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**Key Points:**
- Carbon and nitrogen cycling coupled in streams
- Higher DOC:$NO_3^-$ ratios and DOC concentrations promote the greatest nitrate uptake
- Biostimulation model in high-nitrate streams

**Supporting Information:**
- Supporting Information S1
- Table S1

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# DOC:$NO_3^-$ ratios and $NO_3^-$ uptake in forested headwater streams

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**Abstract** The underlying mechanisms driving the coupled interactions between inorganic nitrogen uptake and dissolved organic matter are not well understood, particularly in surface waters. To determine the relationship between dissolved organic carbon (DOC) quantity and nitrate ($NO_3^-$) uptake kinetics in streams, we performed a series of $NO_3^-$ Tracer Additions for Spiraling Curve Characterization experiments in four streams within the Lamprey River Watershed, New Hampshire, across a range in background DOC concentrations (1–8 mg C/L). Experiments were performed throughout the 2013 and 2014 growing seasons. Across streams and experimental dates, ambient uptake velocity ($V_f$) correlated positively with increasing DOC concentrations and DOC:$NO_3^-$ ratios but was only weakly negatively associated with $NO_3^-$ concentrations. Ambient $NO_3^-$ $V_f$ was unrelated to pH, light, temperature, dissolved oxygen, and Specific Ultraviolet Absorbance at 254 nm. Although there were general tendencies across the entire Lamprey River Watershed, individual sites behaved differently in their uptake kinetics. $NO_3^-$ uptake dynamics in the Lamprey River Watershed are most strongly influenced by DOC concentrations rather than $NO_3^-$ concentrations or physicochemical parameters, which have been identified as regional- to continental-scale drivers in previous research. Understanding the fundamental relationships between dissolved organic matter and inorganic nutrients will be important as global and climatic changes influence the delivery and production of DOC and $NO_3^-$ in aquatic ecosystems.

## 1. Introduction

Major transformations in the nitrogen (N) cycle depend on the availability of carbon (C) as an energy source [*Bernhardt and Likens*, 2002; *Strauss and Lamberti*, 2002; *Dodds et al.*, 2004; *Goodale et al.*, 2005; *Taylor and Townsend*, 2010]. In stream ecosystems moderate changes in dissolved organic carbon (DOC) concentrations can affect N retention in streams [*Goodale et al.*, 2005]. The availability of labile DOC, in particular, can exert strong controls and modify the quantity and form of nitrogen exported from terrestrial watersheds [*Bernhardt and Likens,* 2002] as well as support greater heterotrophic activity [*Strauss and Lamberti,* 2000; *Bernhardt et al.*, 2002; *Strauss and Lamberti*, 2002]. For example, the removal of N from surface water via denitrification is controlled by both labile DOC and $NO_3^-$ availability [*Bernhardt et al.*, 2005; *Taylor and Townsend*, 2010].

Previous studies have exhibited inconsistent relationships between DOC and $NO_3^-$. *Taylor and Townsend* [2010] demonstrated a decrease in $NO_3^-$ concentrations with increasing DOC or particulate organic C concentrations across different ecosystems (soils, streams, estuaries, and oceans) affected by different land use changes (pristine, urban, and agriculture), suggesting that the underlying mechanisms controlling this biogeochemical coupling are similar regardless of ecosystem type or land use. Similar results have been observed with experimental addition of DOC to streams where microbial activity and growth are stimulated resulting in an increased demand for nitrogen and a reduction in $NO_3^-$ concentrations [*Bernhardt and Likens*, 2002; *Sobczak et al.*, 2003; *Bernhardt and McDowell*, 2008]. In contrast, other studies suggest that $NO_3^-$ uptake is often unaffected by the addition of labile DOC [*Richey et al.*, 1985]. The effects of DOC concentrations on nitrate uptake are further complicated by the role that $O_2$ concentrations play in regulating nitrogen dynamics [*Thouin et al.*, 2009]. Although these previous studies have demonstrated strong links between the C and N cycles, the underlying mechanisms of C and N dynamics and their coupling are inconsistent and still not well understood, especially in surface waters.

Many studies have used whole stream nutrient additions to quantify $NO_3^-$ uptake in streams [*Mulholland et al.*, 2008; *Hall et al.*, 2009]. Most demonstrate that $NO_3^-$ uptake plateaus as ecosystems approach N saturation [*Stream Solute Workshop*, 1990; *Dodds et al.*, 2002; *Mulholland et al.*, 2002; *Earl et al.*, 2007; *Hall et al.*, 2009; *O'Brien et al.*, 2007; *Covino et al.*, 2010; *Ribot et al.*, 2013], a pattern that holds across land use and biomes

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[*Mulholland et al*., 2008; *Hall et al*., 2009]. Variation in the nature of uptake kinetics defines how a stream will respond to increases in a given nutrient [*Wollheim et al*., 2014]. Three general patterns are often recognized. Uptake can be directly proportional to concentration of the manipulated solute [*Dodds et al*., 2002; *Ribot et al*., 2013; *O'Brien et al*., 2007], can follow a Michaelis-Menten saturation curve [*Dodds et al*., 2002; *O'Brien et al*., 2007], or can follow an efficiency loss model where the increase of uptake declines relative to the increase in concentration [*O'Brien et al*., 2007].

To further understand the relationships between DOC availability and $NO_3^-$ uptake, we manipulated $NO_3^-$ concentrations in multiple headwater streams across a range of DOC concentrations in the Lamprey River Watershed, New Hampshire. We used the Tracer Additions for Spiraling Curve Characterization (TASCC) [*Covino et al*., 2010] method which allows for the quantification of uptake kinetics. The metrics described by TASCC include dynamic uptake (a stream's response across the full range of concentrations encountered during the nutrient addition) and ambient uptake (uptake rate in the absence of added nutrients) [*Covino et al*., 2010]. Here we focus on uptake velocity, the vertical movement of solutes into the benthos that represents uptake efficiency. Uptake velocity is well suited for cross-system comparisons as it is normalized for discharge and differences in ambient concentrations [*Peterson et al*., 2001; *Bernhardt et al*., 2002; *Hall et al*., 2002; *Fellows et al*., 2006].

We predicted that streams with higher DOC concentrations would promote the greatest $NO_3^-$ removal from the water column because of greater heterotrophic activity [*Bernhardt and McDowell*, 2008]. Also, we expected $NO_3^-$ uptake velocity will decrease with increased $NO_3^-$ concentrations as the ecosystem reaches N saturation and the lowest uptake at high $NO_3^-$ and low DOC concentrations. Although our overarching objective is to assess the role of C in $NO_3^-$ removal, we also wanted to consider other potential drivers of $NO_3^-$ uptake like physicochemical parameters (i.e., DO, temperature, light, and pH). We predicted that ambient $NO_3^-$ uptake kinetics will also be related to the abiotic parameters that control stream metabolism [*Hall and Tank*, 2003; *Fellows et al*., 2006; *Mulholland et al*., 2006; *Hall et al*., 2009]. Identifying the controls on $NO_3^-$ uptake and processing in streams is needed to better understand the fate of $NO_3^-$ and its downstream transport, which can contribute to the degradation of receiving bodies of water.

## 2. Methods

### 2.1. Study Site

The Lamprey River Watershed (479 $km^2$) is located in southeastern New Hampshire, drains mostly forested land (68% of the watershed is forested), and discharges into the Great Bay Estuary. Great Bay has been classified as nitrogen impaired [*New Hampshire Department of Environmental Services*, 2009] due to chronic $NO_3^-$ inputs resulting in a loss of eelgrass and low DO in tidal rivers. Four sites were chosen within the Lamprey River Watershed; Wednesday Hill Brook (WHB) and Dowst-Cate Forest (DCF) for the 2013 growing season and Rum Brook (RMB) and Saddleback Mountain (SBM) were added in 2014 (Figure 1 and Table 1).

The selected streams varied in their background $NO_3^-$ and DOC concentrations as well as benthic substrate (Table 2). WHB is a first order stream with an average $NO_3^-$ concentration of 804 μg N/L and average DOC concentration of 4.42 mg C/L. The experimental stream reach has a silty stream bottom as well as various fallen branches and logs creating small debris dams. DCF is a second order stream draining a wetland with an average $NO_3^-$ concentration of 55 μg N/L and average DOC concentration of 7.44 mg C/L. The stream bottom at DCF is mostly cobble and large rocks and a riffle pool sequence. RMB is a first order stream with average $NO_3^-$ concentration of 63 μg N/L and average DOC concentration of 7.48 mg C/L. The experimental stream reach is mostly composed of short riffles and long runs with the stream bottom mostly made up of cobble and larger rocks. SBM is a first order steep mountainous stream following a step riffle pool sequence with large rocks and a mossy stream bottom. The stream has an average $NO_3^-$ concentration of 2 μg N/L and average DOC concentration of 1.19 mg C/L.

### 2.2. TASCC Additions and Uptake Metrics

A series of short-term stream enrichments were performed at all sites between April and November 2013 and June through September 2014 (Table 3) following the methods for Tracer Additions for Spiraling Curve Characterization (TASCC) [*Covino et al*., 2010]. Enrichments consisted of $NO_3^-$ as sodium nitrate ($NaNO_3$) along with sodium chloride (NaCl) as a conservative tracer mixed in stream water where we increased

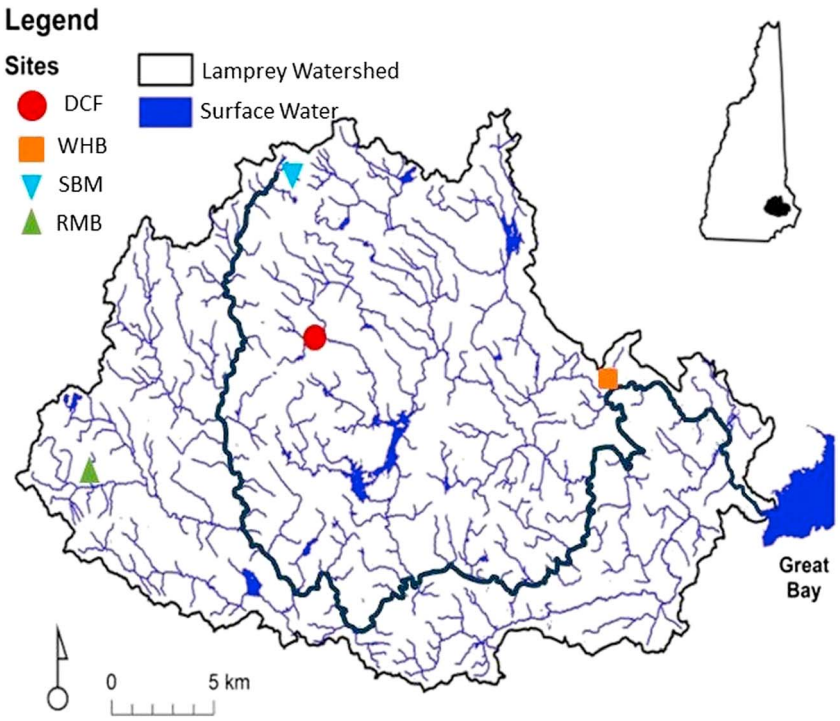


**Figure 1.** Map of the Lamprey River Watershed with the four study sites Dowst-Cate Forest (DCF) (red circle), Wednesday Hill Brook (WHB) (orange square), Saddleback Mountain (SBM) (blue triangle), and Rum Brook (RMB) (green triangle), in respect to Great Bay and the state of New Hampshire. The darker line outlines the Lamprey River main stem.

$NO_3^-$ and Cl between 2X and 3X background concentrations (Table 3). Experimental reaches ranged between 50 and 100 m in length and were selected so that large pools, wetlands, culverts, and inputs from overland flows and tributaries were excluded from our study reaches. Solutes were released at the top of the experimental reach near a riffle to facilitate mixing. Background samples were collected in triplicate before every experiment at the top and bottom of the experimental reach.

Discharge measurements were taken the day before each experiment, to calculate the required amount of solute for each addition and after every experiment using a Flowtracker Handheld ADV (SonTek, San Diego, CA) which automatically calculates discharge using depth and velocity. When low flow conditions prevented the use of the Flowtracker, we used dilution gaging [*Kilpatrick and Cobb*, 1985] to calculate discharge. Sodium chloride (NaCl) was dissolved in stream water and added as an instantaneous slug addition. Conductance was logged at 5 s intervals throughout the break through curve (BTC) with a HOBO conductivity data logger (Onset, Bourne, MA) or YSI $EXO_2$ multiparameter sonde (YSI, Yellow Springs, OH).

Calculations for dynamic and ambient uptake parameters followed the TASCC method as developed by *Covino et al*. [2010]. For all TASCC additions a dynamic uptake length ($S_{w\ Add\text{-}dyn}$) was calculated as the negative inverse of $k_w$, the longitudinal uptake rate determined by the rate of change of the natural log of the N:Cl

**Table 1.** Coordinate Location and Land Use Characteristics for Wednesday Hill Brook (WHB), Dowst-Cate Forest (DCF), Rum Brook (RMB) and Saddleback Mountain (SBM)

| Site | Coordinates | Area ($km^2$) | Population ($km^2$) | % Land Wetland[a] | % Land Developed[a] | % Land Agriculture[a] | % Land Forested[a] |
|---|---|---|---|---|---|---|---|
| WHB | 43.122°N, 71.0040°W | 1.0 | 155.8 | 4.1 | 12.3 | 17.1 | 62.6 |
| DCF | 43.134°N, 71.183°W | 7.0 | 25.3 | 4.2 | 0.5 | 5.8 | 82.2 |
| RMB | 43.053°N, 71.034°W | 4.9 | 105.2 | 6.8 | 7.4 | 13.5 | 65 |
| SBM | 43.184°N, 71.215°W | 0.3 | 32.9 | 0 | 0 | 0 | 98.6 |

[a]Data obtained from *NOAA's Coastal Change Analysis Program* [2006].



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**Table 2.** Average Background Nutrient Concentrations During Experiments

| Site | $NO_3^-$ (mg N/L) | DOC (mg C/L) | $NH_4^+$ (μg N/L) | $PO_4^{3-}$ (μg P/L) | DON (mg N/L) | TDN (mg N/L) |
|---|---|---|---|---|---|---|
| WHB | 0.727 | 3.10 | 17.0 | 8.16 | 0.20 | 0.38 |
| DCF | 0.051 | 7.61 | 7.77 | 5.88 | 0.31 | 0.42 |
| RMB | 0.063 | 7.48 | 25.2 | 6.24 | 0.33 | 0.91 |
| SBM | 0.002 | 1.20 | [a] | 1.89 | 0.23 | 0.10 |

[a]Concentration below detection.

ratio over the stream reach length for each grab sample along the BTC. Using $S_{w\ Add\text{-}dyn}$ both dynamic areal uptake ($U_{Add\text{-}dyn}$) and uptake velocity ($V_{f\ Add\text{-}dyn}$) can be determined as

$$U_{Add-dyn} = \frac{Q\ x\ \left[NO_3^- N_{Add-dyn}\right]}{S_{w\ Add-dyn}\ x\ W}$$

$$V_{f\ Add-dyn} = \frac{U_{Add-dyn}}{\left[NO_3^- N_{Add-dyn}\right]}$$

where $Q$ is stream discharge, $[NO_3^- - N_{Add\text{-}dyn}]$ is the geometric mean concentration of $NO_3^-$ (added $NO_3^-$ and predicted $NO_3^-$; see *Covino et al.* [2010] for further details) of the individual grab samples and $W$ is the wetted stream width in the experimental reach for each grab sample along the BTC.

Spiraling measurements encompass the added nutrient (Add-dyn) and the ambient (Amb) conditions in the stream. For this reason it is critical to use total spiraling values in order to correctly characterize kinetic models [*Covino et al.*, 2010]. Total dynamic areal uptake ($U_{Tot\text{-}dyn}$) is the sum of ambient areal uptake ($U_{Amb}$) and the dynamic areal uptake ($U_{Add\text{-}dyn}$) calculated for each grab sample along the BTC. Total dynamic uptake velocity ($V_{f\ Tot\text{-}dyn}$) is determined by the quotient of $U_{Tot\text{-}dyn}$ and total observed $NO_3^-$. From here on, when we refer to dynamic uptake velocity, we are referring to the total dynamic uptake velocity.

Ambient uptake length ($S_{w\text{-}Amb}$) was estimated as the $y$ intercept of the linear regression between $S_{w\ Add\text{-}dyn}$ and $NO_3^-$ concentration [*Payn et al.*, 2005]. Ambient areal uptake ($U_{Amb}$) and ambient uptake velocity ($V_{f\text{-}Amb}$) are determined by the same equation as dynamic $U$ and $V_f$ but with ambient $NO_3^-$ concentrations.

### 2.3. Water Chemistry

We collected samples throughout the experiment in acid washed bottles which were then filtered through precombusted Whatman GF/F glass fiber filters within the same day of collection. Samples were transported

**Table 3.** Background $NO_3^-$ and DOC Concentrations, Discharge, $SUVA_{254}$ Index, $NO_3^-$ Concentrations at the Peak of the BTC, and the Raw Amount of $NaNO_3$ Added for Each Experiment Conducted at Wednesday Hill Brook (WHB), Dowst-Cate Forest (DCF), Rum Brook (RMB), and Saddleback Mountain (SBM)[a]

| Site | Date | $NO_3^-$ (μg N/L) | DOC (mg/L) | $Q$ (L/s) | SUVA ($L\ mg^{-1}\ m^{-1}$) | Peak $NO_3^-$ (mg/L) | Added $NO_3^-$ (g) | Ambient $S_w$ (m) | Ambient $U$ ($\mu g\ m^{-2}\ s^{-1}$) | Ambient $V_f$ ($mm\ min^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| WHB | 4/25/13 | 357 | 3.85 | 13.1 | 3.87 | 5.17 | 182 | −583[b] | −0.369[b] | −1.72[b] |
| | 6/21/13 | 343 | 3.72 | 6.88 | 3.71 | 8.39 | 180 | [c] | [c] | [c] |
| | 8/7/13 | 1036 | 2.29 | 2.36 | 3.43 | 4.35 | 46.5 | 640 | 0.223 | 0.214 |
| | 9/11/13 | 776 | 3.55 | 2.64 | 2.79 | 2.45 | 38.0 | 314 | 0.520 | 0.666 |
| | 6/30/14 | 1156 | 1.77 | 2.62 | 4.22 | 13.42 | 218 | 3302 | 0.063 | 0.054 |
| | 8/15/14 | 533 | 4.9 | 7.26 | 3.91 | 15.53 | 450 | 928 | 0.199 | 0.376 |
| | 9/11/14 | 882 | 1.63 | 1.57 | 3.38 | 1.08 | 46.0 | 570 | 0.148 | 0.168 |
| DCF | 5/31/13 | 45 | 7.06 | 73.6 | 4.66 | 0.28 | 65.0 | 212 | 0.269 | 6.73 |
| | 7/10/13 | 33 | 8.50 | 63.3 | 4.13 | 0.47 | 99.0 | 144 | 0.260 | 98.61 |
| | 8/15/13 | 78 | 9.02 | 19.2 | 3.20 | 0.51 | 54.0 | [c] | [c] | [c] |
| | 10/5/13 | 35 | 7.34 | 30.0 | 3.83 | 0.25 | 40.0 | 115 | 0.263 | 6.60 |
| | 7/9/14 | 42 | 8.64 | 70.8 | 4.64 | 0.19 | 30.0 | [c] | [c] | [c] |
| | 8/22/14 | 41 | 7.27 | 40.0 | 4.17 | 0.08 | 113 | 50 | 0.506 | 12.7 |
| | 9/26/14 | 92 | 5.46 | 22.3 | 5.55 | 0.13 | 37.0 | 57 | 0.912 | 10.1 |
| RMB | 7/2/14 | 80 | 6.26 | 8.23 | 4.33 | 0.19 | 5.50 | 488 | 0.028 | 0.360 |
| | 8/20/14 | 44 | 9.92 | 13.0 | 4.86 | 0.35 | 65.0 | 43 | 0.237 | 5.94 |
| | 9/19/14 | 71 | 6.26 | 2.92 | 7.70 | 0.09 | 20.5 | 112 | 0.040 | 0.567 |
| SBM | 7/11/14 | 2 | 1.2 | 1.76 | 2.19 | 0.47 | 11.5 | 117 | 0.001 | 0.560 |

[a]Ambient uptake length ($S_w$), uptake velocity ($V_f$), and areal uptake ($U$) are reported for every experiment.
[b]Negative ambient uptake values that were obtained from kinetics that showed uptake.
[c]Ambient uptake values that were not attainable due to negative dynamic uptake values.

to the lab on ice and frozen until analysis. We analyzed samples for DOC and TDN using high temperature catalytic oxidation in a Shimadzu TOC-V CPH/TNM. Ions ($Cl^-$ and $NO_3^-$) were analyzed with ion chromatography using an Anion/Cations Dionex ICS-1000 with AS40 autosampler. $NH_4^+$ and $PO_4^{3-}$ analyses were done using a SmartChem 200 discrete automated colorimetric analyzer using the alkaline phenate ($NH_4^+$) and molybdate ($PO_4^{3-}$) standard methods. DON was determined arithmetically by subtracting TDN and DIN concentrations. The total mass of added Na, Cl, and N used in each experiment was determined based on the mass of salt used in each experiment and the elemental content of each salt.

### 2.4. In Situ Physicochemical Data

Ambient physicochemical data were available for WHB, DCF, and SBM from a permanent in situ YSI $EXO_2$ multiparameter sonde (YSI, Yellow Springs, OH), which measures pH, DO, temperature, and specific conductance, and a Photosynthetically Active Radiation (PAR) logger (Odyssey, Christchurch, New Zealand). RMB is not equipped with a permanent sensor suite therefore sensor data are only available for the dates when we deployed a temporary YSI $EXO_2$ instrument during the experiment.

### 2.5. SUVA

Specific Ultraviolet Absorbance (SUVA) ($L\,mg\,C^{-1}\,m^{-1}$) was determined for background samples of all the additions following the methods presented by *Weishaar et al*. [2003]. Absorbance was measured using a Genesis 10 UV spectrophotometer at 254 nm. UV absorbance is the absorbance of the sample at 254 nm and [DOC] is the DOC concentration of the sample.

$$SUVA_{254} = \frac{\text{UV Absorbance}}{[DOC]}$$

### 2.6. Statistics

We used simple linear regressions to determine how much of the variation in uptake metrics was explained by total $NO_3^-$, DOC concentrations, DOC:$NO_3^-$ ratios as well as physicochemical parameters, and ambient background nutrient concentrations. Ambient uptake velocities, DOC:$NO_3^-$ ratios, DOC concentration, and $NO_3^-$ concentration were log transformed to normalize data across dates and sites. Significance was determined by $p < 0.05$, and all statistical analyses were performed in JMP Pro 12 (SAS Institute 2013).

## 3. Results

### 3.1. Ambient Uptake Kinetics, Nutrients, and Physicochemical Parameters

Across the Lamprey River Watershed ambient $NO_3^-$ uptake velocities ($V_f$) correlated negatively with background $NO_3^-$ concentrations ($r^2 = 0.33$, and $p = 0.03$; Figure 2a). In contrast, ambient $NO_3^-$ $V_f$ increased with DOC concentrations ($r^2 = 0.56$, and $p = 0.001$; Figure 2b) and DOC:$NO_3^-$ ratios ($r^2 = 0.54$, and $p = 0.001$; Figure 2c).

### 3.2. Spatial Variability in Dynamic $NO_3^-$ Uptake Kinetics

Uptake kinetics in the Lamprey River Watershed varied among individual sites and experiments. As expected, the most common uptake kinetic trend across all sites was a negative correlation between dynamic $NO_3^-$ $V_f$ and total $NO_3^-$ concentrations. However, the shape of the line describing this relationship varied among sites including both linear and exponential functions. This negative correlation was seen in WHB in April 2013 ($r^2 = 0.44$, and $p < 0.01$; Figure 3a) and September 2013 ($r^2 = 0.61$, and $p = 0.06$; Figure 3d), DCF in October 2013 ($r^2 = 0.95$, and $p < 0.0001$; Figure 4d) and September 2014 ($r^2 = 0.80$, and $p < 0.0001$; Figure 4g), and RMB in July 2014 ($r^2 = 0.39$, and $p = 0.03$; Figure 5a) and August 2014 ($r^2 = 0.97$, and $p < 0.0001$; Figure 5b).

The second most common trend seen across sites was a positive and linear correlation between dynamic $NO_3^-$ $V_f$ and total $NO_3^-$ concentrations. This positive relationship was most common at WHB seen in August 2013 ($r^2 = 0.89$, and $p < 0.0001$; Figure 3c), June 2014 ($r^2 = 0.55$, and $p < 0.0001$; Figure 3e), August 2014 ($r^2 = 0.47$, and $p < 0.0001$; Figure 3f), and September 2014 ($r^2 = 0.99$, and $p < 0.0001$; Figure 3g). This trend was also detected at DCF in August 2014 ($r^2 = 0.27$, and $p = 0.03$; Figure 4f) and RMB in September 2014 ($r^2 = 0.64$, and $p < 0.0001$; Figure 5c).

We also found trends that occurred occasionally at given sites. The experiments in May 2013 ($r^2 = 0.00$, and $p = 0.99$; Figure 4a) and July ($r^2 = 0.06$, and $p = 0.33$; Figure 4b) at DCF did not show significant relationships between dynamic $NO_3^-$ $V_f$ and total $NO_3^-$ concentrations. The experiment from June 2013 (Figure 3b) at



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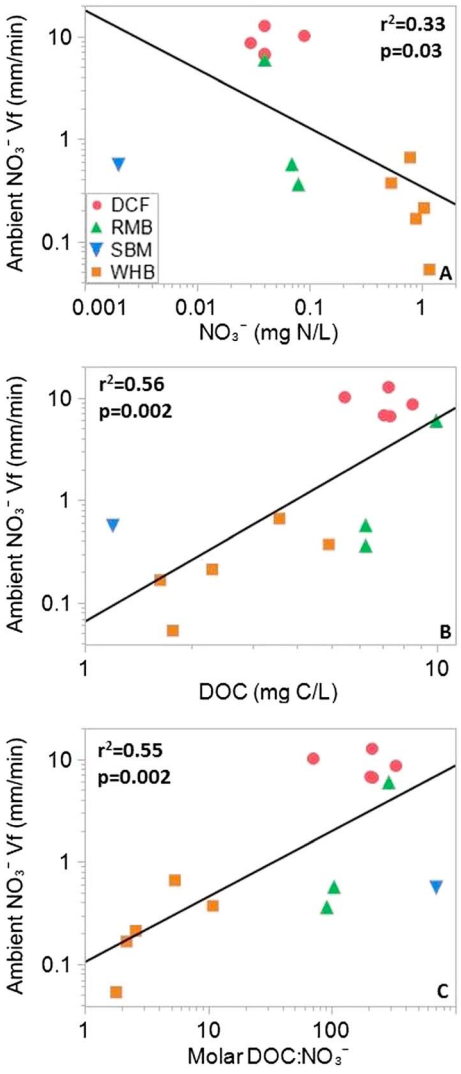


**Figure 2.** Log transformed ambient $NO_3^-$ uptake velocities ($V_f$) versus log transformed background (a) $NO_3^-$ concentration, (b) DOC concentration, and (c) DOC:$NO_3^-$ ratios for all experiments performed across all sites: Dowst-Cate Forest (DCF), Wednesday Hill Brook (WHB), Saddleback Mountain (SBM), and Rum Brook (RMB). August 2013 and July 2014 DCF, and May and June 2013 WHB were excluded because uptake was undetectable or negative values.

WHB resulted in negative uptake values that became more negative with increasing $NO_3^-$ concentrations. This was also observed at DCF in August 2013 (Figure 4c) and July 2014 (Figure 4e). We also detected one experiment that exhibited a counter clockwise hysteresis at SBM in July 2014 ($r^2 = 0.55$, and $p < 0.0001$; Figure 6) where the greatest uptake occurred during the falling limb. Only one experiment was executed at SBM due to its ephemeral nature.

### 3.3. Ambient Uptake and Physicochemical Parameters

Ambient uptake velocity was unrelated to physicochemical parameters such as pH, PAR, DO, and temperature. Ambient $V_f$ was also unrelated to stream geomorphology as described by slug travel time from release to the peak of BTC ($r^2 = 0.01$; $p = 0.73$). Although $NO_3^-$ uptake is closely linked to DOC concentrations and DOC:$NO_3^-$ ratios, ambient uptake was unrelated to DOC composition as described by $SUVA_{254}$.

## 4. Discussion

### 4.1. $NO_3^-$ Uptake Kinetics and Nutrients

Across the Lamprey River Watershed, ambient uptake of $NO_3^-$ was tightly linked to DOC:$NO_3^-$ ratios as well as DOC concentrations. Although we did not alter DOC concentrations in our experiments, we found similar results to studies that have manipulated C [*Bernhardt and Likens*, 2002; *Sobczak et al.*, 2003; *Bernhardt and McDowell*, 2008; *Thouin et al.*, 2009]. Collectively, these results demonstrate the strong influence of DOC on $NO_3^-$ removal in aquatic ecosystems. Specifically, streams with greater DOC concentrations are more efficient at removing $NO_3^-$ from the water column in the Lamprey River Watershed.

The moderately high DOC concentrations found at our highest DOC sites appear to provide the microbial community with a sufficiently large energy pool to support heterotrophic activity in streams that are otherwise $NO_3^-$ limited. Because sites with higher DOC had higher $NO_3^-$ uptake efficiency, our data suggest that $NO_3^-$ concentrations and DOC interact to drive overall rates of N uptake [*King et al.*, 2014]. Similar to *Bernhardt and McDowell* [2008], we observed that low DIN coupled with higher DOC provides a favorable environment for rapid $NO_3^-$ removal. Whether or not low DIN is a consequence of heterotrophic metabolism or characteristics of the stream drainage, our study demonstrates a strong relationship between DOC concentration and $NO_3^-$ uptake.



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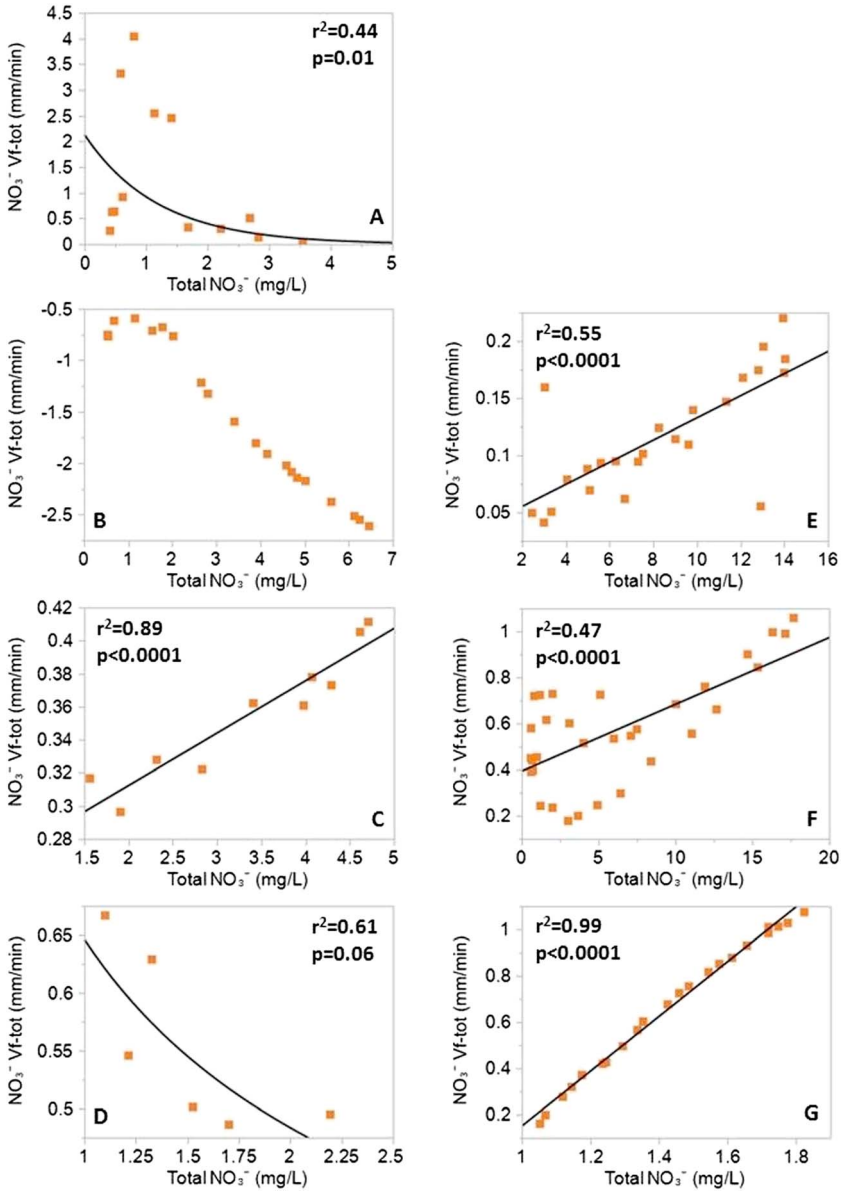


**Figure 3.** Individual experimental dynamic uptake velocities ($V_f$) from $NO_3^-$ TASCC additions for all the experiments at Wednesday Hill Brook (WHB) for (a) April 2013 ($\log Y = 0.75 - 0.84x$), (b) June 2013, (c) August 2013 ($Y = 0.25 + 0.032x$), (d) September 2013 ($\log Y = -0.44 - 0.42 \log x$), (e) June 2014 ($Y = 0.036 + 0.010x$), (f) August 2014 ($Y = 0.39 + 0.029x$), and (g) September 2014 ($Y = -1.03 + 1.18x$).

The ratio of DOC:$NO_3^-$ is surprisingly effective in predicting the uptake of $NO_3^-$ in streams both locally in the Lamprey River Watershed and at the continental scale (Figure 7). This result is evident across a wide range of DOC and $NO_3^-$ concentrations and across multiple land use types including streams draining urban, agricultural, and forested watersheds across the US and Puerto Rico that were included in the second Lotic Intersite Nitrogen eXperiment (LINX II) [*Mulholland et al*., 2008; *Hall et al*., 2009]. It thus appears that the role of DOC:$NO_3^-$ ratios in aquatic systems may be analogous to the role of substrate C:N ratios in driving N sequestration and organic matter decomposition more generally [*Schlesinger*, 1997; *Strauss and Lamberti*, 2002]. Previous work on N uptake in streams does show that the C:N ratio of various types of decomposing organic matter in the stream channel can also affect N uptake. For example, *Dodds et al*. [2004] saw greater N retention and N uptake in high C:N aquatic compartments (i.e., woody debris, leaf litter, and detritus). Our increase in $NO_3^-$ uptake efficiency with increasing DOC:$NO_3^-$ ratios suggests that carbon-nitrogen interactions in



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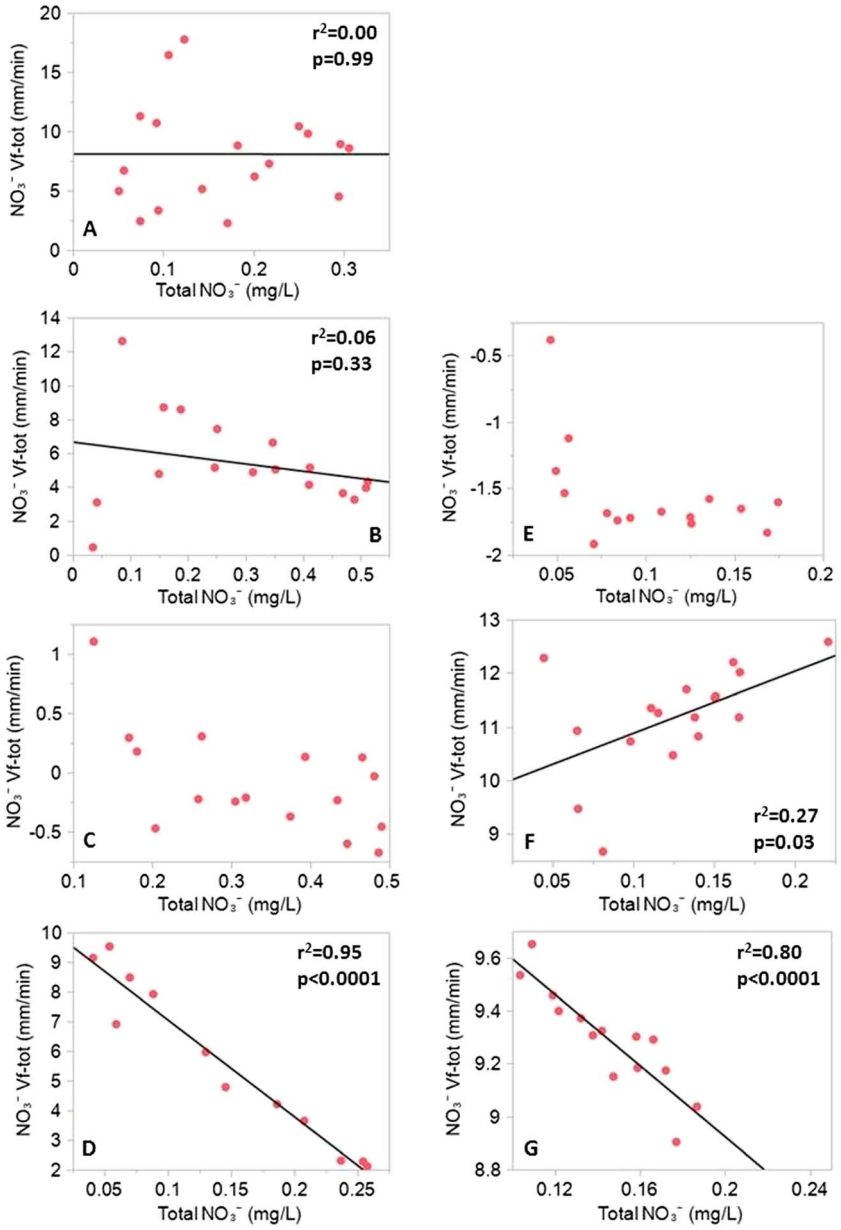


**Figure 4.** Individual experimental dynamic uptake velocities ($V_f$) from $NO_3^-$ TASCC additions for all the experiments at Dowst-Cate Forest (DCF) for (a) May 2013 ($Y = 8.09 - 0.06x$), (b) July 2013 ($Y = 6.60 - 4.30x$), (c) August 2013, (d) October 2013 ($Y = 10.32 - 32.70x$), (e) July 2014, (f) August 2014 ($Y = 9.72 + 11.57x$), and (g) September 2014 ($Y = 10.26 - 6.72x$).

both the water column and the stream bed can affect N uptake in streams. The cross-biome and land use comparison, as described by the LINX II data set, suggests that the coupling between C and N closely depends on C availability regardless of system type (e.g., temperate, desert, tropical, and steppe) or land use type (i.e., forested, agricultural, and urban).

The general negative correlation between ambient $NO_3^-$ uptake velocity and $NO_3^-$ concentrations is similar to results found in previous studies, in which $NO_3^-$ uptake velocity reaches saturation and thereby decreases the ability of the microbial community to take up more $NO_3^-$ [*Dodds et al.*, 2002; *Earl et al.*, 2007; *O'Brien et al.*, 2007; *Covino et al.*, 2010]. The negative correlation observed in this study between ambient $V_f$ and $NO_3^-$ concentrations is also consistent with patterns observed across biomes and land uses [*Mulholland et al.*, 2008; *Hall et al.*, 2009]. Although these studies encompass streams from various biomes across the U.S. and Puerto Rico, our study streams were individual tributaries that drained largely forested watersheds with



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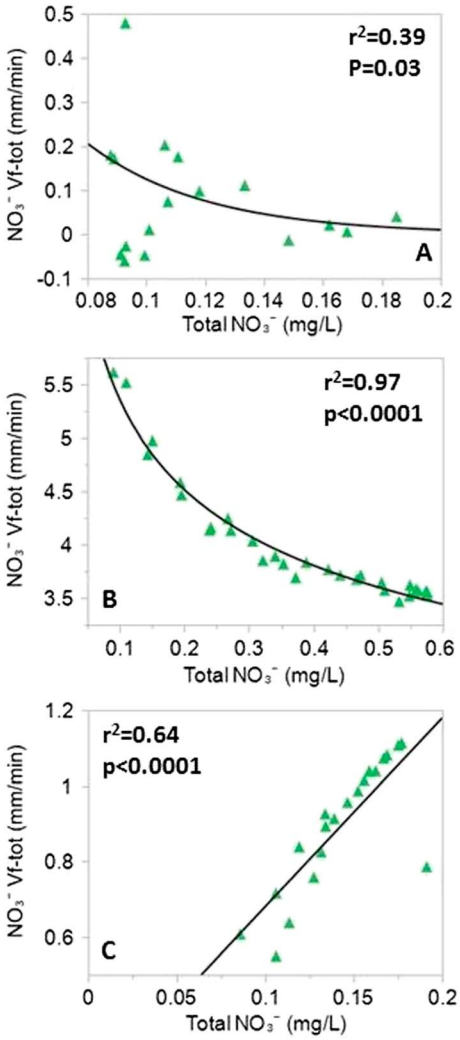


**Figure 5.** Individual experimental dynamic uptake velocities ($V_f$) from $NO_3^-$ TASCC additions for all the experiments at Rum Brook (RMB) for (a) July 2014 ($\log Y = 0.42 - 25x$), (b) August 2014 ($\log Y = 1.11 - 0.25 \log x$), and (c) September 2014 ($Y = 0.18 + 4.99x$).

relatively low light levels in a single drainage basin. Our results demonstrate that $NO_3^-$ concentration is not the best predictor for $NO_3^-$ uptake across streams that are otherwise similar in many respects. Although $NO_3^-$ is not the best predictor for $NO_3^-$ uptake, lower efficiency of $NO_3^-$ removal from the water column was seen under higher $NO_3^-$ conditions in the Lamprey River Watershed. This is similar to *Ribot et al.* [2013] where high N sites promoted lower uptake efficiency of $NO_3^-$. High DIN concentrations could promote saturation of assimilative processes [*O'Brien et al.*, 2007] thus reducing the ability to take up $NO_3^-$.

Our ambient $V_f$ values ranged between 0.05 and 12.65 mm/min and coincide with values reported in earlier studies (0.0001 to 54 mm/min) [e.g., *Ensign and Doyle*, 2006; *O'Brien et al.*, 2007; *Mulholland et al.*, 2008; *Hall et al.*, 2009; *Hoellein et al.*, 2012]. Our values also agree but fall within the lower range of values reported by other studies using the TASCC method [*Covino et al.*, 2010, 2012; *Arce et al.*, 2014; *Wollheim et al.*, 2014; *Gibson et al.*, 2015] with ambient $V_f$ values ranging between 0.10 and 39.4 mm/min. Our ambient areal uptake ($U$) values (0.0012 and 0.912 $\mu g\, m^{-2}\, min^{-1}$) are within the lower end of earlier studies (0.007–75,000 $\mu g\, m^{-2}\, min^{-1}$) [e.g., *Ensign and Doyle*, 2006; *O'Brien et al.*, 2007; *Mulholland et al.*, 2008; *Hall et al.*, 2009; *Rasmussen et al.*, 2011; *Sudduth et al.*, 2011] as well as other TASCC studies (2.36–28,920 $\mu g\, m^{-2}\, min^{-1}$) [*Arce et al.*, 2014; *Wollheim et al.*, 2014] . The efficiency of the microbial community to take up $NO_3^-$ is rather low in our streams. However, when uptake rates are standardized by velocity and depth, (i.e., areal uptake, $U$), overall uptake appears to be relatively low which can be associated with the generally low $NO_3^-$ concentrations in these headwater streams of the Lamprey River Watershed.

### 4.2. Spatial Variability in Dynamic $NO_3^-$ Uptake Kinetics

Our data conformed to several accepted models of uptake kinetics. Most experiments across sites and dates exhibited saturation kinetics or efficiency loss, where uptake velocity decreases with increasing $NO_3^-$ concentrations, as seen in many earlier studies [*Stream Solute Workshop*, 1990; *Dodds et al.*, 2002; *Mulholland et al.*, 2002; *Earl et al.*, 2007; *O'Brien et al.*, 2007; *Hall et al.*, 2009; *Covino et al.*, 2010; *Ribot et al.*, 2013]. In some experiments, however, we observed an unusual increase in uptake velocity at higher $NO_3^-$ concentrations. There is no clearly established mechanism to explain this increase in uptake efficiency at high $NO_3^-$ concentrations, but *Covino et al.* [2012] found that a stream with chronic N inputs exhibited a decrease in uptake length (length a molecule travels before being intercepted by the benthos) with higher added N concentrations. They attributed the decreasing uptake lengths to a fertilization effect,



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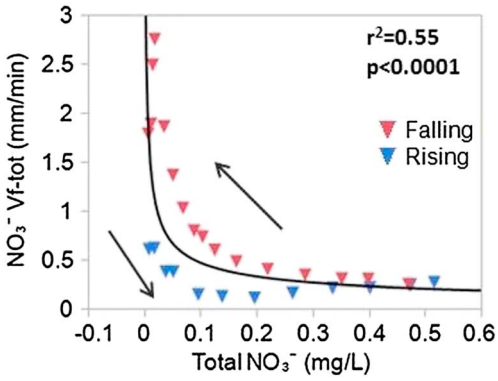


**Figure 6.** Individual experimental dynamic uptake velocities ($V_f$) from a $NO_3^-$ TASCC addition at Saddleback Mountain (SBM) in July 2014 ($\log Y = -1.95 - 0.52 \log x$) showing counterclockwise hysteresis. Blue triangles denote rising limb and red triangle the falling limb of the break through curve.

where the increased loading of N increased the retention capacity and caused changes in biological community structure (i.e., increased biomass and metabolic activity) resulting in an increase in uptake at high concentrations. We also observed this potential fertilization effect in the stream with the highest ambient concentrations of $NO_3^-$ (WHB) which has been termed the biostimulation model [*Diemer et al*., 2015]. Similar to *Covino et al*. [2012], WHB has a history of chronic $NO_3^-$ inputs from the surrounding landscape which could cause the microbial community to have adapted to high $NO_3^-$, and it thus may be able to take up $NO_3^-$ during a sudden nutrient pulse. However, we also observed biostimulation in both DCF and RMB (Figures 4f and 5c) which are low-$NO_3^-$ streams and are similar to the stream conditions where *Diemer et al*. [2015] observed biostimulation. These DCF and RMB patterns suggest that the mechanisms behind biostimulation may be complex and might be related to the large addition of nutrients that occur during a TASCC addition. Background $NO_3^-$ concentrations as well as antecedent $NO_3^-$ data collected at a fine resolution demonstrated that there are no clear precursor conditions that are particularly conducive to biostimulation. This biostimulation trend has received very little attention in the literature despite the vast amount of research conducted on N kinetics in streams.

Uptake of $NO_3^-$ was undetectable for several experiments where we saw constant N:Cl ratios (both tracers traveled conservatively) or moderately negative uptake values. *Arce et al*. [2014] and *Gibson et al*. [2015] also found a lack of $NO_3^-$ retention in their $NO_3^-$ TASCC additions. Undetectable uptake due to little $NO_3^-$ retention can be a consequence of stream saturation where $NO_3^-$ concentrations reach a level where microbes cannot process additional $NO_3^-$ [*O'Brien et al*., 2007], thus transporting unused $NO_3^-$ downstream. Negative values can also occur when not enough solute is added to increase background concentrations sufficiently in order to detect uptake against ambient variation in background concentrations of N or Cl. Undetectable uptake can also be the consequence of very high discharge that leads to uptake metrics tending toward infinity [*Hall and Tank*, 2003]. Our ambient uptake lengths (Table 3) often exceed the experimental reach length, making quantification of uptake more difficult.

Hysteresis in uptake kinetics reflects the dominance of in-channel hydrologic transport of the solute during the rising limb and the role of transient storage sites during the falling limb [*Gibson et al*., 2015]. Counter clockwise hysteresis demonstrates that the greatest uptake occurs in the falling limb where the added solute has had a longer residence time due to transient storage. In steep mountainous streams like SBM, transient storage zones like small pools dominate the experimental reach. The presence of hysteresis during TASCC additions has received very little attention in the literature (but see *Gibson et al*. [2015]), although it does show considerable promise in elucidating differences in hydrologic characteristics among streams and their biotic implications.

We have demonstrated several different uptake models using $V_f$, but these models can also be similarly interpreted with uptake length ($S_w$). The most common models such as saturation or efficiently loss exhibit increasing uptake lengths with increasing concentrations, which is due to a molecule traveling longer distances before being taken up by the benthic community. Alternatively, biostimulation presents the opposite pattern where $S_w$ decreases with increased concentrations because the added nutrient is quickly taken up by the biota thus causing the molecule to travel shorter distances due to greater demand. These same increasing and decreasing patterns would be mirrored in a hysteresis model, depending on the direction of the hysteresis (i.e., clockwise or counterclockwise) as both increasing and decreasing trends can be found in $S_w$ for one experiment [*Trentman et al*., 2015].



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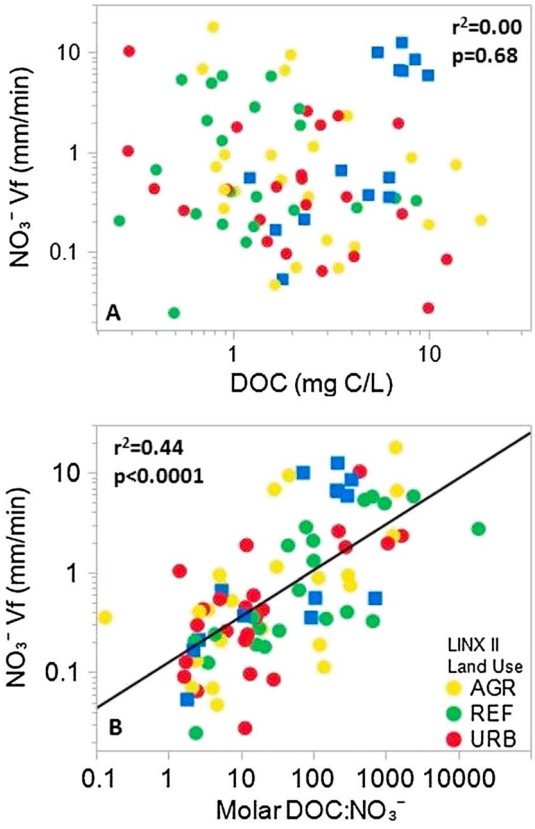


**Figure 7.** Log transformed $NO_3^-$ uptake velocity ($V_f$) and log transformed (a) DOC concentrations and (b) DOC:$NO_3^-$ ratios for LINX II sites (yellow denotes agricultural sites, green denotes reference sites, and red denotes urban sites across the U.S. and Puerto Rico) and data from the Lamprey River Watershed, New Hampshire (blue squares). LINX II data obtained from *Mulholland et al*. [2015].

### 4.3. $NO_3^-$ Uptake Kinetics and Physicochemical Parameters

Contrary to our initial hypotheses, ambient $V_f$ was unrelated to physicochemical parameters, probably due to canopy closure during most of the growing season. Forested headwater streams such as our study sites are considered strongly heterotrophic [*Fisher and Likens*, 1973; *Vannote et al*., 1980; *Hall and Meyer*, 1998; *Hoellein et al*., 2007], and therefore, it is unlikely that $NO_3^-$ uptake would correlate with the parameters controlling autotrophic processes (e.g., light, temperature, and DO). It is possible that for streams in northeast temperate forests, controls on $NO_3^-$ uptake are driven purely by stream chemistry, specifically by DOC concentrations. And while we found no relationships between physicochemical parameters of uptake, the different kinetic models found within a given site demonstrate the potential for temporal variability in nutrient uptake kinetics that should be further explored.

## 5. Conclusion

We have demonstrated the tight linkage between DOC and $NO_3^-$ in streams within the Lamprey River Watershed. Specifically, DOC concentrations are the best predictor and driver of $NO_3^-$ uptake at the local scale, while DOC:$NO_3^-$ ratios seem to be the best at explaining continental-scale variation. Although nutrient addition experiments do not allow clear discrimination among the biological processes responsible for uptake, the loss of $NO_3^-$ from the water column suggests that uptake is potentially due to denitrification or assimilatory processes [*Bernhardt and Likens*, 2002; *Mulholland et al*., 2009]. Our results also provide a potential mitigation strategy to reduce the concentrations and the transport of $NO_3^-$ in streams. Key landscape features like riparian zones or adjacent wetlands can aid in reducing N transport by maintaining carbon inputs into streams, thus increasing $NO_3^-$ uptake and reducing downstream transport. With the likelihood of ongoing urban development in many regions and the potential for increased N loads into streams, it is imperative to better understand how these systems process $NO_3^-$. Uptake kinetics can provide insight into N cycling and transport in streams, especially in how a stream responds to sudden pulses of nutrients. This is of great importance to systems that drain into N-impaired bodies of water like Great Bay in New Hampshire, into which the Lamprey River discharges.

The TASCC method provides a rich data set as well as a quick and cost effective method to characterize nutrient uptake, but it also has presented some potential challenges yet to be explained. For example, ambient uptake metrics are extrapolated from the linear regression between uptake length ($S_w$) and total $NO_3^-$ concentration. This relationship is not always linear or statistically significant. For example, *Trentman et al*. [2015] found positive and negative slopes in the rising and falling limbs of their relationship between $S_w$ and $NH_4^+$ during TASCC additions. This lack of good fit in the linear regression propagates error into the ambient uptake metrics as well as the calculation of total dynamic uptake. Similar issues are associated with calculations of ambient uptake with plateau uptake experiments [e.g., *Payn et al*., 2005]. We found that the TASCC experimental approach



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can be used to document a wide variety of new uptake kinetic models [see *Gibson et al*, 2015], not all of which are adequately understood or documented in the literature (e.g., biostimulation) since they veer away from traditional assumptions of first order and saturation kinetics. With the prospect of this method becoming more popular, it is important to implement best practices for analyzing samples from TASCC experiments. Some laboratory instrumentation cannot handle such wide ranges in concentrations experienced in TASCC additions, and there will be an increasing need for labs to be accustomed to performing analyses on samples with ranges similar to those of pristine to highly impacted systems.

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