

RESEARCH ARTICLE

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Key Points:

- We observed low biological uptake of nitrate in stream reaches in Rocky Mountain National Park, potentially due to saturation of biological demand
- Due to low in-stream biological uptake, gross gains and losses of water and nitrate to and from the stream exerted primary constraint on nutrient retention
- Nutrient injections and ambient flux data, used in concert, can enhance understanding of stream and valley controls on nutrient retention

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Evaluating Controls on Nutrient Retention and Export in Wide and Narrow Valley Segments of a Mountain River Corridor

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Abstract Over the past few decades, nitrate-nitrogen (NO₃-N) concentrations have increased within streams of the central Rockies, a pattern linked to regional N deposition trends. As NO₃-N concentrations increase, in-stream biological demand may become saturated and stream N export may increase. In mountain landscapes, streams generally flow through steep, narrow valleys with limited riparian area and strong stream-hillslope connectivity. Interspersed between the narrow valleys are wide segments where substantial floodplain riparian areas can develop. Here, we coupled measures of stream reach NO₃-N flux balances with nutrient enrichment experiments along two stream reaches of contrasting valley morphology in Rocky Mountain National Park. The stream reaches were (1) a narrow valley segment with limited floodplain riparian area and (2) a longitudinally adjacent (directly downstream) wide valley segment with extensive floodplain riparian area. We found that in-stream biological uptake of added NO₃-N was limited in both segments, presumably as a consequence of saturating conditions. Assessment of mass flux indicated that the narrow valley segment was a consistent source of water and NO₃-N across flow states, while the wide segment was a sink at high flow and a source at low flow. Due to low in-stream biological retention, gross gains and losses of water and NO₃-N to and from the stream exerted primary constraint on segment mass balances. Our results suggest that the exchange of water and nutrients between the stream and adjacent landscape can exert strong control on reach-scale nutrient export, particularly in streams experiencing or approaching N saturation.

1. Introduction

Mountain environments provide numerous ecosystem services important to humans, and over half the world's population is dependent on water resources from mountain headwaters (Barnett et al., 2005; Debarbieux & Price, 2012). Streams draining the mountains of Colorado supply water resources to at least 5 million people in Colorado and comprise substantial proportions of the headwaters of the Colorado, Platte, and Arkansas River basins. Although mountain environments provide a variety of beneficial services to human populations, they also tend to be sensitive to environmental perturbation (Beniston, 2003).

Historically, mountain headwater systems of Colorado have received chronically low deposition of bioavailable nitrogen (e.g., nitrate-nitrogen, NO₃-N; ammonium-nitrogen, NH₄-N), but a pattern of increasing N deposition on the eastern flank of the Colorado Front Range has been observed since the 1970s (Lewis & Grant, 1980). High-elevation mountain ecosystems, such as those of Rocky Mountain National Park (RMNP), are particularly sensitive to increased N deposition (Baron et al., 2000). The consequences of increased N deposition in RMNP have included changes to terrestrial (Bowman et al., 1993, 2006) and aquatic biota (Wolfe et al., 2003) and increased N concentrations in soils (Bowman et al., 2012), streams (Campbell et al., 1995), and lakes (Baron, 1983; Williams et al., 1996). The observation of increased N concentrations in lakes and streams during the growing season suggests that current N deposition exceeds terrestrial N demand and excess nutrients leak to aquatic ecosystems (Baron et al., 2000; Mast et al., 2014; Williams et al., 1996). This situation, where N supply exceeds N demand, is known as N saturation and has consequences for ecosystem function (Vitousek et al., 1997) and downstream N export (Aber et al., 1998; Dodds et al., 2002; Earl et al., 2006; O'Brien et al., 2007).

Watershed or stream reach NO₃-N export represents the balance between NO₃-N inputs and retention. Hydrologic connectivity between hillslopes and adjacent streams regulates the delivery of water and

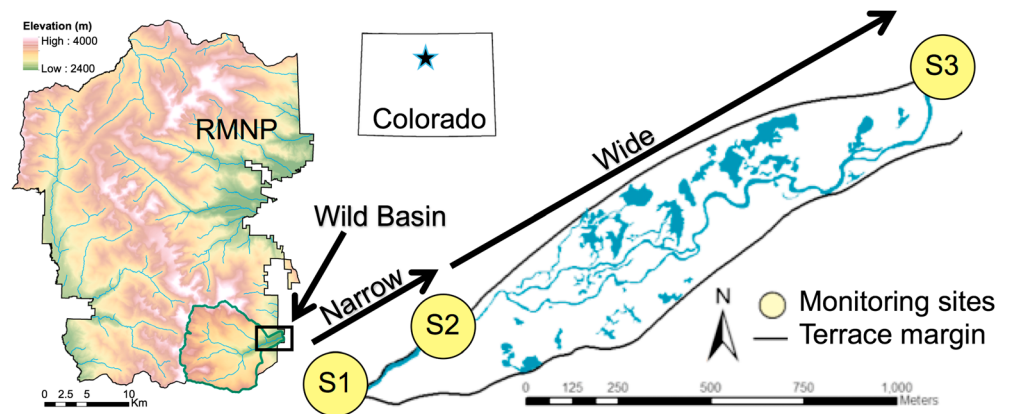


Figure 1. (top middle) Site location in north-central Colorado. (left) Outline of Rocky Mountain National Park (RMNP) and outline of Wild Basin in the southeast corner of RMNP. The continental divide longitudinally transverses RMNP and Wild Basin is situated on the eastern flank of the continental divide. The box at the outflow of Wild Basin indicates our study reaches, which are shown in more detail to the right. (right) Expanded view of stream reaches in Wild Basin. The stream reaches consist of a narrow and a wide valley segment. The wide valley segment is directly downstream from the narrow segment. We present data from stream monitoring sites S1, S2, and S3. S1 and S2 bracket the narrow segment and S2 and S3 bracket the wide segment.

nutrients to the stream network (Jencso et al., 2009; Stieglitz et al., 2003) and sets the initial template of channel network nutrient concentrations. For instance, stream reaches that are strongly connected to their adjacent hillslopes will likely receive greater hillslope loading, while reaches that are less strongly connected to the uplands, due to riparian buffering (Jencso et al., 2010; Pacific et al., 2010), will receive less lateral loading. Subsequent to delivery to the stream network, numerous processes including hyporheic exchange (Battin, 1999; Mulholland, 1997; Zarnetske et al., 2011), stream-floodplain interactions (Junk et al., 1989; Meyer et al., 1997; Tockner et al., 1999), and in-channel biogeochemical processing (Kothawala et al., 2015), control the downstream transport of nutrients.

Streams of RMNP, and in mountain watersheds in general, tend to flow through steep narrow valley segments that are occasionally interrupted by wide, flat valley segments (Wohl & Beckman, 2014). The steep and narrow segments tend to have very limited riparian area, while expansive floodplain riparian areas can develop in the wide segments. Riparian areas in wide valley segments can influence downstream nutrient export through stream-riparian interactions that facilitate nutrient uptake and processing (Battin et al., 2008; Hill, 1996). Additionally, valley width can influence stream-hillslope connectivity because broad riparian

Table 1

Physical Characteristics for the Narrow and Wide Valley Segments of Upper North Saint Vrain Creek in Wild Basin, Rocky Mountain National Park

	Narrow valley segment	Wide valley segment
Catchment area at segment outlet (km ²)	82	84
Average elevation (m)	2560	2540
Average floodplain width (m)	97	254
Average channel width (m)	9.4	8.0
Riparian buffer ratio ^a	0.06	0.28
Valley length (m)	390	1540
Channel confinement	Confined ^b /unconfined ^c	Unconfined ^b /unconfined ^c
Channel gradient (%)	2.5	0.7
Channel sinuosity	1.1	1.4
Channel morphology	Pool-riffle	Pool-riffle

^aRiparian area divided by hillslope area. Riparian and hillslope areas were calculated as the downstream minus the upstream contributing areas for each segment. ^bConfinement as defined by Brierley and Fryirs (2005), in which a channel is confined if >90% of the channel length contacts a confining feature (i.e., terrace) and unconfined if <10% of the channel length contacts a confining feature. ^cConfinement as defined by the ratio of channel width to floodplain width, in which a channel is confined if the floodplain width is less than twice the channel width, and unconfined if the floodplain width is over 8 times the channel width.

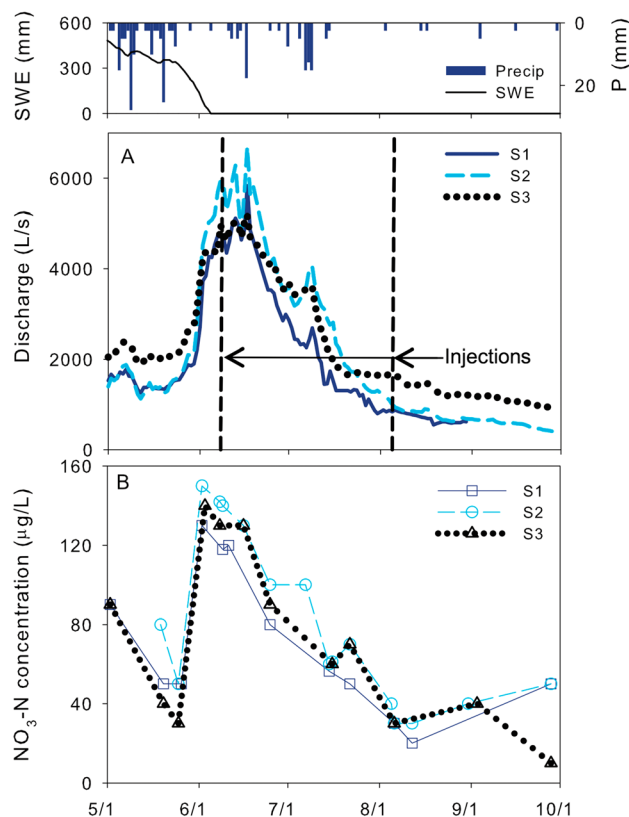


Figure 2. (top) Precipitation (P) and snow water equivalent (SWE) with (a) daily mean discharge and (b) ambient nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations at S1, S2, and S3 from May to October 2015. S1 and S2 bracket the narrow segment, and S2 and S3 bracket the wide valley segment. The vertical lines in Figure 2a indicate timing of high (8–9 June) and low flow (5–6 August) injection experiments.

areas of wide valley segments can interrupt stream-hillslope connections, thus buffering hillslope nutrient delivery to the stream (McGlynn & Seibert, 2003). As such, floodplain riparian areas have the potential to buffer downstream export through lateral stream-riparian interaction and diminished hillslope nutrient delivery to the stream. For these reasons, wide valley segments may be important locations of nutrient retention in mountain environments. Given the increased N deposition in portions of the Colorado Rockies, including RMNP (Bowman et al., 2012), understanding nutrient retention in these landscapes is required for mitigating potential ecological and water quality impacts.

Experiments that quantify stream nutrient retention typically involve injecting nutrients into the stream and quantifying the loss of that nutrient at a downstream sampling point (Stream Solute Workshop, 1990). Injection studies reflect in-stream (Triska et al., 1989) and hyporheic (Mulholland et al., 1997) nutrient uptake and provide information on the ability of the stream to retain nutrient inputs (Peterson et al., 2001). In addition to nutrient injection experiments, nutrient mass balances can be used to evaluate watershed (Bormann & Likens, 1967; Hetherington, 1984) or stream reach (Roberts & Mulholland, 2007) nutrient export and incorporate stream connections to hillslopes, riparian areas, and the watershed. We used nutrient injection experiments and stream-valley segment flux balances to evaluate in-stream and valley controls on nutrient retention along two morphologically contrasting, but longitudinally adjacent, segments of North Saint Vrain (NSV) Creek, RMNP.

2. Study Site

This research occurred during May–October 2015 along Upper NSV Creek, which drains the 88 km² Wild Basin Watershed (40°13'N, 105°32'W; Figure 1). Wild Basin is located above a Pleistocene glacial

moraine in the southeast corner of RMNP, Colorado, and overlies predominantly Precambrian biotite schist and granite bedrock (Braddock & Cole, 1990). Upland vegetation consists of Engelmann spruce (*Picea engelmannii*), subalpine fir (*Abies lasiocarpa*), and lodgepole pine (*Pinus contorta*), and valley bottom vegetation includes quaking aspen (*Populus tremuloides*), dense stands of willow (*Salix* spp.), and other riparian shrubs. In 2015, mean annual temperature was 6 °C, with a summer average of 15 °C and a winter average of 1 °C. Total precipitation in 2015 was 813 mm with 64% (519 mm) in the form of snowfall (snow telemetry, #412). A persistent snowpack is typical in higher elevations of the watershed and extended from October 29 to June 5 in 2015 (Wild Basin snow telemetry, #1042, 2914 m). Melting of the snowpack drives the NSV hydrograph, which typically rises to peak flows in June and recedes to baseflow by late summer or early autumn. The portions of NSV we studied were (1) a pool-riffle sequence that flows through a moderately sloped, narrow valley directly followed by (2) a low-gradient, wide valley bottom with extensive floodplain riparian areas (Figure 1 and Table 1). The two segments are longitudinally adjacent but vary substantially with respect to valley width, channel slope, floodplain riparian area, and channel planform complexity (Table 1).

3. Methods

3.1. Stream Physical and Chemical Characteristics

We placed three stream monitoring stations, “S1,” “S2,” and “S3” at the inflows and outflows of the narrow and wide segments, so that S1 and S2 bracket the narrow segment and S2 and S3 bracket the wide segment (Figure 1). At each monitoring station, we measured stream stage and water temperature at 15-min intervals from May to October 2015 using capacitance rods (TruTrack Inc., Christchurch, New Zealand) with ±1-mm precision.

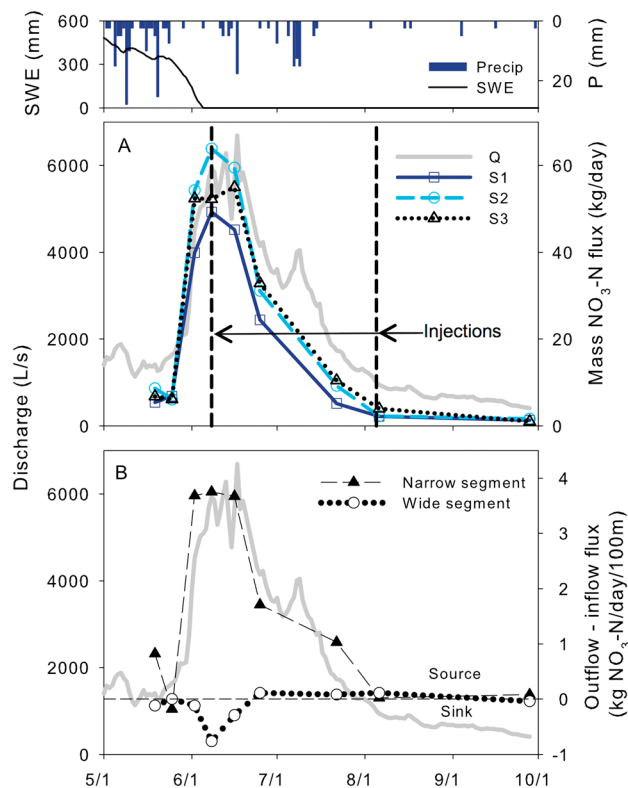


Figure 3. (top) Precipitation (P) and snow water equivalent (SWE) with (a) daily mean discharge (Q) at S2 and ambient nitrate-nitrogen ($\text{NO}_3\text{-N}$) fluxes at S1, S2, and S3, and (b) daily mean discharge (Q) at S2 and ambient $\text{NO}_3\text{-N}$ flux balances for the narrow and wide valley segments. The vertical lines in Figure 3a indicate the timing of high flow (8–9 June) and low flow (5–6 August) injection experiments. Segment balances in Figure 3b are given per 100 m of valley length to account for differences in total length between the segments.

discharge. For instance, the narrow valley segment water balance was calculated as flow at S2 minus flow at S1. For $\text{NO}_3\text{-N}$, we calculated flux as the product of grab sample $\text{NO}_3\text{-N}$ concentrations and sampling location discharge. Net segment $\text{NO}_3\text{-N}$ flux balances were determined as the difference between flux measured at segment outflow minus inflow. We calculated segment $\text{NO}_3\text{-N}$ flux balances for nine dates where inflow and outflow were sampled simultaneously. Positive values indicate that the segment was a net source of water or $\text{NO}_3\text{-N}$, while negative values indicate that the segment was a net sink. Flux balances for each segment were divided by segment valley length, or the length of a straight line running in the down-valley direction (Table 1), to account for differences in valley length.

3.3. Stream Nutrient Injection Experiments

We performed stream nutrient injection experiments during high flows ($5 \text{ m}^3/\text{s}$) from 8 to 9 June and low flows ($1 \text{ m}^3/\text{s}$) from 5 to 6 August along the narrow and wide valley segments of NSV. For each experiment, we instantaneously coinject NaCl and Potassium nitrate (KNO_3) at the segment inflow (S1 for the narrow segment and S2 for the wide segment; Figure 1) and quantified Cl and $\text{NO}_3\text{-N}$ concentrations at the segment outflow (S2 for the narrow segment and S3 for the wide segment; Figure 1). At the downstream sampling locations (segment outflows) we recorded real-time (2-s) conductivity breakthrough curves using Campbell 547A conductivity and temperature probes attached to Campbell CR1000 data loggers (Campbell Scientific Inc., Logan, UT). Using real-time conductivity data to guide sample collection, we collected stream water grab samples across the conductivity breakthrough curves, filtered the samples in the field through $0.7\text{-}\mu\text{m}$ glass fiber filters (GF/F Whatman International, Ltd., Maidstone, UK) into acid-washed and stream-rinsed 125-mL high-density polyethylene bottles, and froze the samples until analysis. Samples were analyzed for chloride

Once a week, we used velocity area (Dingman, 2002) or dilution gauging (Kilpatrick & Cobb, 1985) approaches to measure discharge at S1, S2, and S3 across flow states. During dilution gauging, we injected dissolved sodium chloride (NaCl) 50 to 75-m upstream of the measurement site (i.e., a mixing length). At the measurement site, we recorded specific conductivity (SC) at 2-s intervals prior to the injection of NaCl to determine background concentrations, through the arrival of NaCl, and after the stream returned to background conditions. We used an empirical calibration to convert SC to NaCl concentrations and determined discharge (Q) from equation (1):

$$Q = \frac{\text{NaCl}_{\text{MA}}}{\int_0^t \text{NaCl}_c(\tau) d\tau} \quad (1)$$

where NaCl_{MA} is the mass of NaCl added to the stream and NaCl_c is the background corrected NaCl concentration through the breakthrough curve. Using weekly discharge data, we developed rating curves between stage and discharge to transform continuous (i.e., 15-min) stage data to a continuous discharge time series.

At S1, S2, and S3, we collected grab samples ($n = 12$ at S1 and S3, $n = 15$ at S2) at weekly to monthly intervals from mid-May to October. We field-filtered each sample through $0.7\text{-}\mu\text{m}$ glass fiber filters (GF/F Whatman International, Ltd., Maidstone, UK) into acid-washed and stream-rinsed 125 mL high-density polyethylene bottles, placed into a dark cooler, and kept frozen until analysis. Nitrate concentrations were analyzed at the Rocky Mountain Research Station in Fort Collins (Pierson et al., 2016) using a Dionex ICS-3000 ion chromatograph with $\pm 5\text{-}\mu\text{g/L}$ precision for concentrations below $100\text{-}\mu\text{g/L}$ and $\pm 5\%$ precision for values above $100 \mu\text{g/L}$, and a method detection limit of $10\text{-}\mu\text{g/L}$ $\text{NO}_3\text{-N}$.

3.2. Segment Water and $\text{NO}_3\text{-N}$ Flux Balances

We determined water and ambient $\text{NO}_3\text{-N}$ flux balances for each segment. Water flux balances were determined as outflow minus inflow

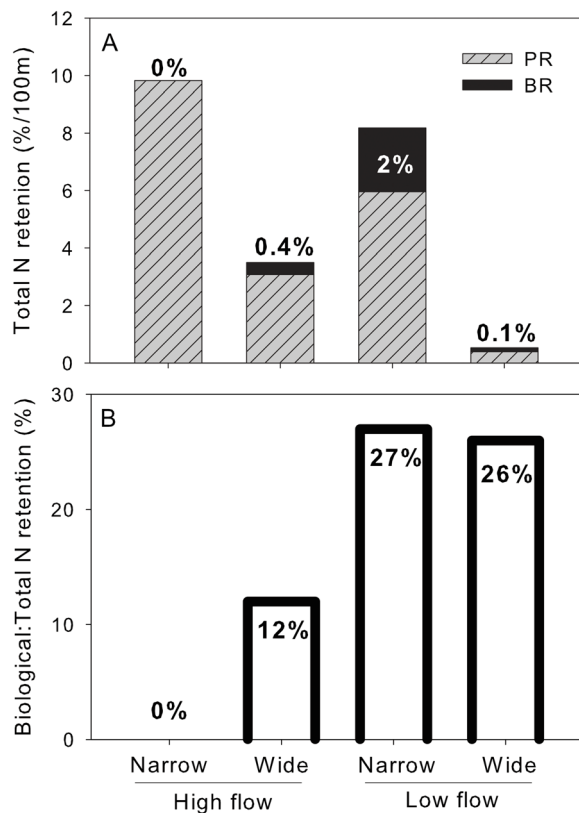


Figure 4. (a) Physical (hashed, PR) and biological (black, BR) contributions to total nitrate-nitrogen ($\text{NO}_3\text{-N}$) retention during nutrient injection experiments. Data are shown for high and low flow injections along the narrow and wide segments and are given per 100 m of valley length to account for differences in total valley length between the segments. The numbers along the bars in Figure 4a refer to biological contributions to total retention. (b) The ratio of biological to total retention given as a percentage. The numbers along the bars give specific percentages of biological:total retention ratios.

Biological retention of $\text{NO}_3\text{-N}$ (BR_N) represents in-channel/hyporheic biological uptake of injected N. Additionally, when the nutrient of concern is nonlimiting (i.e., saturating ambient conditions), nutrient injection experiments will fail to detect uptake. We standardized total, biologic, and physical retention by injected tracer mass (i.e., percent retained; %) and by segment valley length (%/100 m). Our measures of biological and physical retention represent the uptake (biological retention) and hydrologic (physical retention) processes that attenuate downstream nutrient flux.

3.4. Stream Gross Gains and Losses of Water and $\text{NO}_3\text{-N}$

We calculated gross gains and losses of water and $\text{NO}_3\text{-N}$ along the narrow and wide valley segments during the high and low flow nutrient injection experiments using mass balance, as shown in equation (6):

$$Q_{\text{Net}} = Q_{\text{Gain}} - Q_{\text{Loss}} \quad (\text{or}) \quad N_{\text{Net}} = N_{\text{Gain}} - N_{\text{Loss}} \quad (6)$$

Net changes were determined as the differences in water (Q) or $\text{NO}_3\text{-N}$ (N) flux between the outflows and inflows of each segment. Gross loss was determined from mass recovery during the injection experiments. Hydrologic gross loss is determined from Cl mass recovery (see Covino et al., 2011), and nutrient mass loss is determined from $\text{NO}_3\text{-N}$ mass recovery. The gain term of the mass balance is then determined by difference.

4. Results

4.1. Stream Physical and Chemical Characteristics

Discharge was predominantly driven by seasonal snowmelt, with only slight increases in response to summer storm events (Figure 2a). Discharge rose abruptly following snowmelt in late May to maximums of 5,830 L/s at

(Cl^-) and nitrate (NO_3^-) using a Dionex ICS-3000 ion chromatograph at Rocky Mountain Research Station, Fort Collins, Colorado. We quantified tracer mass recoveries for both Cl and $\text{NO}_3\text{-N}$ for the injections as

$$\text{TMR} = Q \int_0^t T_c(\tau) d\tau \quad (2)$$

where TMR is the tracer mass (g) recovery, and T_c is the time-integrated background corrected tracer concentrations (g^*/L) for either Cl or $\text{NO}_3\text{-N}$. We used injected tracer mass recoveries at each sampling site to calculate total retention (TR), as shown in equation (3):

$$\text{TR} = \text{mass of tracer injected} - \text{TMR} \quad (3)$$

Total retention of $\text{NO}_3\text{-N}$ (TR_N) represents the amount of injected $\text{NO}_3\text{-N}$ that did not arrive at the downstream sampling location due to hydrologic loss (physical retention) and in-channel/hyporheic biological uptake (biological retention). To calculate the physical retention of $\text{NO}_3\text{-N}$ (PR_N), we multiplied the fraction of Cl retained during the tracer injection by the mass of injected $\text{NO}_3\text{-N}$, as shown in equation (4):

$$\text{PR}_\text{N} = \frac{\text{TR}_\text{Cl}}{\text{mass of Cl injected}} * \text{mass of N injected} \quad (4)$$

Physical retention is defined as water and nutrients that leave the stream and enter subsurface or overbank flow paths that do not intersect with the downstream sampling site during the timescale of the experiment (Covino et al., 2010). The $\text{NO}_3\text{-N}$ physically retained by hydrologic loss may subsequently encounter a variety of fates including long-term storage in the valley aquifer, storage in floodplain waterbodies (i.e., side channels, ponds, or marshes), denitrification in floodplain waterbodies or shallow subsurface zones, uptake by riparian vegetation or soil microbes, or eventual reentry into the channel. As such, physical retention can delay downstream transport and provide increased opportunity for biological uptake (Battin et al., 2008). We then calculated biological $\text{NO}_3\text{-N}$ retention (BR_N) using equation (5)

$$\text{BR}_\text{N} = \text{TR}_\text{N} - \text{PR}_\text{N} \quad (5)$$

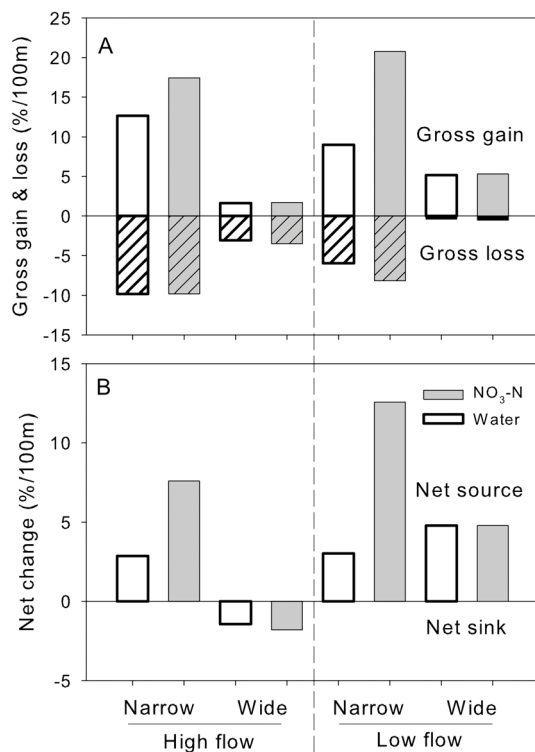


Figure 5. (a) Gross gains and losses of water and nitrate-nitrogen ($\text{NO}_3\text{-N}$) along narrow and wide segments during high and low flow experiments. Gross losses are indicated by hashing, and water is open bars while $\text{NO}_3\text{-N}$ is gray bars. Data are presented in percent gain/loss per 100 m of valley length to account for differences in segment lengths. (b) Net change in water and $\text{NO}_3\text{-N}$ along the narrow and wide valley segments during high and low flow experiments. Again water is open bars and $\text{NO}_3\text{-N}$ is gray. Positive values indicate the segment was a net source, while negative values indicate the segment was a net sink. Gross losses were determined from $\text{NO}_3\text{-N}$ mass recovery during injection experiments, net changes were determined from ambient mass flux balances (i.e., outflow – inflow flux), and gross gains were calculated as the difference between the two.

we measured no biological nutrient uptake during the high flow experiment in the narrow segment (Figure 4a). The biological contribution to total retention ranged from 0 to 28% and was largest during the low flow experiments (Figure 4b).

Analysis of ambient flux balances across the stream-valley segments provided contrasting results relative to tracer injection data. While nutrient injection experiments indicated greater total retention of added $\text{NO}_3\text{-N}$ along the narrow segment relative to the wide segment, these gross losses were offset by gross gains

S1, 6,690 L/s at S2, and 5,190 L/s at S3 between 4 June and 22 June, and decreased to minimums of 340 L/s at S1, 410 L/s at S2, and 940 L/s at S3 by the end of monitoring. From May to October, average discharge increased with downstream distance, with values of 2,018 L/s at S1, 2,125 L/s at S2, and 2,318 L/s at S3. Water temperatures also increased slightly with downstream distance, with an average ($\pm$ standard deviation) of $7.4 \pm 3.4^\circ\text{C}$ at S1, $7.7 \pm 3.4^\circ\text{C}$ at S2, and $8.4 \pm 3.6^\circ\text{C}$ at S3 from May to October. During the May–October period stream temperatures ranged from $2.1\text{--}13.5^\circ\text{C}$ at S1, $2.0\text{--}13.7^\circ\text{C}$ at S2, and $2.3\text{--}14.4^\circ\text{C}$ at S3.

Nitrate-N concentrations were similar between all three sites, with an average ($\pm$ standard deviation) of $70 \pm 35\text{ }\mu\text{g/L}$ at S1, $80 \pm 41\text{ }\mu\text{g/L}$ at S2, and $72 \pm 42\text{ }\mu\text{g/L}$ at S3 (Figure 2b). Nitrate-N concentrations were related to discharge and peaked on the rising limb of the seasonal snowmelt hydrograph to maximums of $130\text{ }\mu\text{g/L}$ at S1, $150\text{ }\mu\text{g/L}$ at S2, and $140\text{ }\mu\text{g/L}$ at S3 and decreased with the falling limb of the hydrograph to minimums of $20\text{ }\mu\text{g/L}$ at S1, $30\text{ }\mu\text{g/L}$ at S2, and $10\text{ }\mu\text{g/L}$ at S3 by the end of monitoring (Figure 2b).

4.2. Segment Flux Balances and $\text{NO}_3\text{-N}$ Retention

Nitrate-N fluxes followed the snowmelt hydrograph with peak values of 49.3 kg/day at S1, 63.9 kg/day at S2, and 55.0 kg/day at S3 during June high flows, and minimum values of 1.3 kg/day at S1, 1.6 kg/day at S2, and 1.1 kg/day at S3 by late summer baseflow (Figure 3a). Nitrate-N fluxes were generally higher at S2 (narrow segment outflow) than S1 (narrow segment inflow), such that the narrow segment was a net source of $\text{NO}_3\text{-N}$ across flows (Figure 3b). In contrast, the relative magnitudes of N fluxes at S3 (wide-segment outflow) and S2 (wide-segment inflow) indicated variable sink-source behavior along the wide segment across flows (Figure 3b).

During all nutrient injection experiments, there was limited biological uptake response to nutrient addition, which indicates the potential for stream N saturation. Total retention of injected $\text{NO}_3\text{-N}$ per unit valley length was higher in the narrow segment relative to the wide segment during high and low flow experiments (Figure 4a). Total retention was dominated by physical retention during all experiments, and

Table 2

Flows, Ambient $\text{NO}_3\text{-N}$ Concentrations, and Gross Gains and Losses of Water and $\text{NO}_3\text{-N}$ During Tracer Injection Experiments

Segment	Date	Stream temperature ($^\circ\text{C}$)	Ambient $\text{NO}_3\text{-N}$ ($\mu\text{g/L}$)	$\text{NO}_3\text{-N}$ gain (%/100 m)	$\text{NO}_3\text{-N}$ loss (%/100 m)	$\text{NO}_3\text{-N}$ net (%/100 m)	Segment inflow Q (L/s)	Segment outflow Q (L/s)	Q net (L/s)	Q gain (%/100 m)	Q loss (%/100 m)	Q net (%/100 m)
Narrow	9 June (HF)	5.2	134 (85)	17.4	−9.8	7.6	4750	5280	530	12.7	−9.8	2.9
Wide	8 June (HF)	5.4	124 (89)	1.7	−3.5	−1.8	5970	4650	−1320	1.6	−3.1	−1.4
Narrow	6 August (LF)	12.5	38 (73)	20.8	−8.2	12.6	850	950	100	9.0	−6.0	3.0
Wide	5 August (LF)	12.5	34 (87)	5.3	−0.5	4.8	950	1650	700	5.2	−0.4	4.8

Note. Parentheses in date column refer to high flow (HF) and low flow (LF) experiments. Parentheses in ambient $\text{NO}_3\text{-N}$ column indicate the proportion of dissolved inorganic N from $\text{NO}_3\text{-N}$.

(Figure 5a). The larger magnitude of gross gains relative to gross losses of N along the narrow segment resulted in net source behavior during high and low flow experiments (Figure 5b and Table 2). Gross $\text{NO}_3\text{-N}$ and water gains were lower across the wide segment than across the narrow segment (Figure 5a). During high flows along the wide segment, gross losses exceeded gross gains resulting in net sink behavior (Figure 5b and Table 2). Both the narrow and wide segments were net sources for water and $\text{NO}_3\text{-N}$ during low flow experiments (Figure 5 and Table 2).

5. Discussion

The capacity of streams to retain $\text{NO}_3\text{-N}$ during nutrient injection experiments varies considerably, with higher biologic uptake typically observed in $\text{NO}_3\text{-N}$ limited relative to $\text{NO}_3\text{-N}$ -enriched sites (Marti et al., 2004). In NSV, in-stream biologic uptake of added $\text{NO}_3\text{-N}$ was a relatively small proportion (<28%) of total retention, which suggests the stream is approaching or experiencing N saturation (O'Brien et al., 2007). Low biologic retention is expected in streams in which the ambient (i.e., preinjection) supply exceeds the biologic demand for that nutrient (Newbold et al., 1981). In RMNP and other portions of the Colorado Rockies, increased stream $\text{NO}_3\text{-N}$ concentrations have been observed (Lewis & Grant, 1980; Williams et al., 1996) and this pattern has been linked to regional atmospheric deposition patterns (Clow et al., 2015; Mast et al., 2014). Other work on dissolved inorganic N (DIN) uptake in RMNP streams, including NSV, has documented low $\text{NO}_3\text{-N}$ use efficiency and biological preference for $\text{NH}_4\text{-N}$ (Day & Hall, 2017). Additionally, Day and Hall (2017) observed that up to 19% of injected $\text{NH}_4\text{-N}$ was immediately nitrified. As such $\text{NH}_4\text{-N}$ is likely supporting much of the in-stream DIN demand in NSV and other RMNP streams. Consequently, we would expect that $\text{NH}_4\text{-N}$ injections would reveal stronger biological, and greater total, retention of added N relative to the $\text{NO}_3\text{-N}$ retention documented here. The stronger affinity for $\text{NH}_4\text{-N}$ was reflected in N concentrations at NSV, where $\text{NO}_3\text{-N}$ accounted for 73–89% of total DIN (Table 2). Because $\text{NO}_3\text{-N}$ accounts for the majority of DIN, future patterns of NO_x deposition will likely be reflected in watershed $\text{NO}_3\text{-N}$ export patterns. This suggests that regulation of emissions is likely to be effective in protecting high-elevation ecosystems of RMNP and improving water quality of watershed exports (Mast et al., 2014).

Information obtained from nutrient injection experiments is challenging to interpret in isolation and needs to be evaluated with complementary information. In fact, the contrasting information we obtained from injection experiments and segment mass balances would have led to different conclusions when interpreted in isolation of one another. For example, although total retention of injected tracer was greater along the narrow segment, these losses were offset by gross gains. This resulted in net source behavior for $\text{NO}_3\text{-N}$ along the narrow segment, even though it had a higher per unit total retention rate. While total $\text{NO}_3\text{-N}$ retention per unit length was lower along the wide segment, gross gains were minimal resulting in net sink behavior along the wide segment during high flow. Because the wide segment can store (net sink) water and N at high flows it has the potential to provide ecosystem and water quality benefits at times when N fluxes are highest (Ocampo et al., 2006) and in-stream uptake efficiencies are low due to high concentrations (Dodds et al., 2002; Earl et al., 2006), high streamflow velocities (Bukaveckas, 2007), and cold temperatures (Demars et al., 2011). A growing body of literature suggests that wide valley segments can act as key locations of water, sediment, and nutrient storage in mountain watersheds (Bellmore & Baxter, 2014; Hauer et al., 2016; Wohl et al., 2017). However, the ability of wide valley segments to store water and nutrients during peak flows, providing important water and ecosystem services, needs to be evaluated in more settings and should ultimately be more fully integrated into understanding water and nutrient export in mountain systems.

The pattern of gross gains and losses, and resulting net behavior, along the two segments is potentially related to stream-valley interactions and riparian buffering of hillslope input (Jencso et al., 2010). This is because interactions between the stream and the adjacent landscape are regulated by valley morphology (Hynes, 1975) with implications for hydrologic (Ward et al., 2012, 2017) and nutrient processes (Gregory et al., 1991; Hauer et al., 2016). The results we present here, although limited to one location, suggest that stream-valley interactions can exert important controls on segment nutrient flux balance. The gross loss of $\text{NO}_3\text{-N}$ through hydrologic exchange or biological uptake can be offset by gross gains, which, in turn, depend upon factors such as stream-hillslope connectivity (Jencso et al., 2009) and width of the riparian area (Vidon & Hill, 2004). The riparian buffer ratio, or the ratio of local riparian area divided by the lateral contributing area, can be used to describe the capacity of the riparian zone to modulate lateral inputs from the hillslope

(McGlynn & Seibert, 2003). In our study, the narrow segment is strongly connected to the adjacent hillslopes and has limited riparian area. This results in a low riparian buffer ratio relative to the wide segment, which is largely disconnected from adjacent hillslopes. In fact, the riparian buffering ratio was 4.7 times higher in the wide relative to the narrow valley segment (Table 1). These differences in valley morphology, stream-hillslope connectivity, stream slope, and sinuosity resulted in differences in gains and losses along the narrow and wide segments. Because biological uptake was a small proportion of total retention of injected N along both reaches, gross gains and losses exerted primary constraints on total retention patterns. Hydrologic controls on N retention are likely to be particularly pronounced in streams approaching or experiencing N saturation. Under N saturation, N concentration and export patterns along the stream network may be related to valley width, hillslope connectivity, and riparian buffering. A hypothesis that derives from this is that streams nearing or experiencing N saturation will preserve terrestrial loading signatures (Brookshire et al., 2009), while N-limited streams will transform terrestrial loading signatures (Bernhardt et al., 2005). Because our research is limited to two stream-valley segments in one watershed, we suggest that future research is required to determine how valley morphology influences N concentration and export patterns in N-limited and N-enriched sites.

6. Conclusion

We evaluated $\text{NO}_3\text{-N}$ retention processes along two longitudinally adjacent but morphologically contrasting segments of Upper NSV Creek, Colorado. We found that biological uptake was a minor component (from 0% to 28%) of total retention of $\text{NO}_3\text{-N}$ added during nutrient injection experiments. The low biological uptake of injected N may be related to high atmospheric deposition of N along the Front Range of Colorado (Baron et al., 2000; Mast et al., 2014; Williams et al., 1996) that may satisfy biological demand. As stream ecosystems become N saturated, hydrologic connectivity between the stream, hillslopes, and riparian areas may become increasingly important in controlling export patterns. Along NSV, longitudinal variations in valley width, hillslope connectivity, and riparian buffer ratios impacted gross gains and losses of water and $\text{NO}_3\text{-N}$ and associated segment flux balances. Although per unit valley length total retention rates were higher along the narrow segment, this retention capacity was overwhelmed by input (i.e., gross gain) from adjacent hillslopes resulting in net positive flux balances (source behavior). While the narrow segment was a net source of $\text{NO}_3\text{-N}$ across flows, the wide valley segment was a sink during high flows and source during low flows. This sink behavior during high flows suggests that stream-riparian interaction in wide valley segments can be important to water and N storage in mountain settings. However, landscape controls on stream reach nutrient flux balances that may be masked by biological uptake in N-limited systems, and these relative controls on nutrient export require further investigation across various landscapes. Further, we suggest that the relative importance of in-stream and valley controls on nutrient retention be evaluated using a combined nutrient injection and ambient flux approach that can provide complementary, but sometimes contrasting, results.

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