2.08 ± 0.54 |
| Study reach length (m) | 180 | 175 |
| Width (m) | 1.81 | 1.70 |
| A_s/A | 0.18 | 0.17 |
| Water exchange rate coefficient (1/min) from flowing water column to the storage zone | 2.03×10^{-3} | 2.44×10^{-3} |
| Lateral inputs (%) | 4.5 | 16.8 |
| O_2 exchange rate coefficient (1/min) | 0.013 | 0.035 |

V_f declined as a power function of NO_3^- concentration (mg/L) ($105.35x^{-0.7607}$, $p = 0.004$, $R^2 = 0.8406$). The relationship appears to apply across the 2 sites, despite their different characteristics (Fig. 2).

TABLE 3. Uptake length (S_w) and uptake velocity (V_f) from NO_3^- additions at Cedar Swamp Creek and Cart Creek. NO_3^- values are the effective concentration observed at the 1st monitoring station downstream of the addition point in each stream reach (30 m and 25 m in Cedar Swamp Creek and Cart Creek, respectively). N_{AMB} = ambient N concentration, N/A = too dilute to detect. * indicates regression used to calculate S_w and V_f was statistically significant ($p < 0.05$).

| Site | Addition | Added NO_3^- (mg N/L) | NO_3^- (mg N/L) | S_w (m) | V_f (m/y) |
|-------------------|----------------------|--|--------------------------|-----------|-------------|
| Cedar Swamp Creek | ^a Ambient | 0 | 0.00 | 15 | 3202 |
| | NO_3^- | 0.02 ($2.1 \times N_{\text{AMB}}$) | 0.04 | 12 | 3981 |
| | NO_3^- | 0.06 ($5.0 \times N_{\text{AMB}}$) | 0.14 | 94* | 311* |
| | NO_3^- | 0.29 ($19.6 \times N_{\text{AMB}}$) | 0.44 | 357* | 132* |
| | NO_3^- | 1.74 ($110.6 \times N_{\text{AMB}}$) | 2.26 | 714 | 66 |
| Cart Creek | Ambient | 0 | 0.46 | 517 | 126 |
| | NO_3^- | 0.13 ($1.3 \times N_{\text{AMB}}$) | 0.64 | N/A | N/A |
| | NO_3^- | 0.45 ($2.0 \times N_{\text{AMB}}$) | 0.91 | 556* | 117* |
| | NO_3^- | 1.24 ($3.8 \times N_{\text{AMB}}$) | 1.71 | 909 | 72 |
| | NO_3^- | 5.40 ($13.2 \times N_{\text{AMB}}$) | 4.84 | 1429 | 46 |

^a Ambient calculated with Payn et al. (2005) method

DOC and DO conditions during C and O_2 manipulations

Fluxes of DOC and DO during experimental plateau compared with ambient fluxes demonstrate that the methods used to manipulate DOC and DO concentrations at Cedar Swamp Creek and Cart Creek were successful (Table 4). We observed clear plateaus of DO during the DO addition in Cedar Swamp and the DO removal in Cart Creek (Fig. 3A, B). Furthermore, all O_2 manipulations at Cedar Swamp and Cart Creek created O_2 concentrations and transects that were significantly different ($p < 0.05$) from those in experiments that did not involve O_2 manipulation (Fig. 4A, B). The sodium sulfite method successfully removed most of the DO at Cart Creek before the 1st sampling station at 25 m. DO fluxes increased slowly through the reach as reaeration occurred. We also observed lower SO_4^{2-} and NO_3^- flux entering the stream reach. Similar to DO, an increase in SO_4^{2-} flux between 25 m and 50 m attests to the fact that full reactivity of the sodium sulfite was realized before the start of the study reach.

DOC additions successfully increased DOC flux during DOC additions, except during the concurrent DO and DOC addition at Cedar Swamp Creek, when DOC was below ambient values. The focus of our experiments was to understand the influence of DOC and DO concentrations on net NO_3^- dynamics, but our data showed a surprising increase in the apparent metabolism of organic matter. During the combined DOC and DO addition at Cedar Swamp Creek, the plateau concentration of DOC at the 1st sampling station was 17.17 mg C/L lower than ambient levels before any DOC addition (Table 4). Downstream of the 1st sampling station, DOC concentrations gradually returned to ambient levels with distance along the transect (Fig. 5A). The immediate removal of the

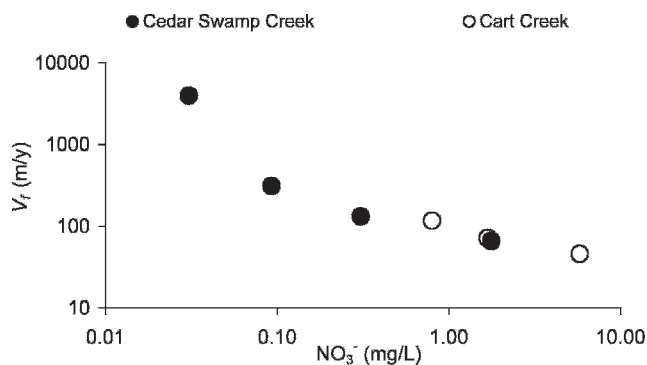


FIG. 2. Whole-reach NO_3^- uptake velocity (V_f) vs NO_3^- concentration during solute additions at Cedar Swamp Creek and Cart Creek in 2005.

ambient and labile DOC between the point of addition and the 1st sampling station represents a DOC V_f equivalent to 1074 m/y. Concentrations of DON along the experimental transect showed a similar pattern to DOC (Fig. 5B). The concentration of DON removed from the water column corresponds to a V_f of 1809 m/y. Furthermore, decreasing levels of DON in the water column corresponded with elevated levels of NH_4^+ (Fig. 5C). NH_4^+ concentrations at the 1st sampling station accounted for ~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. A net NO_3^- increase of 0.047 mg N/L was observed over this transect (Fig. 5D). 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 decreased 0.013 mg N/L, and concentrations of NH_4^+ and NO_3^- increased 0.002 and 0.019 mg N/L respectively. However, these trends were far less obvious than those observed at Cedar Swamp.

NO_3^- response to DOC and DO manipulations

Transects of NO_3^- concentration during experimental plateau were significantly different than their ambient counterparts for all DOC and DO manipulations (paired *t*-test, $p < 0.05$).

Addition of DOC had different effects on NO_3^- dynamics at Cedar Swamp Creek and Cart Creek. Under ambient conditions at Cedar Swamp Creek, NO_3^- flux increased through the study reach. Addition of DOC alone to Cedar Swamp Creek (low DO stream) resulted in slower flux increases through the study reach ($p = 0.0508$; Table 5), a result indicating that the addition caused a net increase in NO_3^- uptake (positive ΔU ; Fig. 6A). At Cart Creek (high DO stream), ambient NO_3^- flux decreased with

TABLE 4. Nutrient concentrations observed during ambient and plateau conditions of the dissolved organic C (DOC) and dissolved O_2 (DO) manipulations at Cedar Swamp Creek and Cart Creek. Concentrations were measured at the 1st sampling station downstream of points of addition (30 m in Cedar Swamp Creek, 25 m in Cart Creek) or are transect averages. Boldface indicates constituents specifically targeted in manipulations. + indicates addition, - indicates removal.

| Site/addition/ nutrient | Experiment | Nutrient | Ambient concentration (mg/L) | | Plateau concentration (mg/L) | |
|----------------------------|------------|-----------------|---------------------------------|---------------|---------------------------------|---------------|
| | | | 1 st station | Transect | 1 st station | Transect |
| Cedar Swamp Creek | +DOC | NO_3^- | 0.061 | 0.076 | 0.056 | 0.068 |
| | | DO | 3.350 | 3.798 | 3.880 | 3.550 |
| | | DOC | 42.572 | 44.529 | 51.332 | 51.668 |
| | +DO | NO_3^- | 0.067 | 0.081 | 0.072 | 0.092 |
| | | DO | 3.060 | 3.531 | 5.800 | 5.456 |
| | | DOC | 48.700 | 46.951 | 37.259 | 39.816 |
| | +DOC, +DO | NO_3^- | 0.067 | 0.081 | 0.073 | 0.096 |
| | | DO | 3.060 | 3.531 | 5.900 | 5.596 |
| | | DOC | 48.700 | 46.951 | 31.528 | 43.992 |
| Cart Creek | +DOC | NO_3^- | 0.270 | 0.260 | 0.296 | 0.279 |
| | | DO | N/A | N/A | 7.910 | 7.868 |
| | | DOC | 5.732 | 5.752 | 11.901 | 10.275 |
| | -DO | NO_3^- | 0.270 | 0.256 | 0.262 | 0.241 |
| | | DO | 8.100 | 8.383 | 0.990 | 2.682 |
| | | DOC | 5.905 | 6.056 | 4.822 | 4.413 |
| | +DOC, -DO | NO_3^- | 0.248 | 0.232 | 0.225 | 0.183 |
| | | DO | 7.940 | 7.590 | 1.080 | 2.168 |
| | | DOC | 4.807 | 4.979 | 11.808 | 11.024 |

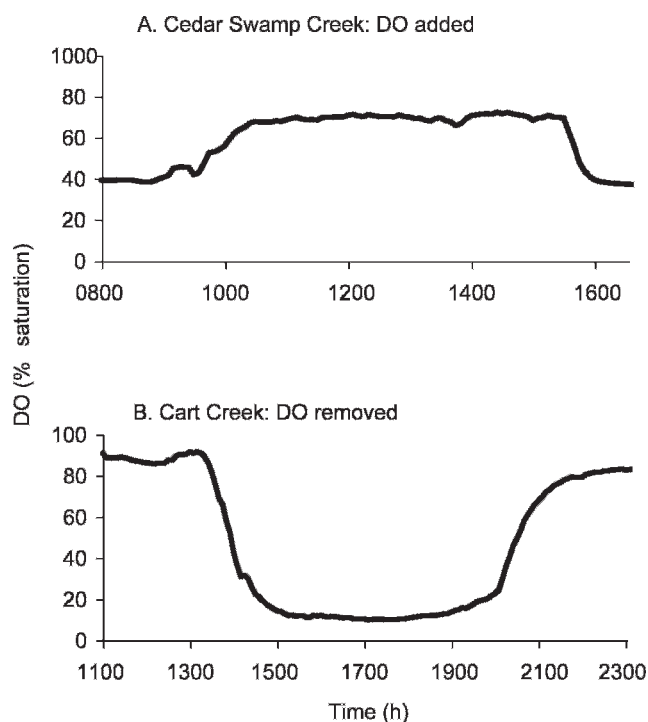


FIG. 3. A.—Time series of dissolved O_2 (DO) in Cedar Swamp Creek 60 m downstream of the DO addition site during the DO-addition experiments. O_2 was added from 0950 to 1515 h. B.—Time series of DO in Cart Creek 60 m downstream of the sodium sulfite addition during the combined dissolved organic C (DOC) addition and DO removal experiment. Sodium sulfite was used to remove DO and was added between 1145 and 1815 h.

distance through the reach. Addition of DOC alone resulted in increasing NO_3^- flux, a result indicating reduced net NO_3^- uptake (negative ΔU ; Fig. 6B).

DO manipulations created relatively small changes in net NO_3^- uptake. Addition of DO to DOC-rich Cedar Swamp Creek caused a statistically insignificant increase in NO_3^- flux through the reach (Table 5), a result indicating a small decline in net NO_3^- uptake (Fig. 6A). This result is consistent with results in Cart Creek where high DOC and high DO were paired. DO removal at Cart Creek had little effect on net NO_3^- uptake, indicating a small increase in $\text{NO}_3^- F_s$ through the reach and a decrease in net NO_3^- uptake (Fig. 6B).

Concurrent manipulations of DOC and DO produced the strongest changes in net NO_3^- uptake in Cedar Swamp Creek and Cart Creek (Fig. 6A, B). Concurrent addition of DOC and DO in Cedar Swamp led to increased NO_3^- flux through the reach ($p = 0.0517$) and a larger decline in net NO_3^- uptake than during the DO addition only experiment (Table 5). At Cart Creek, simultaneous removal of DO and addition of DOC decreased NO_3^- flux below ambient conditions ($p = 0.0574$), indicating increased net NO_3^- uptake (Fig. 6B).

Discussion

NO_3^- additions

Despite the lack of significance observed in several of the individual NO_3^- regressions used to calculate

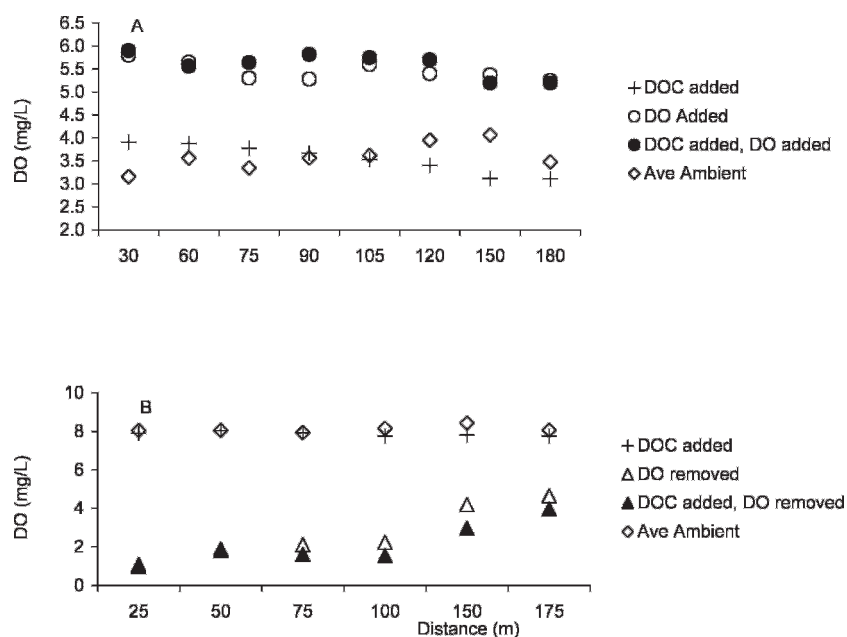


FIG. 4. Dissolved O_2 (DO) concentrations along stream transects at the plateau of each experiment and including average (ave) ambient concentrations at Cedar Swamp Creek (A) and Cart Creek (B). DOC = dissolved organic C, ave = average.

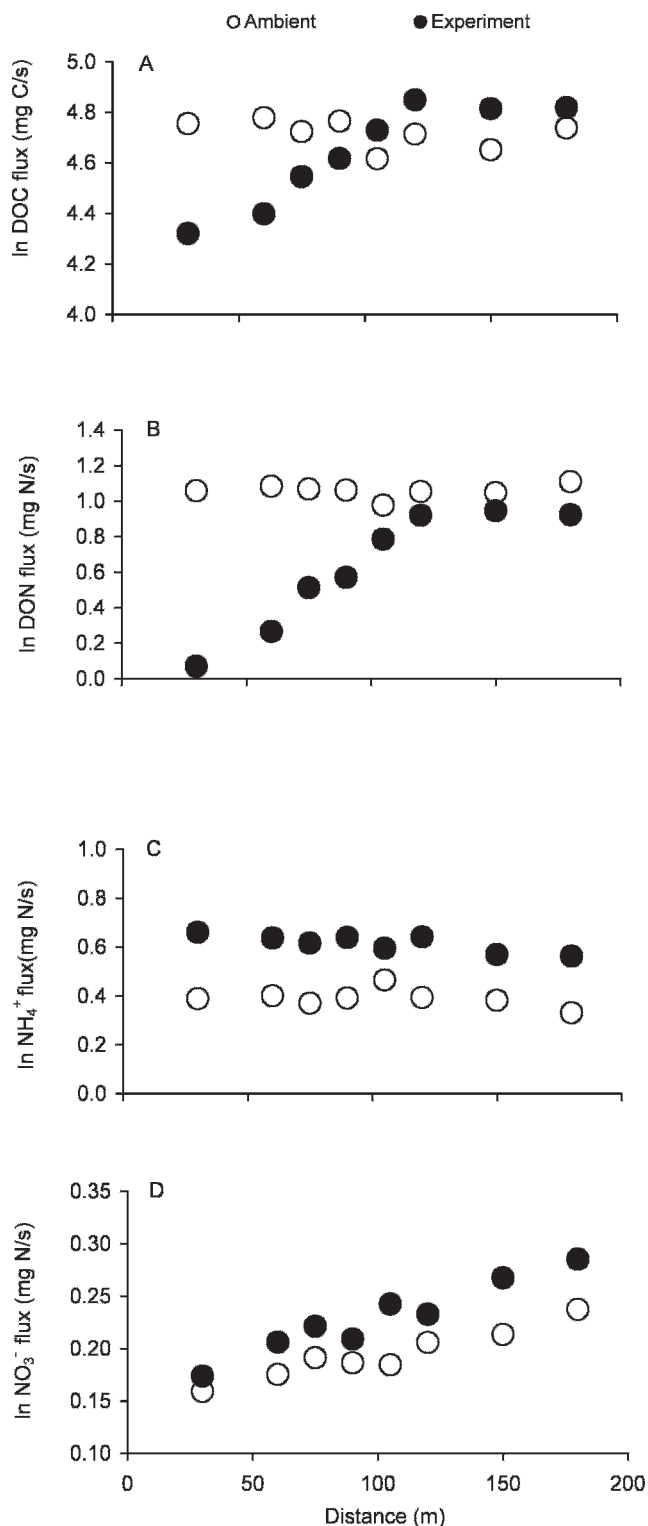


FIG. 5. Ambient and plateau chemistry of dissolved organic C (DOC) (A), dissolved organic N (DON) (B), NH_4^+ (C), and NO_3^- (D) at Cedar Swamp Creek from the concurrent addition of DOC and dissolved O_2 .

S_W and V_f in Cedar Swamp Creek and Cart Creek, together these data show trends with increasing NO_3^- concentration that are consistent with both the unique biogeochemistry of these streams and the results of other stream NO_3^- studies. $\text{NO}_3^- V_f$ in Cedar Swamp Creek was extremely high compared to those in other streams. The values were above the interquartile range from 52 studies in other 1st-order streams (420–2208 m/y; Ensign and Doyle 2006). The high ambient V_f in Cedar Swamp Creek suggests severe NO_3^- limitation. However, the decline in V_f as experimental NO_3^- concentrations increased (20–110% above ambient concentration) indicates that NO_3^- limitation was removed at moderate NO_3^- concentrations. At Cart Creek, the V_f values quantified from NO_3^- additions and the estimated ambient V_f were an order of magnitude lower than the mean value of 1472 m/y reported in Ensign and Doyle (2006). However, our estimate of ambient $\text{NO}_3^- V_f$ at Cart Creek (126 m/y) is similar to that estimated in this stream during the Lotic Intersite Nitrogen Experiment II (LINX II) with tracer ^{15}N additions (172 m/y; Mulholland et al. 2008). V_f at Cart Creek did decline with increasing NO_3^- concentration, but the decline was not as extreme as at Cedar Swamp Creek.

The results from the multiple additions at the 2 sites show a consistent inverse relationship between NO_3^- concentration and $\text{NO}_3^- V_f$. The consistent trend both within and across sites in our study suggests that NO_3^- concentration is a key control on NO_3^- dynamics in these streams and can be approximated with a power function (Fig. 7). Our finding of efficiency loss based on a series of short-term N additions to individual streams is consistent with similar results based on multiple streams with a range of chronically elevated NO_3^- levels (O'Brien et al. 2007, Mulholland et al. 2008). Similar to results of Mulholland et al. (2008), the overlapping trends of $\text{NO}_3^- V_f$ vs concentration across our 2 stream sites suggests that efficiency loss is a common phenomenon within, as well as across, streams. The V_f data from our study, particularly Cedar Swamp Creek, are elevated compared to the overall results of LINX II (Mulholland et al. 2008). Typically, ^{15}N tracer additions result in higher V_f than when short-term solute additions are used (Mulholland et al. 2002). In our study, the depleted O_2 conditions in Cedar Swamp Creek probably established a truly NO_3^- -limited system that excelled at NO_3^- removal via denitrification, particularly at low NO_3^- concentration. High background concentration of PO_4^{3-} in Cedar Swamp Creek also would have caused greater N limitation and might have influenced assimilatory demand.

TABLE 5. Linear slope (m) and intercept (b) values of NO_3^- flux (mg/s) along transects during ambient and plateau conditions of the dissolved organic C (DOC) and dissolved O_2 (DO) manipulations at Cedar Swamp Creek and Cart Creek. The change in flux (ΔF_s) was determined from the difference between experiment and ambient fluxes through the reach. p -values for slope and intercepts of ΔF_s are shown in parentheses. + indicates addition, - indicates removal. Boldface indicates value significantly different from 0 ($p < 0.05$).

| Experiment | Ambient | | Plateau | | ΔF_s | |
|-------------------|----------------|----------------|----------------|----------------|-------------------|-------------------|
| | m | b | m | b | m | b |
| Cedar Swamp Creek | | | | | | |
| +DOC | 0.00058 | 0.16274 | 0.00044 | 0.15504 | -0.00014 (0.0508) | -0.00770 (0.2648) |
| +DO | 0.00048 | 0.1456 | 0.00061 | 0.15832 | 0.00012 (0.2502) | 0.01272 (0.2852) |
| +DOC, +DO | 0.00048 | 0.1456 | 0.00071 | 0.1582 | 0.00023 (0.0517) | 0.01260 (0.2714) |
| Cart Creek | | | | | | |
| +DOC | -0.00031 | 0.72831 | -0.00009 | 0.75898 | 0.00022 (0.3655) | 0.03070 (0.2665) |
| -DO | -0.00007 | 0.45061 | -0.00006 | 0.41783 | 0.00001 (0.9506) | -0.03280 (0.1496) |
| +DOC, -DO | -0.00010 | 0.43436 | -0.00066 | 0.39612 | -0.00055 (0.0574) | -0.03824 (0.1687) |

Effect of DO and DOC concentrations on dissolved organic matter

DOC was removed from the water column more rapidly under higher DO conditions in both streams (Table 5). Others also have found that addition of DOC under aerobic conditions can increase metabolism in streams (Wiegner et al. 2005). Adding only DO

to Cedar Swamp Creek reduced DOC concentrations, but the loss of dissolved organic matter (DOC and DON) from the water column at Cedar Swamp Creek during the concurrent addition of DOC and DO was particularly striking because the estimated value of DOC V_f within the first 30 m reached levels 5× higher than average levels recorded in the literature (Wiegner et al. 2005). This mass removal of organic

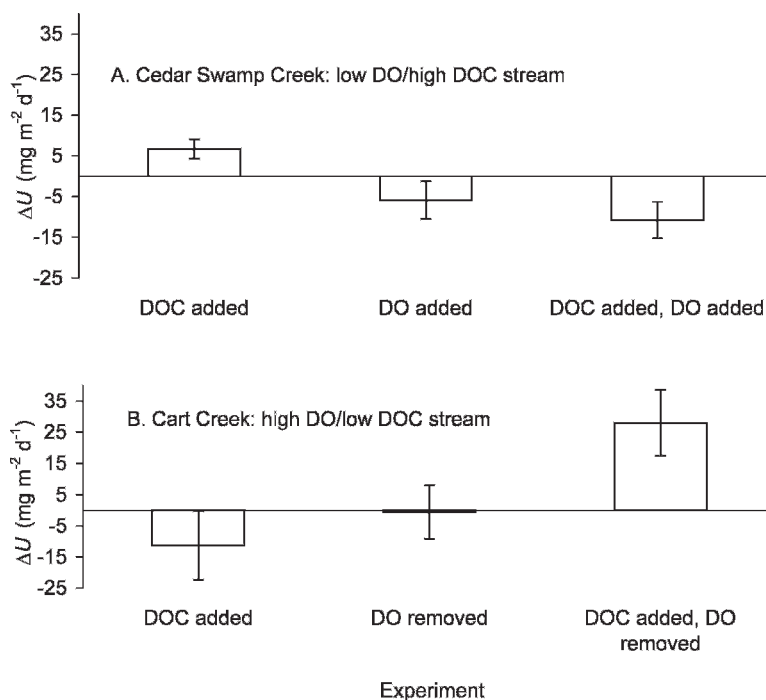


FIG. 6. Mean (± 1 SE) change in net NO_3^- uptake (ΔU ; difference in net NO_3^- uptake between manipulated and ambient conditions) resulting from the experimental manipulations at Cedar Swamp Creek (A) and Cart Creek (B). Positive values reflect increased net NO_3^- uptake, and negative values reflect increased net NO_3^- production caused by the manipulation. Error bars refer to the SE of the slope of ΔNO_3^- flux (ΔF_s) through the reach. DO = dissolved O_2 , DOC = dissolved organic C.

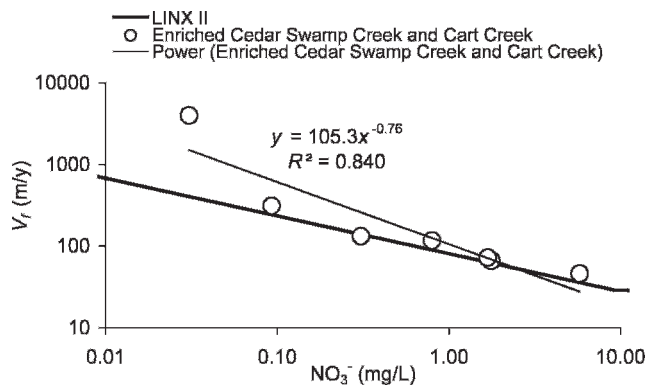


FIG. 7. Total NO_3^- uptake velocity (V_f) vs NO_3^- concentration determined from $^{15}\text{NO}_3^-$ additions by Lotic Intersite Nitrogen Experiment II (LINX II; Mulholland et al. 2008) and from NO_3^- additions to Cedar Swamp Creek and Cart Creek during our study.

matter might be explained, in part, by flocculation of dissolved organic matter into particulate organic matter (POC) (Lush and Hynes 1973) and by abiotic adsorption of dissolved organic matter to sediments (McDowell 1985). However, the concurrent decline in DON concentration and rise in NH_4^+ during the addition of DOC and DO at Cedar Swamp Creek is consistent with remineralization of organic matter (Scott and Binkley 1997). This phenomenon of labile DOC increasing the use of ambient organic matter has not been reported before 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 heterotrophic system contains high levels of organic matter relative to systems in other studies involving DOC additions (Wiegner et al. 2005) and because Cedar Swamp Creek was simultaneously primed with DO, which increased the potential for aerobic remineralization. DO concentrations were still fairly low at Cedar Swamp during the DO additions, but the relative effect of doubling DO availability in this chronically O_2 -poor ecosystem created significant biological results and highlighted the effect of DO on the N cycle.

We suggest that concentrations of DOC and DON were reestablished and maintained near an equilibrium concentration downstream of the priming effects by leaching from the highly organic stream bottom. The increase in concentration of DOC over this 150-m reach was large (20 mg/L, or 65% of initial influx), but previous reports support our interpretation that in-channel leaching of stored benthic organic matter can be a significant source of DOC (Meyer et al. 1998, Wiegner et al. 2005). McDowell (1985) also found that

ambient dissolved organic matter stored in the benthos contributed to water-column DOC. Thus, the organic matter content in the stream bottom might determine equilibrium concentrations and cause a return to ambient levels as water flowed through the experimental reach.

Effect of DO and DOC concentration on net NO_3^- uptake

Results from the manipulations of DOC and DO suggest that DOC alone does not lead to increased net NO_3^- uptake, but magnifies the dominant biological processes determined by ambient O_2 levels. Goodale et al. (2005) suggested that higher DOC concentrations aid NO_3^- retention or removal, but we found that higher DOC concentrations increased NO_3^- retention only under depressed O_2 conditions. Thus, observed relationships between NO_3^- and DOC (e.g., Goodale et al. 2005) might be influenced, in part, by covariation of DOC and DO in natural systems. Based on our findings, we suggest that DO concentrations in stream ecosystems determine the dominant processes that influence net NO_3^- uptake and that addition of DOC serves to fuel the dominant metabolic activity. In DO-deficient systems, such as Cedar Swamp Creek, nitrification is depressed (Kemp and Dodds 2001), whereas conditions for denitrification are favorable. As a result, NO_3^- concentrations remain low, whereas NH_4^+ concentrations are elevated. The reverse is true in DO-rich streams.

DOC accelerates the dominant processes determined by overall O_2 conditions. Under anaerobic conditions, DOC can enhance denitrification (Inwood et al. 2005). Under aerobic conditions, we would expect additional DOC to enhance net NO_3^- uptake through immobilization by heterotrophs (Bernhardt and Likens 2002). However, we did not see this effect because of enhanced remineralization caused by priming followed by nitrification in our organic-matter-rich system. As a result, net NO_3^- uptake declined. Our results suggest that NO_3^- , DOC, and DO dynamics are tightly coupled, and the relative strength of various N processes will depend on the relative abundance of each of these constituents.

Summary and conclusions

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^- additions suggest that NO_3^- uptake efficiency decreases with increasing concentration in local headwater streams, and that the NO_3^- buffering capacity of these systems can be overwhelmed. The results from these DOC and

DO manipulations suggest that DO concentrations in headwater streams significantly influence net NO_3^- uptake by determining the dominant respiratory pathway of stream ecosystems as being either: 1) a predominantly aerobic system with the potential for efficient organic matter metabolism, ammonification, nitrification, and net NO_3^- production or 2) a predominantly anaerobic system with low and inefficient organic matter metabolism, limited nitrification, and NO_3^- limitation. Our results also suggest that short-term increases in the availability of labile DOC in both low- and high-DO streams increases metabolic activity and accentuates existing DO-dependent processes that determine net NO_3^- uptake and production. Therefore, wetland streams with characteristically low DO and high DOC are 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 $\text{NO}_3^- V_f$ 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 reaeration rates, such as those dominated by riffles, might serve as sources of net NO_3^- production via remineralization and nitrification. Coupling of environments, such as the natural riffle and pool sequences inherent in stream ecosystems (Dunne and Leopold 1978), that link net NO_3^- sources and NO_3^- sinks might be a critical component in longitudinal removal of N. Quantifying the abundance and linkages of different stream types relative to source areas at river-network scales is necessary to assess the effect of entire river systems on the export of NO_3^- from watersheds with high N inputs.

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