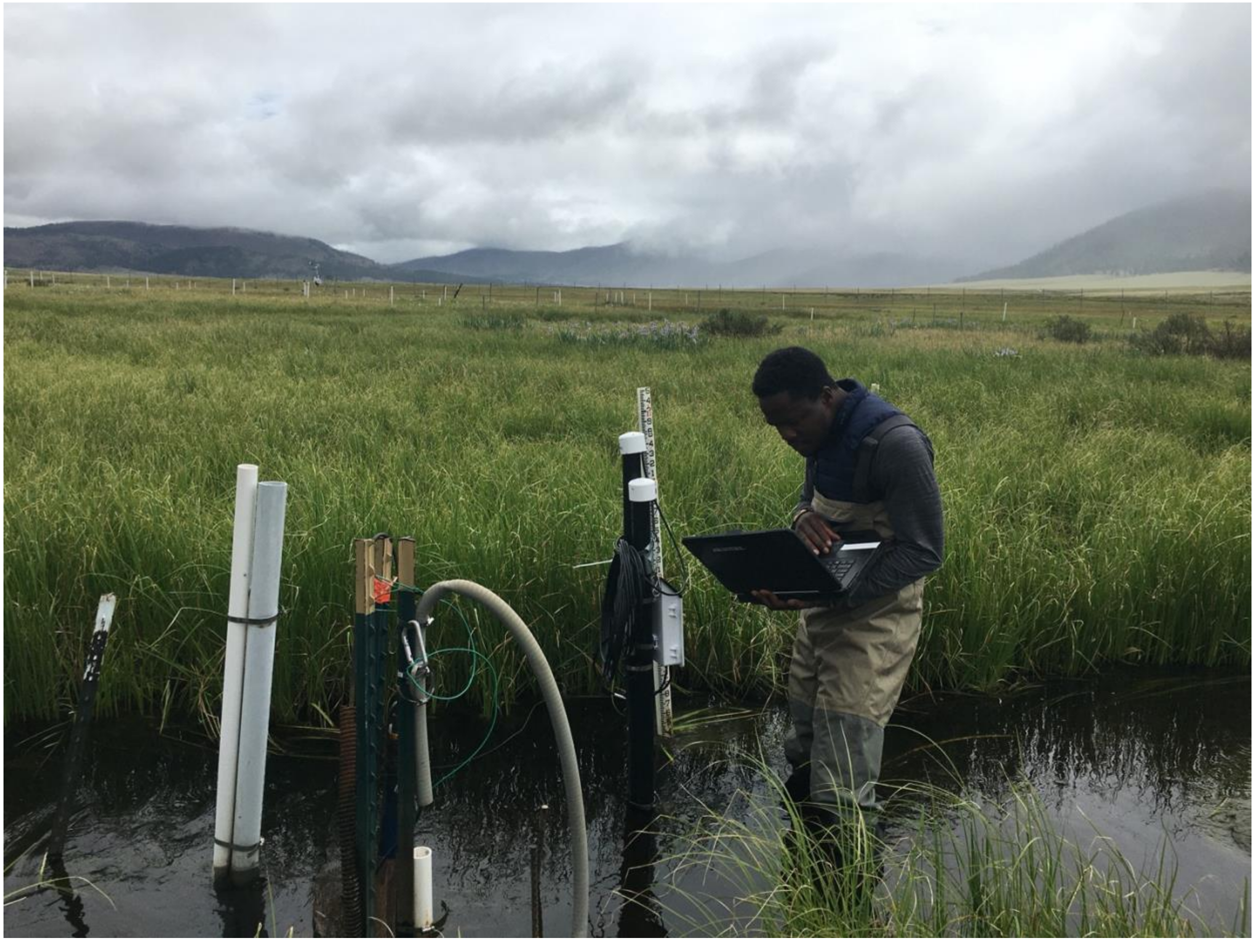
NMWRRI 2020 Final Report

Transport and biogeochemical controls on nutrient retention along stream corridors



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Problem Statement and Objectives

The 2018-2020 New Mexico Integrated Water Quality Assessment Report suggests that ~1.2 of the ~7 thousand miles of assessed streams and rivers suffer from nutrient-related impairment (New Mexico Environment Department Surface Water Quality Bureau, 2018). Due to the interconnected, fractal nature of stream networks, these impacts propagate from headwater streams to downstream rivers, lakes, aquifers, and coastal waters that are highly susceptible to nutrient loadings. Complex transport and biogeochemical dynamics influence the fate of nutrient loadings, and most of the nutrient reactions occur in a biolayer called the hyporheic zone, which is found below the surface of the streambed (Knapp, González-Pinzón, and Haggerty 2018; Li et al. 2017; Harvey, Judson W., Gooseff 2015). This zone is a rich site of surface water and groundwater interaction where organics accumulate, diverse microbial communities flourish, and complex redox zonation occurs (Battin et al. 2016). Due to the complexity of the synchronous transport and reaction processes taking place in the hyporheic zone, decoupling them is challenging and limits our understanding of when, where and why streams sometimes behave effectively as pipes and other times as reactive lagoons. Furthermore, solute-specific analyses dominate the existing literature, disregarding the significance that stoichiometric controls may have on the biological uptake of nutrients.

This study aims to address two research questions: 1) How do resource supply and stoichiometric limitations influence the efficiency of nutrient uptake in stream ecosystems? And 2) how do complex transport dynamics and biogeochemical reactions limit nutrient uptake? We achieved this goal by conducting four sets of nutrient addition experiments combining the conservative tracer chloride (as sodium chloride) to reactive tracers injections, creating cocktails of N (as $NaNO_3$), C (as $C_2H_3NaO_2$), and P (as KH_2PO_4) following the Redfield ratio of 106C:16N:1P. We present a combined method result to provide a synchronized perspective on the interactions of hydrologic exchange and stoichiometric demands/limitations to determine the relative contribution of each in controlling nutrient retention as observed at the stream reach scale.

Methods

Site location

This study was conducted at the Catalina-Jemez Critical Zone Observatory (CJCZO) on the East Fork Jemez River (EFJR). The EFJR is a snowmelt-driven stream that originates in a coniferous forest of approximately 350 km^2 in the Valles Caldera National Preserve (VCNP). The East Jemez River flows as a 1st order stream for approximately 6.5 km. The river transitions to a 2nd order stream for 3 km until the confluence with Jaramillo Creek, where it continues as a 3rd order stream until the confluence with the San Antonio Creek, ~18 km downstream (Summers et al. 2020). Elevations within the CJCZZO range from 2300 m to 3050 m (see Figure 1) and precipitation between 480-850 mm/y. Mean air temperature is 6°C, discharge between 100-2000 L/s, and water quality parameters ranges of 0.04-022 mg/L for NO3, 6.5-9.0 for pH, 0.1 to 5.5 mg/L for Cl, and 1.6-8.8 mg/L in DOC.

Nutrient Enrichment Injections and sampling

A total of four nutrients enrichment injections were conducted. Each of nutrient injections included the co-injection of the conservative tracer sodium chloride (NaCl) and the combination of C, N, and P. The four nutrient experiments included: nitrate injection (N only), nitrate and carbon (106C:16N), nitrate and phosphorus (16N:1P), and a combination of carbon, phosphorus, and nitrogen (106C:16N:1P). For all of our experiments, grab sampling coupled with live sensor monitoring from tracer breakthrough curves (BTC) measured in the stream main channel was done 320 m downstream from the injection site. For each grab sample, 20 mL aliquots were collected throughout the experiment. All samples were filtered immediately after collection using a 0.7 µm GF/F filter (Sigma-Aldrich) and kept frozen at 20º F until it was time to analyze them. All samples were thawed and ran on a Dionex ICS-1100 Ion Chromatograph (IC) using a Dionex IonPac AS23/G23 analytical guard column and a 25-µL injection loop. The IC's setup analytical detection limits were 0.05 mg/L to 15 mg/L for NO_3-N and 0.15 mg/L to 20 mg/L for Cl- (Thermo Fisher Scientific Inc.; Sunnyvale, California). We were unable to detect PO4 on the IC due to low concentrations; therefore, PO4 was not included in the BTC analyses but was used as a known forcing function.

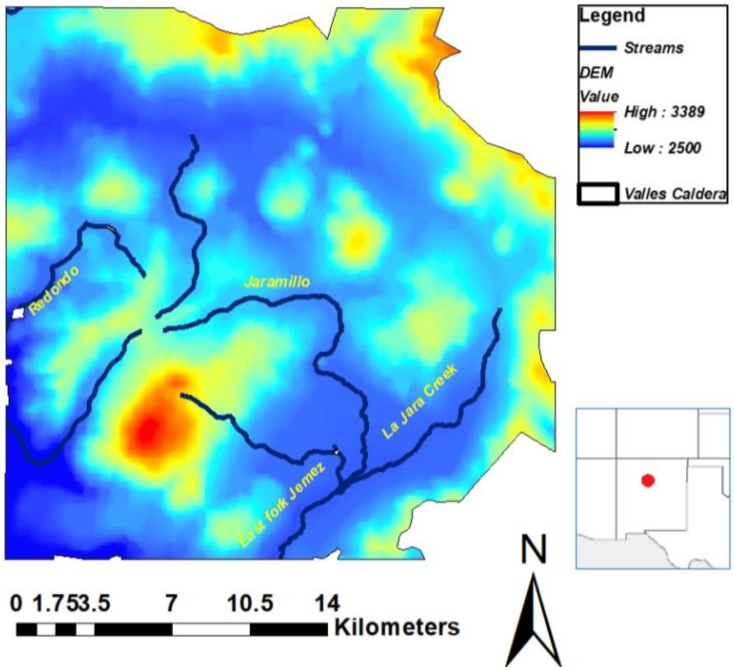

Figure 1. Digital elevation map (DEM) of the Valles Caldera National Preserve along with streams. The values on the DEM are in meters.

Modeling

Solute transport parameters were estimated using the transient storage model (Bencala 1983) with reaction to simulate in-stream transport with hyporheic exchange. We assumed in our model that the hyporheic zone is a single, well-mixed, transient storage zone that undergoes a linear exchange with the main channel. Our model is similar to what was used in Gootman et al., 2020 and Knapp et al., 2017. The governing equation for the TSM are:

$$\frac{\partial c_i}{\partial t} + R_i A_{rel} \frac{\partial c_{hz,i}}{\partial t} + v \frac{\partial c_i}{\partial x} - D \frac{\partial^2 c_i}{\partial x^2} = A_{rel} r_{hz,i} + q_{in}(c_{in,i} - c_i) \quad (1);$$

$$R_i \frac{\partial c_{hz,i}}{\partial x} = k_i(c_i - c_{hz,i}) + r_{hz,i} \quad (2);$$

where c_i is the tracer concentration of compound i in the stream channel, $c_{hz,i}$ is the concentration in the hyporheic zone, v is the advective in-stream velocity, D the dispersion coefficient and R_i is compound-specific retardation factor in the hyporheic zone. A_{rel} represents the dimensionless ratio between the area of the hyporheic zone and the main channel, k_i is the mass-transfer rate coefficient for the exchange between the main channel and the hyporheic zone. $q_{in}(s^{-1})$ is the dilution factor; $c_{in,i}$ is the concentration of ground water inflow. We assumed $c_{in,i} = 0$ for all tracers. $r_{hz,i}$ is the reaction of compound i in the hyporheic zone following a first-order (linear) reaction kinetics:

$$r_{hz,i} = -\gamma_{1,hz} c_{hz,1} \quad (3);$$

with the reaction coefficient $\gamma_{1,hz}$ describing the uptake of nitrate. For an instantaneous injection:

$$c_i(x, t = 0) = c_{hz,i}(x, t = 0) = 0 \ \forall x \quad (4);$$

$$\left(vc_i - D\frac{\partial c_i}{\partial x}\right)|_{x=0} = \frac{M_i}{A}\delta(t) \quad (5);$$

$$\lim_{x \to \infty} c_i(x, t) = 0 \ \forall t \quad (6).$$

where M_i is the mass injected for tracer i and A is the area of the reach.

Calculating uptake parameters

Based on our simulated results, uptake parameters were calculated using the Tracer Addition for Spiraling Curve Characteristics (TASCC) (Covino, Mcglynn, and Mcnamara 2010) to estimate nitrate uptake dynamic for each tracer breakthrough curve. The TASCC method allows for rapid investigation of in-stream nutrient metrics and nutrient concentrations across the tracer breakthrough curve to quantify uptake kinetics (Covino, Mcglynn, and Mcnamara 2010). Prior to the development of TASCC, uptake kinetics were often quantified by using multiple continuous injections with different steady-state conditions (e.g., Dodds et al., 2002; Ensign & Doyle, 2006; P. J. Mulholland et al., 2002). Uptake length (S_w), uptake velocity (V_f) and uptake rate (U) from each pair of co-sampled conservative (i.e., Chloride) and reactive (e.g., nitrate) concentrations across the breakthrough curves observed in each experiment are calculated as:

$$S_{w\,NO_3-N} = -\frac{L}{k_w} \quad (7);$$

$$V_{f\,NO3-N} = \frac{Q}{S_{w\,NO_3-N} * w} \quad (8);$$

$$U = \frac{Q * C_{NO_3-N_{obs}}}{S_{w\,NO_3-N} * w} \quad (9);$$

where L is the length of the sampling distance, Q is the flow rate along the reach, and w is the reach's width. $k_w[L^{-1}]$ is the longitudinal uptake rate and is calculated as:

$$k_w = \left[\ln\left[\frac{C_{NO_3-N_{obs}}}{C_{Cl_{obs}}}\right] - \ln\left[\frac{C_{NO_3-N_{inj}}}{C_{Cl_{inj}}}\right]\right] \quad (10).$$

The subscript 'obs' is the background corrected observed concentrations, and 'inj' is the injectate's concentration.

Damköhler number analysis

To decouple transport and stoichiometric processes, we used the Damköhler number ($D_a[-]$). The Damköhler number is calculated as a function of the hyporheic residence time ($\tau_{hz}[h]$) and the total transformation rate coefficient ($\lambda_1[h]$).

$$D_a = \tau_{hz}\lambda_1 \quad (11)$$

The mean hyporheic zone residence times for the study reach, τ_{hz} (s), were determined from the inverse of the fitted transient storage model first-order exchange rate coefficient, k (s^{-1}):

$$\tau_{hz} = \frac{1}{k} \quad (12)$$

The ideal value for D_a must be near or equal to one, which indicates a balance between transport and reaction timescales. For $D_a \ll 1$, nutrient processing is suboptimal and can be classified as reaction limited. Similarly, if $D_a \gg 1$, nutrient processing is suboptimal and is transport limited (González-Pinzón, Haggerty, and Myrold 2012).

Results and Discussion

Breakthrough curve simulation

A total of eight tracer breakthrough curves were simulated using the transient storage model. Results from our simulations showed a regression value (R) between 1.64 and 1.00. The root-mean-square errors of our simulations were between 0.001 and 0.000 for all the fitted breakthrough curves (see Table 1). Minor differences were observed in the transport parameters (e.g., advective velocity) for all injection experiments, except the stoichiometrically balanced C:N:P tracer experiment. Based on the minor changes in transport parameters, we can assume that differences in transport across experiments had less of an impact on nutrient uptake during our study.

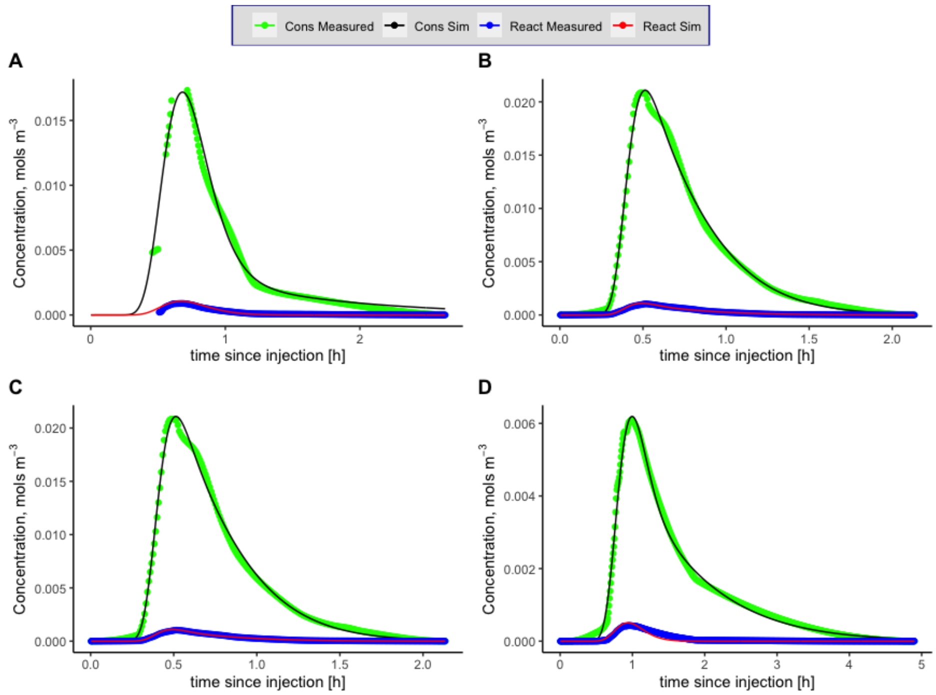

Figure 2. Tracer BTCs of measured (dotted) and best models fit simulations (lines) based on the transient storage model for A) N injection, B) NC injection, C) NP injection, and D) CNP injection.

Nutrient uptake across injection

We observed strong differences in the distribution of the uptake velocity. For example, the N and CNP injections show a broader range of uptake velocity relative to the median value than the NP and NC injection, where much of the uptake values are closer to the median (see Figure3). These differences in the distribution of the uptake velocity can be attributed to the high the higher uptake values during the N and CNP.

Stoichiometry plays an essential role on nutrient uptake as it defines and mediates transport and reaction-limited conditions, i.e., it opens the notion that high or fast hydrologic exchange does not guarantee adequate supply (e.g., transport limitation could be caused by nutrient limitation regardless of mass exchange rates) and that reaction-limitation could be caused by the inability of microbial communities to take up substances or grow due to stoichiometric imbalances. Considering the N injection as our reference case (thus, the dotted line in Figure 3), we can observe from Figure 3 that both the NC and NP injections fall below our reference point while the stoichiometrically balanced injection experiment with ratios of 106C:16N:1P led to a significant increase in nutrient uptake. The increase seen in the CNP injection has been reported in other studies and has been found to result from microorganisms in natural systems dependence on the ratios of these key macronutrients.

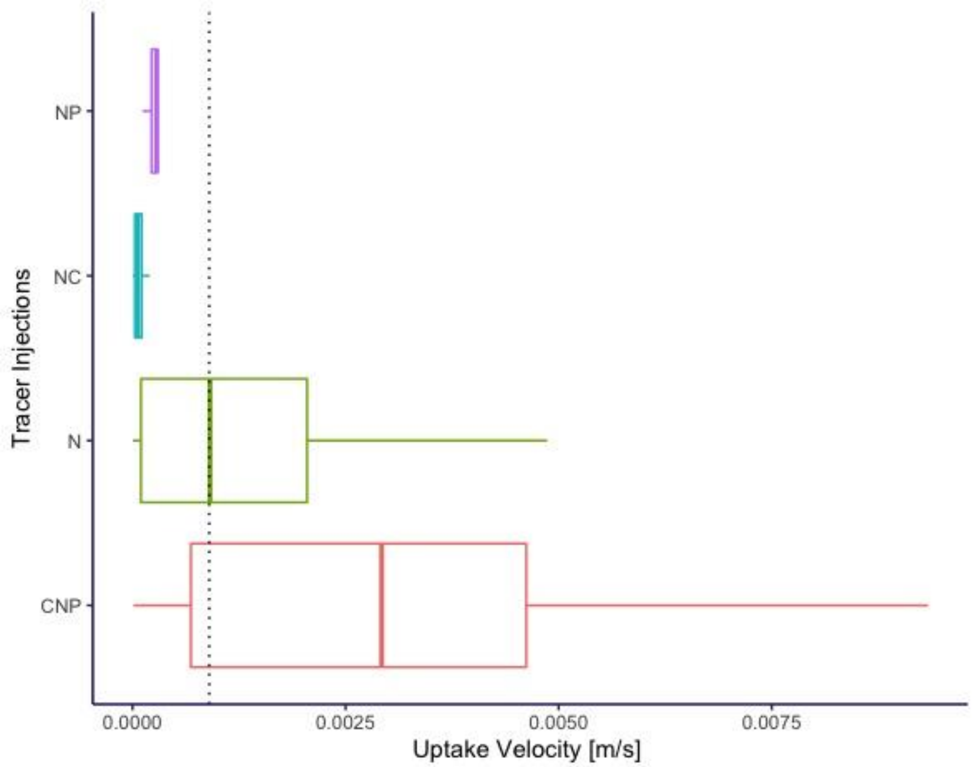

Figure 3. Boxplot of uptake velocities for the four tracer injection experiments. The dotted line is to show the median uptake velocity value of our reference case (N injection).

Overall nutrient uptake pattern

For all our experiments, the nutrient retention efficiency (i.e., high uptake velocity and low uptake length) decreased with total nutrient concentration, respectively (Figure 4A and C). Overall regression slopes for all uptake metrics show a hysteresis behavior. For example, the loop shown in Figure 4B shows that uptake rates both increase and decreases across the tracer breakthrough curve. For uptake velocity, we noticed that the early part of the hysteresis loop (Figure 4C) follows more of a linearly decreasing trend compared to the exponential behavior observed in the latter part of the loop. These differences in the rising and falling limbs creates a hysteresis loop that follows a clockwise behavior and can be observed for all injection experiments (i.e., N, NC, NP, and CNP). Several studies (e.g., Covino et al., 2010; Li et al., 2020) have suggested using a variable travel time approach to address these hysteresis behaviors; however, due to the scope of this study, we assumed that this approach would not lead to increase interpretation of the metrics. The alternative to the variable travel time approach would be to use only the falling limb of the tracer breakthrough curve. While this approach will eliminate the hysteresis pattern we observed, we could lose information relative to biological nutrient uptake in our study reach. Our experiments assumed that calculated solute-specific uptake rates were not sensitive to abiotic sorption (Covino et al., 2010) because we did not use NH_4^+. Therefore, the increase in nutrient uptake during the falling limb is primarily due to abiotic factors such as hyporheic flow paths which affects the velocity of the solute parcel moving through the subsurface, leading to differences in contact time between the solute and the streambed sediment during the rising and falling limbs. Uptake observed in the rising limb is mainly influenced by biological activities.

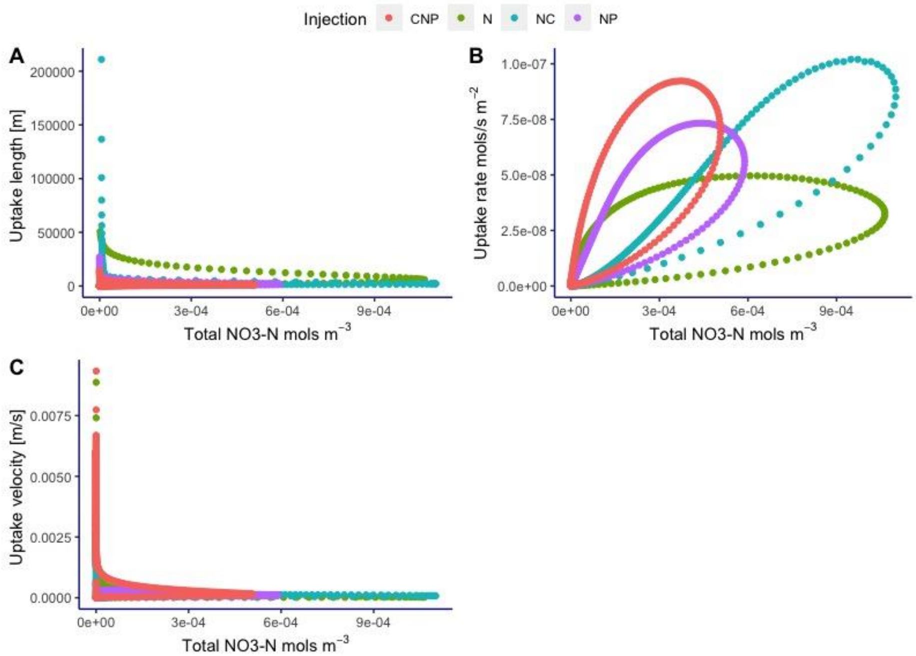

Figure 4. Uptake metrics plotted as a function of total NO_3-N concentration for A) uptake length, B) uptake rate, and C) uptake velocity.

Damköhler analysis

We were able to decouple the effect of transport and stoichiometric processes on nitrate uptake using the non-dimensional Damköhler number [-]. Low Damköhler number ($D_a \ll 1$) values were observed during the NP and NC injections, while higher values of the Damköhler number ($D_a \gg 1$) were observed during the N and CNP injections. While the type of limitation (transport vs. reaction) correlates closely with the uptake velocity values in Figure 3, we cannot make a definitive statement to these correlations as it could lead to sporous correlations. However, we recommend that a similar experiment be conducted across varying discharge conditions. This result highlights the importance of stoichiometric conditions in controlling reach-scale metabolism and its complexity.

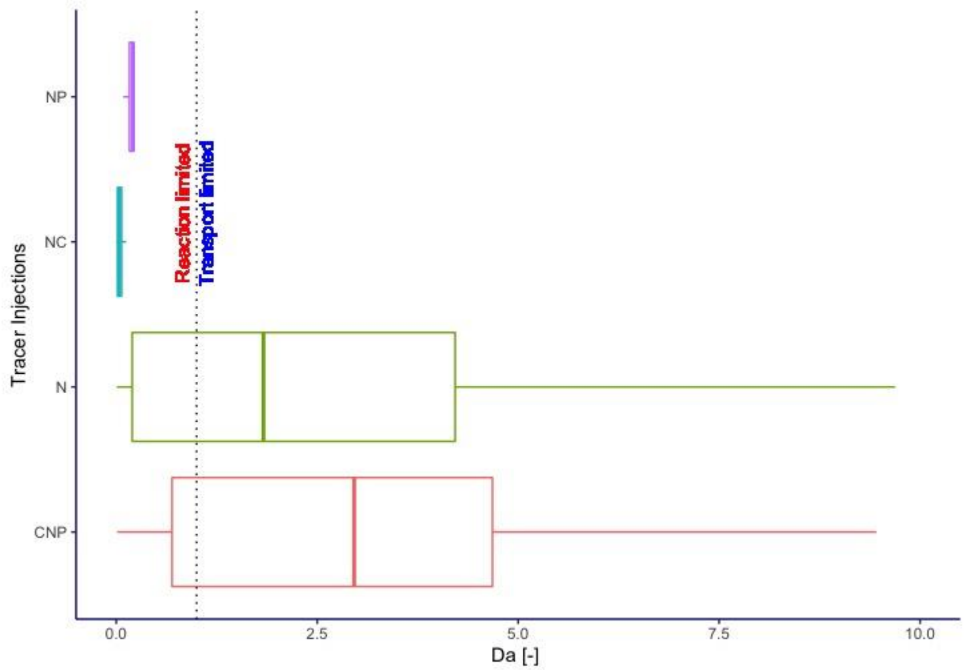

Figure 5. Damköhler numbers (D_a) compared across nutrients injections. Reaction-limited conditions were observed for the NC and NP injection, while transport limited conditions is observed for the N and CNP tracer injection experiments.

<u>Conclusions</u>

This study aimed to address two research questions: 1) How do resource supply and stoichiometric limitations influence the efficiency of nutrient uptake in stream ecosystems? And 2) how do complex transport dynamics and biogeochemical reactions limit nutrient uptake? We conducted four sets of nutrient addition experiments combining the conservative tracer chloride (as sodium chloride) to reactive tracers' injections, creating cocktails of N (as $NaNO_3$), C (as $C_2H_3NaO_2$), and P (as KH_2PO_4) following the Redfield ratio of 106C:16N:1P to address these questions. Our results showed that nitrate uptake was more efficient when the ideal stoichiometric ratio of 106C:16N:1P was injected into the stream.

For our overall trend in nitrate uptake metric across injection experiments, we observed a hysteresis behavior. For all these metrics, higher uptake of nitrate was observed in the falling limb of the tracer BTC compared to the rising limb. Therefore, we can conclude that this is primarily due to abiotic factors such as hyporheic flow paths affecting the velocity of the solute parcel moving through the subsurface, leading to differences in contact time between the solute and the streambed sediment while uptake in the rising limb can be attributed to biological processing of nitrate.

Who will benefit from your research results?

The results generated from this project can provide a means to evaluate previously unexplored solutions to restoring impaired streams, rivers, and lakes via stoichiometric manipulations. Stream restoration is the most prominent area (a multi-billion-dollar industry) of applied water-resource science but is mainly focused on physical alterations such as the creation of pool-riffle sequences. Therefore, findings from this research could also help lower the high cost associated with restoring impaired ecosystems and explore new measures to prevent the impairment of streams and river ecosystems.

How have you spent your grant funds?

Table 1: Proposed budget and actual cost for completing experiment

	Proposed	***Actual***
Salary and Benefits (undergraduate student)	$2440.00	$3050.00
Supplies/equipment/services	3,481.96	$3,327.02
Travels	$1,267.00	$711.94
Total	$7,088.96	$7,088.96

Presentations you have made related to the project.

UNM CWE Mini Conference 2021

Upcoming AGU 2021

Upcoming NM WRRI's 66th Annual New Mexico Water Conference

List publications or reports under preparation.

I plan to work more towards doing more analysis of my results and subsequently submitted my findings to a peer-review journal for publication

List of students assisted you with your project.

Trevor Amestoy, undergrad student in the School of Engineering at UNM. Justin Nichols and Aashish Khandelwal, graduate students in the School of Engineering at UNM.

Special recognition awards or notable achievements because of the research including any publicity such as newspaper articles, or similar.

UNM Civil eNews on July 13,2020 (Link: https://civil.unm.edu/news/2020/07/two-graduate-students-in-dr.-gonzalez-pinzons-team-win-research-grants.html)

Information on degree completion and future career plan.

I expect to graduate in the Fall of 2021. For future career plans, I hope to become a tenure-track professor at a university.

Citations

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