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ARE RIVERS JUST BIG STREAMS?

A PULSE METHOD TO QUANTIFY NITROGEN DEMAND IN A LARGE RIVER

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Abstract. Given recent focus on large rivers as conduits for excess nutrients to coastal zones, their role in processing and retaining nutrients has been overlooked and understudied. Empirical measurements of nutrient uptake in large rivers are lacking, despite a substantial body of knowledge on nutrient transport and removal in smaller streams. Researchers interested in nutrient transport by rivers (discharge $>10,000 \text{ L s}^{-1}$) are left to extrapolate riverine nutrient demand using a modeling framework or a mass balance approach. To begin to fill this knowledge gap, we present data using a pulse method to measure inorganic nitrogen (N) transport and removal in the Upper Snake River, WY (7th order, discharge $12,000 \text{ L s}^{-1}$). We found that the Upper Snake had surprisingly high biotic demand relative to smaller streams in the same river network for both ammonium (NH_4^+) and nitrate (NO_3^-). Placed in the context of a meta-analysis of previously published nutrient uptake studies, these data suggest that large rivers may have similar biotic demand for N as smaller tributaries. We also found that demand for different forms of inorganic N (NH_4^+ vs NO_3^-) scaled differently with stream size. Data from rivers like the Upper Snake and larger are essential for effective water quality management at the scale of river networks. Empirical measurements of solute dynamics in large rivers are needed to understand the role of whole river networks (as opposed to stream reaches) in patterns of nutrient export at regional and continental scales.

Key words: nutrient spiraling, uptake length, uptake velocity, nitrate, ammonium, stream, river

1 INTRODUCTION

2 River networks regulate the export of nutrients from the terrestrial landscape, making
3 them critical for mitigating eutrophication of downstream ecosystems (Alexander et al 2000) and
4 we must understand the role of entire river systems (as opposed to stream reaches) in affecting
5 regional and continental nutrient export patterns. Foundational research examining the
6 contribution of rivers to inorganic nitrogen (N) export to coastal systems has shown that simple
7 models can predict N export based on human-influenced point and non-point source loading
8 from fertilizer application and NO_y deposition (Caraco and Cole 1999) or even more simply from
9 population density alone (Howarth et al. 1997, Peierls et al. 1991). These relationships have
10 shaped our worldview on the dominant *external edaphic* factors that control river nutrient export
11 but provide no indication of the role of *internal* nutrient uptake and transformation that may
12 occur in rivers.

13 Our current empirical understanding of fluvial nutrient dynamics is based mainly on
14 research conducted in small, headwater streams (Ensign and Doyle 2006). Particularly for
15 nitrogen, the take-home message is that small streams are processing hotspots with the potential
16 to transform and retain dissolved nutrients (Peterson et al. 2001), and thus may control N exports
17 from river networks because they make up the majority of catchment river miles (Alexander et
18 al. 2000, 2007). Current research on the biogeochemistry of small streams is now focusing on
19 what controls nutrient uptake, how land use modifies those patterns, and what constitutes
20 effective stream restoration (Doyle et al. 2003, Meyer et al. 2005, Bernot et al. 2006, Hoellein et
21 al. 2007, Mulholland et al. in revision).

22 Despite comparatively high N uptake rates in headwater streams, excess nutrients are
23 nevertheless exported to downstream ecosystems (Alexander et al. 2007). Nutrient export from

1 large rivers is receiving considerable attention, for example N loading in the Mississippi River
2 causes periodic hypoxic zones in the Gulf of Mexico (Rabalais et al. 2002, Dodds 2006), and this
3 phenomenon may not be limited solely to river networks with intensive upstream agriculture
4 (Monteiro et al. 2006), as previously assumed. Most often nutrient uptake in rivers is inferred
5 using models based on data from small streams (Wollheim et al. 2006) or estimated from nutrient
6 mass balances (Howarth et al. 1996, Alexander et al. 2000, Alexander et al. 2007). Results from
7 such studies suggest that larger streams and rivers may be responsible for the majority of
8 nitrogen removal because long transport distances result in increased water residence time
9 (Seitzinger et al. 2002, Wollheim et al. 2006). Nevertheless there remains a lack of empirical
10 data on nutrient uptake in larger systems (e.g. discharge $>1000 \text{ L s}^{-1}$). Given the focus on entire
11 river networks as conduits for excess nutrients into coastal zones, the ability of large rivers to
12 process and retain nutrients has been overlooked and understudied.

13 In part, this knowledge gap reflects the current methods for measuring nutrient uptake *in*
14 *situ* that are impractical for quantifying nutrient cycling in large rivers. Nutrient spiraling theory
15 was developed in headwater streams and has a long history in stream ecology (e.g. Webster and
16 Patten 1979, Newbold et al. 1981). Spiraling theory represents a conceptual framework for
17 understanding solute dynamics in fluvial systems with a strength being that it combines both
18 hydrological and biological controls on nutrient removal in lotic systems. Nutrient spiraling
19 parameters are typically measured using steady-state solute releases of isotopic tracers (e.g.
20 Peterson et al. 2001, Newbold et al. 1981) or low-level short-term nutrient enrichments (e.g.
21 Mulholland et al. 2002). In either case, nutrient fluxes (a result of discharge and nutrient
22 concentration) are generally too high in rivers to use short term additions delivered using pumps.
23 These methods cannot increase concentrations sufficiently to quantify subsequent decline

1 without great difficulty or prohibitive cost. To date, the majority (~90% of N=625) of nutrient
2 uptake measurements have been made in streams with discharge $<200 \text{ L s}^{-1}$, with almost half of
3 these made in streams $<20 \text{ L s}^{-1}$ (Fig. 1).

4 To address this lack of data, we used a nutrient pulse addition approach to quantify N
5 uptake in a large river. Using methods adapted from small-stream ecology we were able to
6 measure N uptake in the $12,000 \text{ L s}^{-1}$ Upper Snake River in NW Wyoming. Here, we report our
7 data from this technique in the context of a larger meta-analysis of nutrient uptake measurements
8 published to date, and we address the following questions in our analysis: 1) How does nutrient
9 uptake in a large western river compare to smaller streams for which we have numerous
10 measurements? and 2) How does the relative role of biology vs. hydrology in nutrient uptake
11 vary with stream size and form of inorganic N? Surprisingly, we found that the Upper Snake had
12 similar biotic demand for N as smaller streams in the same river network. The Snake River data
13 combined with our meta-analysis suggests that riverine nutrient uptake may scale with stream
14 size; large rivers may have similar demand compared to small tributaries. Yet different forms of
15 inorganic N show different uptake parameters and thus may scale differently with stream size,
16 which may have ramifications for uptake and delivery of N to downstream ecosystems.

17 MATERIALS AND METHODS

18 *Study Site*

21 In July 2005, we conducted solute releases in a 3-km reach of the Upper Snake River
22 (width = 41m, $Q=12,000 \text{ L s}^{-1}$) in John D. Rockefeller National Parkway, WY upstream of
23 Jackson Lake (7th order and catchment area = 1376 km^2). We chose to quantify N uptake in the
24 Snake River during summer because we wanted to test the nutrient pulse method in a larger
25 system where we had previous nutrient uptake data from small tributaries in the same river

1 network. During summer, the cobble/boulder bottom of the Upper Snake supports an active algal
2 assemblage (e.g. filamentous green streamers), which we predicted would result in high rates of
3 biotic N demand, particularly because ambient concentrations were very low (dissolved
4 inorganic N, DIN < 10 µg/L).

5 *Pulse addition method*

6 We conducted pulse additions using a conservative tracer (chloride, Cl⁻) plus a reactive solute
7 (ammonium, NH₄⁺ or nitrate, NO₃⁻ conducted separately). We added the nutrient pulse by filling
8 a 610-L cattle tank with river water and 276 kg of NaCl and 4.3 kg KNO₃ or 5.7 kg (NH₄)₂SO₄,
9 depending on the release and mixing until dissolved. Before the nutrient/conservative tracer
10 additions, we conducted a preliminary release of only conservative tracer, NaCl, and stationed
11 crews at sites downstream (1330, 1430, 1750 and 2610m from the release point) with
12 conductivity meters to estimate travel time and mixing, allowing us to measure the travel
13 distance required for the solute solution to be well mixed across the channel, and to fine tune
14 how much reactive solute we had to add. The key to mixing in the Snake River was placing the
15 first sampling station below a large eddy created from a pool located at a river bend.
16 Considering previous research that has shown that enrichment-type releases can saturate nutrient
17 demand, and thus underestimate nutrient uptake (Mulholland et al. 2002, Payn et al. 2005), we
18 aimed to raise the peak concentrations of NH₄⁺ and NO₃⁻ during the peak of the pulse to ~50
19 µg/L above background concentrations. This increase was analytically detectable, but the highest
20 concentration during the pulse was likely not high enough to saturate demand (Dodds et al. 2002,
21 Earl et al. 2006), and only lasted for a few minutes at most. During each pulse, we collected
22 water samples every 2 minutes at each station to characterize the peak as it passed by a station,
23 while also measuring specific conductance. Upon return to the laboratory, we quantified NO₃⁻

1 using ion chromatography (Dionex Model DX600) with AS14A analytical and guard columns
2 and a 500- μ L injection loop, and NH_4^+ using the phenylhypochlorite technique (Solorzano
3 1969, APHA 1998).

4 *Pulse release calculations*

5 Nutrient spiraling theory (e.g. Webster and Patten 1979, Newbold et al. 1981) uses
6 interrelated metrics to quantify different aspects of nutrient transport and removal in flowing
7 waters. Uptake length (S_w) is the average distance a solute molecule travels prior to removal
8 from the water column. As such, it combines both hydrologic and biological processes, because
9 S_w lengthens with increasing depth and velocity, and shortens with increasing biotic demand.
10 From S_w (in meters, m), we calculated biotic demand relative to concentration (uptake velocity,
11 V_f in mm s^{-1}) using stream discharge (Q in $\text{m}^3 \text{s}^{-1}$) and width (w in m); it is calculated as $V_f =$
12 $(Q/w)/S_w$ (Stream Solute Workshop 1990, Davis and Minshall 1999). Uptake velocity (V_f)
13 normalizes S_w for the effects of depth and velocity ($= Q$ divided by width, w), so streams of
14 different sizes can be directly compared.

15 For each pulse release, we calculated uptake parameters (described above) using a mass
16 balance approach, by calculating the mass of reactive solute passing over each station, relative to
17 the mass of conservative tracer (i.e. area under each curve in Figs. 2A and B; Chapra 1997). We
18 assumed that any reduction in the mass of N relative to conservative tracer at downstream
19 stations was a result of biological uptake between stations as sorption is balanced by desorption
20 throughout the pulse (Stream Solute Workshop 1990). We calculated uptake length (S_w) using
21 background-corrected mass of solute passing over a station divided by background-corrected
22 mass of conservative tracer passing over a station and plotted the natural log of this fraction
23 versus distance downstream where S_w is the absolute value of the inverse of the slope (Stream

1 Solute Workshop 1990). Uptake velocity (V_f) was calculated using equations described above.
2 We independently confirmed our results from the pulse mass balance approach using a one-
3 dimensional advection, dispersion, transient storage solute transport model (OTIS-P, Runkel
4 1998, 2007; Fig.2A, dashed line) to estimate first-order decay rate (λ , min^{-1}) for the solute, using
5 NH_4^+ as an example.

7 RESULTS

8 *Quantifying inorganic N uptake in the Upper Snake River*

9 Using the pulse release method we were able to quantify declines (corrected for dilution
10 and dispersion with the conservative tracer) in the mass of NH_4^+ and NO_3^- passing by stations
11 downstream of the release point (Fig. 2A and B, respectively), allowing us to successfully
12 calculate the uptake length (S_w) and uptake velocity (V_f) for each reactive solute. In the Upper
13 Snake, the uptake length S_w for NH_4^+ was 2000m (linear regression, $r^2= 0.85$, $p=0.07$, Fig. 2A).
14 When scaled for discharge and width, the NH_4^+ uptake velocity, V_f , was 9.3 mm min^{-1} (Table 1).
15 For NO_3^- , the S_w was somewhat longer at 2500m (linear regression, $r^2= 0.80$, $p=0.10$, Fig. 2B)
16 and we calculated a slightly lower V_f at 7.4 mm min^{-1} (Table 1). To corroborate the linear
17 regression approach based on mass loss, the first-order decay rate (λ) estimated using OTIS-P
18 was $2.20 \times 10^{-4} \text{ min}^{-1}$, roughly equivalent to the value ($2.33 \times 10^{-4} \text{ min}^{-1}$) obtained using the mass-
19 balance calculated S_w (Stream Solute Workshop 1990)

20 We can place our NH_4^+ and NO_3^- uptake estimates in the context of the smaller tributaries
21 in the Upper Snake River basin using data from Hall and Tank (2003); discharge in the smaller
22 tributaries ranged from 9 - 231 L s^{-1} (Table 1). For both NH_4^+ and NO_3^- , S_w estimates in the
23 Upper Snake were generally longer than in the smaller tributaries, reflecting the influence of

1 depth and velocity on S_w . However, when we scaled for discharge by calculating V_f (i.e. biotic
2 demand relative to concentration), NH_4^+ and NO_3^- demand were similar, and fell among the
3 higher values, compared to the smaller tributaries (Table 1). Using the nutrient pulse method,
4 NH_4^+ and NO_3^- demand in the Upper Snake River are comparable to biotic demand for small
5 streams in the same catchment (Hall and Tank 2003).

6 *Snake River nitrogen uptake in context of meta-analysis*

7 Using inorganic N uptake data from previously published studies (Appendix A), plus our
8 data for the Upper Snake River (this study), we examined the relationship between S_w and stream
9 size (discharge, Q in L s^{-1}) for both NH_4^+ and NO_3^- . There was a significant relationship between
10 $\text{NH}_4^+ S_w$ and Q , with stream size explaining almost half of the variation in uptake length (linear
11 regression, $r^2 = 0.47$, $p=0.0001$, Fig. 3A). For the largest streams in the dataset, there was the
12 least variation in uptake length, with data points falling very close to the regression line (Fig.
13 3A), recognizing this pattern is confounded by the difference in the number of data points
14 between small and large streams. The Upper Snake River ($S_w = 2000\text{m}$, $Q= 12,000 \text{ L s}^{-1}$) had the
15 same uptake length as the Kansas River, KS ($S_w = 2000$, $Q= 14350 \text{ L s}^{-1}$, Dodds et al. in review),
16 but both were shorter than the Lower Kuparuk River, AK ($S_w = 5360$, $Q = 18,300 \text{ L s}^{-1}$,
17 Wollheim et al. 2001), the largest reported discharge in the literature. Two medium-sized streams
18 demonstrated the potential role of biological demand in modifying the S_w vs. Q relationship as
19 they had significantly shorter NH_4^+ uptake lengths given their discharge. One represents a
20 geothermal stream in Greater Yellowstone (Polecat Creek, WY, $S_w = 75\text{m}$, $Q= 1900 \text{ L s}^{-1}$, Hall et
21 al. 2003) and the other was the phosphorus-fertilized reach of the Upper Kuparuk River, AK (S_w
22 $= 278\text{m}$ $Q= 5010 \text{ L s}^{-1}$, Wollheim et al. 2001); both NH_4^+ uptake “hotspots” are systems where
23 biological processes play a disproportionately large role in controlling uptake length. For NO_3^- ,

1 there was also a significant linear relationship between S_w and Q , but the relationship was more
2 variable, with less of the variation explained (linear regression, $r^2 = 0.15$, $p=0.0003$, Fig. 3B).
3 There are no data available for larger systems, at least within an order of magnitude of discharge
4 of the Snake River; therefore comparison to our Snake River S_w at 12000 L s^{-1} is not possible at
5 this time. However there is no change in the slope of the relationship even when we remove the
6 Snake River data point, and the y-intercept changes only by $<0.5\%$ (see Fig. 3B).

7 *How does nutrient concentration interact with stream size in controlling uptake length?*

8 Although stream size is a major driver of S_w , increasing nutrient concentration also
9 lengthens S_w (Stream Solute Workshop 1990), therefore unexplained variation in the S_w vs. Q
10 relationship may be explained by N availability, either as background or plateau concentration
11 (for those measured using short-term nutrient additions). For NH_4^+ , Fig. 3A identifies estimates
12 made using ^{15}N isotope additions which do not raise background NH_4^+ concentrations; these
13 estimates fall below the regression line, being the least likely to overestimate S_w due to a
14 saturation effect (sensu Mulholland et al. 2002). The ^{15}N tracer estimates contrast with those S_w
15 estimates made with short-term enrichment methods where background enrichment was $>50\mu\text{g}$
16 $\text{NH}_4\text{-N/L}$; these estimates fall above the regression line indicating that excess NH_4^+ , particularly
17 in smaller streams, can result in longer S_w estimates (Fig. 3A). We compared the slope of the
18 regression of Q vs. S_w for all data (Fig. 3A) with the regression of Q vs. ^{15}N tracer data only, and
19 although the regression was also significant for Q vs. $^{15}\text{NH}_4 S_w$ (linear regression, $y = 0.69x +$
20 0.79 , $r^2 = 0.71$, $p < 0.0001$), the slope of 0.69 was significantly greater than that from the Q vs. S_w
21 regression for all data (ANCOVA, $p < 0.0001$, Fig 3A). In contrast, for $\text{NO}_3^- S_w$, ^{15}N tracer
22 estimates did not influence the relationship between S_w and Q (Fig. 3B). When we compared the
23 slope of the regression of Q vs. S_w for all data (Fig. 3B) with the regression of Q vs. ^{15}N tracer

1 data only, the regression was again significant for Q vs. $^{15}\text{NO}_3^- S_w$ (linear regression, $y = 0.42x +$
 2 2.23 , $r^2 = 0.16$, $p < 0.0001$), but the slope of 0.42 was not significantly different than the slope
 3 using all data (ANCOVA, $p = 0.579$, Fig 3B). In summary, $\text{NO}_3^- S_w$ does not appear to be as
 4 sensitive to variation in NO_3^- availability, which contrasts with results from the $\text{NH}_4^+ S_w$ meta-
 5 analysis.

6 We can further explore the secondary influence of ambient concentration by examining it
 7 in the context of the residuals of the S_w vs. Q relationship for each solute. For NH_4^+ , the residuals
 8 of the Q vs. S_w relationship were significantly related to background NH_4^+ concentration
 9 ($r^2 = 0.13$, $p < 0.0001$). In contrast, this was not the case for the residuals of the Q vs. $\text{NO}_3^- S_w$
 10 relationship and NO_3^- concentration ($p = 0.316$). For the meta-analysis, the range in background
 11 concentration of NH_4^+ and NO_3^- varied considerably between the two datasets; background NH_4^+
 12 ranged from $\sim 1\text{-}160 \mu\text{g N L}^{-1}$, whereas the NO_3^- range was almost 40X larger ($\sim 1\text{-}6100 \mu\text{g N L}^{-1}$).
 13 There has been some support in the literature that shows that NH_4^+ is used preferentially over
 14 NO_3^- to satisfy inorganic N demand (e.g. Dortch 1990), supporting our results indicating that
 15 background concentration of NH_4^+ was a major driver in the deviation from the Q vs. S_w
 16 relationship, but the same was not true for $\text{NO}_3^- S_w$.

17 The results from the meta-analysis suggest that NH_4^+ is tightly cycled; after stream size is
 18 accounted for, $\text{NH}_4^+ S_w$ may be under strong biological control because concentration explains
 19 the residual variation in the $\text{NH}_4^+ S_w$ vs. Q relationship. From our limited data it may be that the
 20 influence of biological demand on uptake is less variable among rivers with increasing size.
 21 Alternatively the relationship may be a response to changing sorption kinetics in larger systems.
 22 We acknowledge either mechanism may be biased by the lack of data from larger systems,
 23 nevertheless, we present this hypothesis of strong biological control to fuel future research.

1 We also plotted $\text{NH}_4^+ S_w$ vs. $\text{NO}_3^- S_w$ from the subset of studies (N=132) that quantified
2 both solutes on the same stream (Fig. 3C). If NH_4^+ and NO_3^- were biologically used
3 interchangeably, we would predict that the data would show a 1:1 relationship (dashed line, Fig.
4 3C), but in fact this is not the case (91% of the data fall on or above the 1:1 line). In particular,
5 for the smallest streams (open boxes, Fig 3C), when $\text{NH}_4^+ S_w$ is low (i.e. highest demand), NO_3^-
6 S_w is longer, and it appears that NH_4^+ is meeting the inorganic N demand. For the largest
7 systems, (closed boxes, Fig. 3C), the data (including that for the Upper Snake River) approach
8 the 1:1 line. In streams $>200 \text{ L s}^{-1}$, the demand for NH_4^+ compared to NO_3^- is similar. These
9 results suggest that larger systems appear to behave distinctly different than smaller systems in
10 regards to NH_4^+ vs. NO_3^- cycling.

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DISCUSSION

14 Identification of factors that control nutrient retention in the full size range of fluvial
15 systems in a river network is essential for determining the relative role that biological activity
16 and subsequent nutrient uptake may play in reducing export of elevated nutrient loads to
17 downstream ecosystems. Key papers have pointed to the importance of small streams as
18 locations for high rates of nutrient cycling (Alexander et al. 2000, Peterson et al. 2001, Bernot
19 and Dodds 2005). Alexander et al. (2007) applied their spatially explicit, mass-balance
20 SPARROW model to stream networks in the northeastern US and concluded that first-order
21 streams contribute approximately 40% of the nitrogen flux to downstream ($>4^{\text{th}}$ order) rivers,
22 emphasizing the importance of small streams in N removal and retention, but also highlighting
23 the remaining role of downstream rivers in influencing/preventing export to sensitive coastal
24 ecosystems. Using our empirical approach to quantify inorganic N uptake combined with OTIS-
25 P modeling of the pulse addition, we found the in-stream loss rate (λ) for NH_4^+ in the Snake

1 River to be $2.20 \times 10^{-4} \text{ min}^{-1}$ (or 0.32 day^{-1}). From Alexander et al. (2000), we can compare our in-
2 stream loss rate to a meta-analysis of 112 US rivers that used SPARROW modeling to predict
3 the relationship between in-stream N loss rate and depth. For a river with a depth = 0.45m,
4 similar to the Snake River, SPARROW predicts a mean in-stream loss rate of 0.45 day^{-1} which is
5 slightly higher than our empirical estimate for NH_4^+ alone. If we add NO_3^- demand to that
6 estimate, the Snake River estimate is higher (0.63 day^{-1}) than predicted via the SPARROW
7 analysis (Alexander et al. 2000), but we acknowledge that our rates could be considered an
8 estimate of gross inorganic N removal and the SPARROW modeling represents net N removal.
9 Modeling efforts have suggested that large rivers are important sites of nutrient removal, but the
10 empirical work lags far behind. The lack of information results from the difficulties of applying
11 empirical methodologies for solute dynamics to large river systems. Our results suggest that
12 mass-balance modeling (e.g. SPARROW) may underestimate the potential for river N removal
13 and further study is needed to determine what aspects of rivers promote higher N removal rates
14 (e.g. shallow depth and increased light penetration in the Snake River).

15 Although modeling approaches suggest that larger rivers can potentially play an
16 important role in N removal (Seitzinger et al. 2002, Wollheim et al. 2006) , most empirical
17 measurements have been made in smaller systems (i.e. $<200 \text{ L s}^{-1}$, Fig. 1). Using the nutrient
18 pulse method described here, we show that it is possible to empirically measure nutrient cycling
19 across a range of stream sizes within a river network, allowing us to fill an important gap in our
20 understanding of how nutrient retention and removal scales with increasing size. The pulse
21 addition technique we present here is practical for larger systems because it requires less solute
22 than steady state releases, which are not feasible in systems with high discharge or high nutrient
23 concentrations or both. A second advantage of the pulse addition method is that it is unbiased by

1 transient storage of solutes (Runkel 2007); this bias may lengthen estimates of uptake length
2 when using steady state additions. The pulse addition method will allow us to extend the scaling
3 approaches of Ensign and Doyle (2006) and Wollheim et al. (2006) to examine nutrient uptake in
4 larger rivers.

5 *Three scenarios of large river biotic demand:*

6 We present 3 possible scenarios of how river size would influence N uptake: 1) As river size
7 increases, the relative role of biological demand in nutrient uptake decreases as invoked by
8 Alexander et al. (2000) in their analysis of N export via the Mississippi River network to the
9 Gulf of Mexico. Their modeling results corroborated earlier studies using mass balance
10 approaches (e.g. Howarth et al. 1996). To put it simply, rivers function as ‘pipes’. 2)
11 Alternatively, river size has no effect on biological demand thus it remains constant with
12 increasing size. Wollheim et al. (2006) used this assumption in their model of river N export and
13 concluded that nutrient uptake is mainly a function of river length, which is somewhat analogous
14 to longer travel time. In other words, rivers are just big streams. 3) Finally, biotic demand may
15 increase with increasing river size, potentially due to the simultaneous demand by benthic and
16 water column biotic processes. We could find no previous empirical or modeling efforts that
17 would support or reject this scenario.

18 *What empirical estimates do we have of nutrient uptake in larger systems?*

19 To date, we know of only three rivers with $Q > 10000 \text{ L s}^{-1}$ where N uptake was empirically
20 measured using whole-system techniques comparable to measurements made in smaller systems
21 (Fig. 1). While $\text{NH}_4^+ S_w$ was long in all 3 rivers, despite their geographic separation, $\text{NH}_4^+ S_w$ in
22 the Lower Kupařuk River was more than twice as long ($S_w = 5360\text{m}$, Wollheim et al. 2001),
23 compared to the $\text{NH}_4^+ S_w = 2000\text{m}$ for both the Kansas River, KS (Dodds et al. in review) and

1 the Upper Snake River WY (this study)(Fig. 3A). When we account for differences in discharge
 2 among the 3 rivers ($Q= 12,000\text{--}18,300 \text{ L s}^{-1}$), NH_4^+ demand (expressed as an uptake velocity, V_f)
 3 was also lowest in the arctic Lower Kuparuk at 3.7 mm min^{-1} , compared to the high of 9.3 mm
 4 min^{-1} in the Upper Snake River during summer (this study); the low-gradient Kansas River fell in
 5 between ($V_f = 5.7 \text{ mm min}^{-1}$). Both the Lower Kuparuk River and the Upper Snake River have
 6 very low background inorganic N concentrations ($\text{NH}_4^+ + \text{NO}_3^- = 10 - 20 \text{ ugN/L}$), which would
 7 be expected to result in fairly high V_f estimates, yet the $\text{NH}_4^+ V_f$ from the Upper Snake River was
 8 ~ 2.5 times higher than that of the arctic Lower Kuparuk River, perhaps reflecting differences in
 9 biotic activity influenced by lower (albeit summer) water temperatures (Wollheim et al. 2001).
 10 Notably, these $\text{NH}_4^+ V_f$ from 3 rivers are comparable to those found in smaller streams both
 11 when we compare streams of varying size within a catchment (e.g. Upper Snake River vs.
 12 estimates in Hall and Tank 2003) or among small streams in general (Ensign and Doyle 2006).
 13 Data summarized from Appendix A ($N= 297$ data points) indicate a mean $\text{NH}_4^+ V_f = 7.58 \text{ mm}$
 14 min^{-1} and the median $\text{NH}_4^+ V_f = 3.75 \text{ mm min}^{-1}$. Results from this meta-analysis lend support to
 15 the idea that biological demand may remain constant or even increase with increasing river size,
 16 but clearly more systematic testing of these predictions are needed (sensu Ensign and Doyle
 17 2006). Recent models have assumed that V_f remains constant with increasing stream size, which
 18 means that large rivers can play an important role in mitigating N export, because of the longer
 19 travel time (and thus processing time) associated with larger systems (Wollheim et al. 2006). As
 20 for NO_3^- uptake in particular, our estimate from the Upper Snake River is the only one available,
 21 despite the relevance of NO_3^- export to downstream and coastal eutrophication issues (Seitzinger
 22 et al. 2002, Bernot and Dodds 2005). Clearly, more empirical estimates are needed.

23 *The effect of river size on N uptake may be solute specific:*

1 Our analyses suggest that NH_4^+ and NO_3^- uptake respond differently to river size (Figs. 3A & B).
2 Our data show that NH_4^+ and NO_3^- are not interchangeable forms of N; the slopes of the
3 relationship of each vs. Q were statistically different from each other (0.51 for NH_4^+ and 0.32 for
4 NO_3^-). Further, $S_w\text{-NO}_3^-$ was far longer (often orders of magnitude) than $S_w\text{-NH}_4^+$ measured in
5 the same stream at the same discharge (Fig. 3C). The results from the meta-analysis of those
6 streams that had concomitant measurements for both $S_w\text{-NO}_3^-$ and $S_w\text{-NH}_4^+$ (N=132) are
7 consistent with a smaller subset of data for 10 streams from different biomes presented by
8 Peterson et al. (2001) showing that $S_w\text{-NO}_3^-$ was 10X greater than $S_w\text{-NH}_4^+$. Interestingly, the
9 difference between $S_w\text{-NO}_3^-$ and $S_w\text{-NH}_4^+$ becomes smaller as streams get larger (Fig. 3C, $Q >$
10 ~ 200 L/s), which may suggest that either form of inorganic N may be able to meet biotic demand
11 in rivers, while NH_4^+ is preferred in small streams. This finding is similar to that of Ensign and
12 Doyle (2006) who found that cumulative uptake flux of NO_3^- increased with stream order while
13 the same was not true for NH_4^+ . One reason for this may be that larger systems have increased
14 nutrient demand as a result of the contribution of water-column processes in addition to benthic
15 dynamics (that dominate smaller streams). Further study of this hypothesis is needed.

16 Although researchers often assume that NH_4^+ and NO_3^- are interchangeable with respect
17 to meeting N demand by stream biota (hence measuring only one or the other in N uptake
18 studies), there are several reasons that explain the differences we report here. First, NH_4^+ is a
19 preferred N substrate for both heterotrophic microbes and algae (Rice and Tiedje 1989, Dortch
20 1990), largely because less energy is required for its assimilation into biomass (Hildebrand
21 2005). This preference is so strong, that the addition of NH_4^+ can suppress NO_3^- uptake via
22 repression of nitrate reductase (Van't Riet et al. 1968) and/or inhibition of NO_3^- transport into
23 cells (Creswell and Syrett 1979).

1 Second, $^{15}\text{N-NH}_4^+$ tracer studies have documented that in some streams nitrification can
2 account for a large (ca. 45%) fraction of apparent NH_4^+ removal (reflected in $S_w\text{-NH}_4^+$) (Peterson
3 et al. 2001, Simon et al. 2007). Thus some portion of the $S_w\text{-NH}_4^+$ in the meta-analysis represents
4 NH_4^+ that was nitrified to NO_3^- , which may lead to increased NO_3^- background concentrations
5 (e.g. Bernhardt et al. 2002) and higher variation and magnitude of $S_w\text{-NO}_3^-$ values. For NO_3^- ,
6 dissimilatory nitrate reduction to ammonium (DNRA) could generate ammonium; however, our
7 understanding of this process is lacking, and its prevalence in streams is currently being
8 examined (Burgin and Hamilton 2007).

9 Differences in NH_4^+ and NO_3^- uptake may be related to whole-stream metabolism. For
10 example, if large rivers become more heterotrophic due to larger sediment loads (Vannote et al.
11 1980), we would expect demand for NO_3^- to decline relative to NH_4^+ because NO_3^- uptake has
12 been shown to be correlated with photosynthesis in systems where primary producers dominate
13 (Hall and Tank 2003). The opposite is likely true: most of the small streams in our meta-
14 analysis are low-light, forested systems with uptake likely more driven by heterotrophic
15 processes- hence tightly cycled NH_4^+ .

16 An alternative explanation for the pattern seen in comparing NH_4^+ and NO_3^- uptake is
17 that NH_4^+ uptake can also be influenced by abiotic sorption processes; NH_4^+ uptake could be
18 higher than NO_3^- because the former is subject to cation exchange as well as biological uptake
19 while the latter is primarily controlled by biological mechanisms. In moving from small streams
20 to larger rivers, abiotic controls may change thus shifting the relationship between NH_4^+ S_w and
21 Q . Rivers transporting more particulates may increase the potential for water column driven
22 cation exchange – perhaps replacing benthic exchange as a mechanism for NH_4^+ uptake. This
23 mechanism may work in concert with an increase in water column biotic demand described

1 above. In summary, location in the river network may dictate solute-specific uptake and deserves
2 further study.

3 *Conceptual framework for scaling nutrient spiraling metrics as streams get larger:*

4 Going back to our three scenarios of large river biotic demand (see above), we can
5 summarize the relative influence of hydrology vs. biology on N uptake in a conceptual diagram
6 using the relationships between size and N uptake based on our meta-analysis (Fig. 4). In small
7 streams, the relative demand of NH_4^+ is greater than the demand for NO_3^- , reflected in shorter S_w .
8 Our meta-analysis indicates that as size (as Q) increases, the lines for NH_4^+ and NO_3^- converge,
9 indicating that in larger fluvial systems the demand for these solutes may be similar. But this
10 pattern may be biased by the fact that we have very few estimates of S_w for larger systems, and
11 indeed the slopes may be strongly influenced by the predominance of data for small streams.
12 Conceptually, this pattern allows us to address the three scenarios of large river nutrient uptake.
13 For example, when nutrient uptake is controlled more by hydrologic processes, S_w should fall
14 well above these lines indicating that the N demand is lower than predicted by its discharge
15 (Scenario 1: rivers as pipes). The Upper Snake River data (this study) illustrates Scenario 2 in
16 which biological N demand in rivers is similar to small streams, and equal for NH_4^+ and NO_3^- ,
17 and therefore falls on the intersection of the two lines. Conversely, when biological activity is
18 greater than the influence of hydrology in a river (Scenario 3), it should fall well below these
19 lines, exemplified by the geothermal Polecat Creek (Hall et al. 2003) and the fertilized Kupa-
20 River (Wollheim et al. 2001)(Fig 3A). We predict that riverine conditions, such as productivity
21 and sediment type, will determine where a given river falls on this plot; however, the relative
22 role of hydrology and biology in other large rivers is not currently known due to the lack of
23 empirical measurements (Fig. 4).

1 *The River Continuum Concept and nutrient cycling*

2 While untested with respect to nutrient dynamics, the river continuum concept (RCC)
3 (Vannote et al. 1980, Minshall et al. 1985) gives us an additional conceptual framework for
4 predicting how nutrient demand should change with stream/river size. Previous research across a
5 range of small streams has shown that nutrient demand is tightly coupled with instream
6 metabolism (Hall and Tank 2003, Meyer et al. 2005, Fellows et al. 2006), and we predict that
7 metabolism should continue to regulate nutrient uptake even as streams become rivers.
8 According to the RCC, gross primary production (GPP) relative to community respiration (CR)
9 increases in mid-order rivers (GPP/CR higher); we would predict that mid-order rivers would
10 have higher assimilative nutrient demand than small streams (i.e. fall below lines, Fig. 4).
11 Furthermore, in even larger systems (e.g. 6th-8th order), the RCC predicts that heterotrophic
12 demand by suspended sediments and/or plankton begin to influence the biology of rivers
13 (GPP/CR lower). Our results from the Upper Snake River in comparison to its small tributaries
14 suggest that nutrient demand is similar regardless of stream order. Turbid rivers with high
15 sediment load or suspended plankton may be metabolically dominated by heterotrophic
16 respiration, which again may increase nutrient demand, but for a very different reason than that
17 which would be predicted from clear water streams such as the Snake and its tributaries where
18 uptake is more strongly related to benthic production (Hall and Tank 2003, Fellows et al. 2006).
19 In addition to biological shifts associated with increasing size, channel complexity may further
20 influence nutrient demand in large rivers. Stanford and Ward (1993) extend the RCC to include
21 hyporheic zones, postulating greater surface/subsurface exchange in aggraded river valleys than
22 in headwater streams. Exchange between surface water and subsurface sediments can increase
23 solute uptake (Ensign and Doyle 2006, Runkel 2007, but see Hall et al. 2002). Unregulated

1 western rivers, such as the Upper Snake River, which drain glacial alluvium have gravel bars and
2 side channels which may increase hyporheic exchange (Fernald et al. 2001, Hauer and Lorang
3 2004) and may result higher biotic nutrient demand, compared to small streams (this study), but
4 there are currently not sufficient empirical data to address this hypothesis.

5 *Summary- large river nutrient cycling*

6 Quantifying the potential for large rivers to process nutrients is essential to elucidate the
7 role of large rivers in controlling nutrient export to downstream ecosystems, such as the Gulf of
8 Mexico, reservoirs, and estuaries. Modeling efforts have suggested that large rivers are important
9 sites of nutrient removal (e.g. Wollheim et al. 2006), but empirical estimates lag far behind,
10 mainly as a result of the methodological difficulties in applying small-stream approaches to
11 larger river systems. We have presented a method to quantify nutrient uptake in large rivers and
12 we place our results in the context of a meta-analysis of previous research thereby providing a
13 context in which to place future studies. Empirical measurements of solute dynamics in large
14 rivers are needed to understand the role of whole river networks (as opposed to stream reaches)
15 in patterns of nutrient export at regional and continental scales and ultimately, to manage water
16 quality effectively.

17

18

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- 15
- 16 APPENDIX A: Studies included in the meta-analysis. C_b = background concentration, C_p=
17 plateau concentration. Note that studies not using stable isotopes where S_w >5000m for NH₄ or
18 NO₃ were excluded from dataset to generate Fig. 3. (Ecological Archives EXXX-XXX-XX).
- 19
- 20 APPENDIX B: Full citations for studies included in meta-analysis (Ecological Archives EXXX-
21 XXX-XX).

Table 1. Comparison of physical characteristics and ammonium and nitrate uptake metrics in the Snake River and its smaller tributaries (data from Hall and Tank 2003). N/A signifies that no significant uptake was measurable.

Stream	Q (L s ⁻¹)	Width (m)	W/D ratio	NH ₄ ⁺ (μg L ⁻¹)	NH ₄ ⁺ S _w (m)	NH ₄ ⁺ V _f (mm min ⁻¹)	NO ₃ ⁻ (μg L ⁻¹)	NO ₃ ⁻ S _w (m)	NO ₃ ⁻ V _f (mm min ⁻¹)
Snake River (this study)	12000	41.0	84	5	2000	9.3	5	2500	7.4
Ditch Creek	231	5.8	41	2	249	9.6	5	821	2.9
Glade Creek	149	3.0	20	1	322	9.2	<5	758	3.9
Two Ocean Creek	144	4.1	32	3	384	5.5	10	2412	0.9
Bailey Creek	118	5.4	52	2	833	1.6	5	747	1.7
Spread Creek	87	5.5	55	1	76	12.6	13	108	9.0
Pilgrim Creek	46	4.1	74	1	278	2.4	<5	558	1.3
Paintbrush Creek	39	1.3	20	2	172	1.1	169	N/A	N/A
Moose Creek	35	2.2	25	10	910	1.1	89	N/A	N/A
Lizard Creek	25	2.5	24	1	416	1.4	6	1568	0.4
Moran Bay	9	0.8	6	2	344	1.9	43	N/A	N/A

FIG. LEGENDS

Fig. 1. Distribution of stream nutrient uptake studies for NH_4^+ and NO_3^- grouped by stream size. Majority of estimates are from streams with discharge $<200 \text{ L s}^{-1}$. Numbers above solute additions labeled above each bar. Data summarized from Appendix A.

Fig. 2. (A) Ammonium and (B) nitrate and associated conductivity from pulse releases in the Snake River.

Fig. 3. Meta-analysis of previously published results plus this study shows that uptake length (S_w) of NH_4^+ (A) and NO_3^- (B) increases with stream discharge Q (L s^{-1}). Note that we excluded studies not using stable isotopes where $S_w > 5000\text{m}$ for NH_4^+ or NO_3^- from the dataset in Appendix A. (C) $\text{NH}_4^+ S_w$ plotted vs. $\text{NO}_3^- S_w$ for streams where both solutes were collected ($N=132$). The dashed line represents the 1:1 relationship. We note that plotting $\text{NH}_4^+ V_f$ vs. $\text{NO}_3^- V_f$ would be identical because Q and width are the same for both releases; thus for either plot, biological demand relative to concentration for NH_4^+ is higher than for NO_3^- .

Fig. 4. Hypothesized relationship of uptake length with river size. The dashed lines represent uptake length of a nutrient across the range of stream sizes for NH_4^+ and NO_3^- based on Fig. 3. The dashed arrows show how uptake in rivers may not follow the trajectory for streams.

Fig. 1

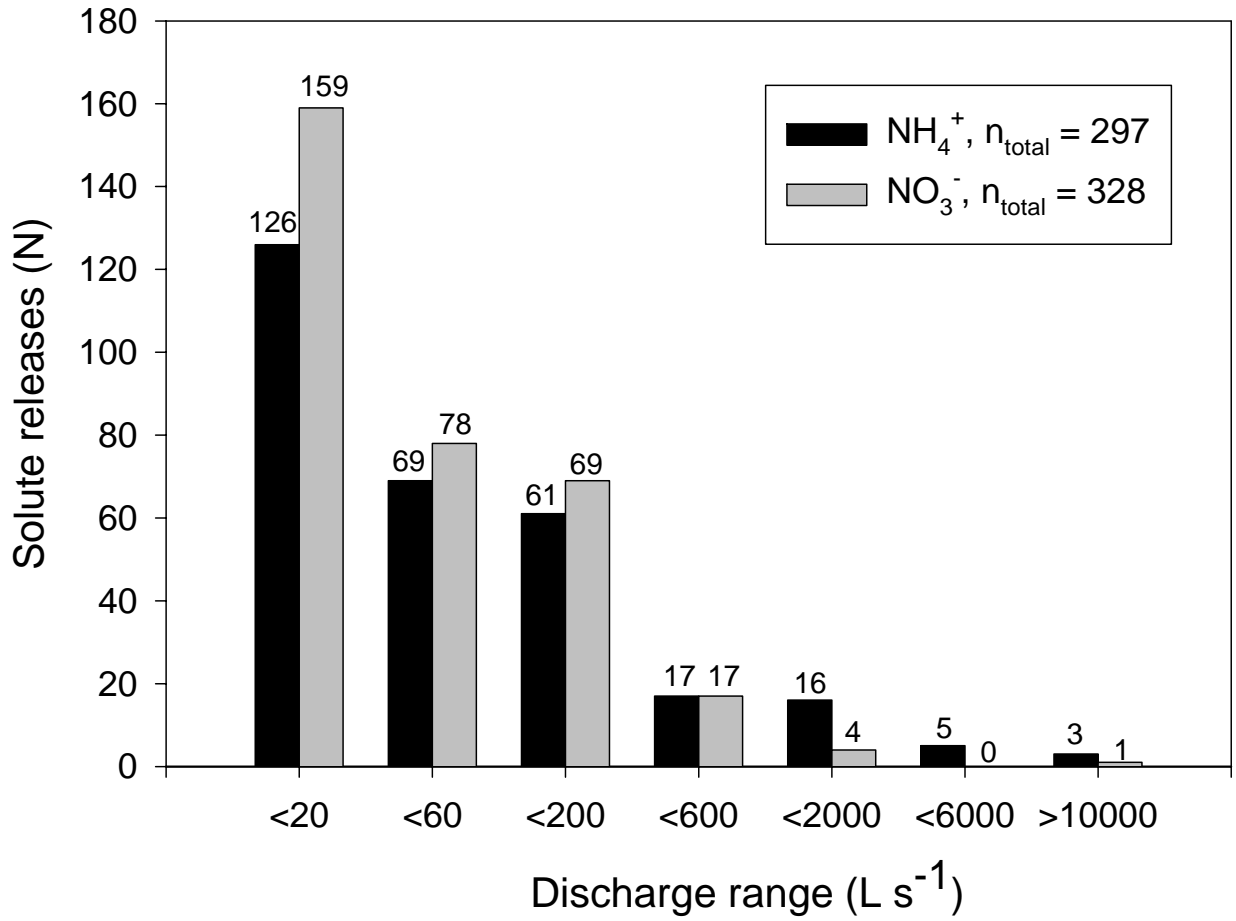


Fig. 2

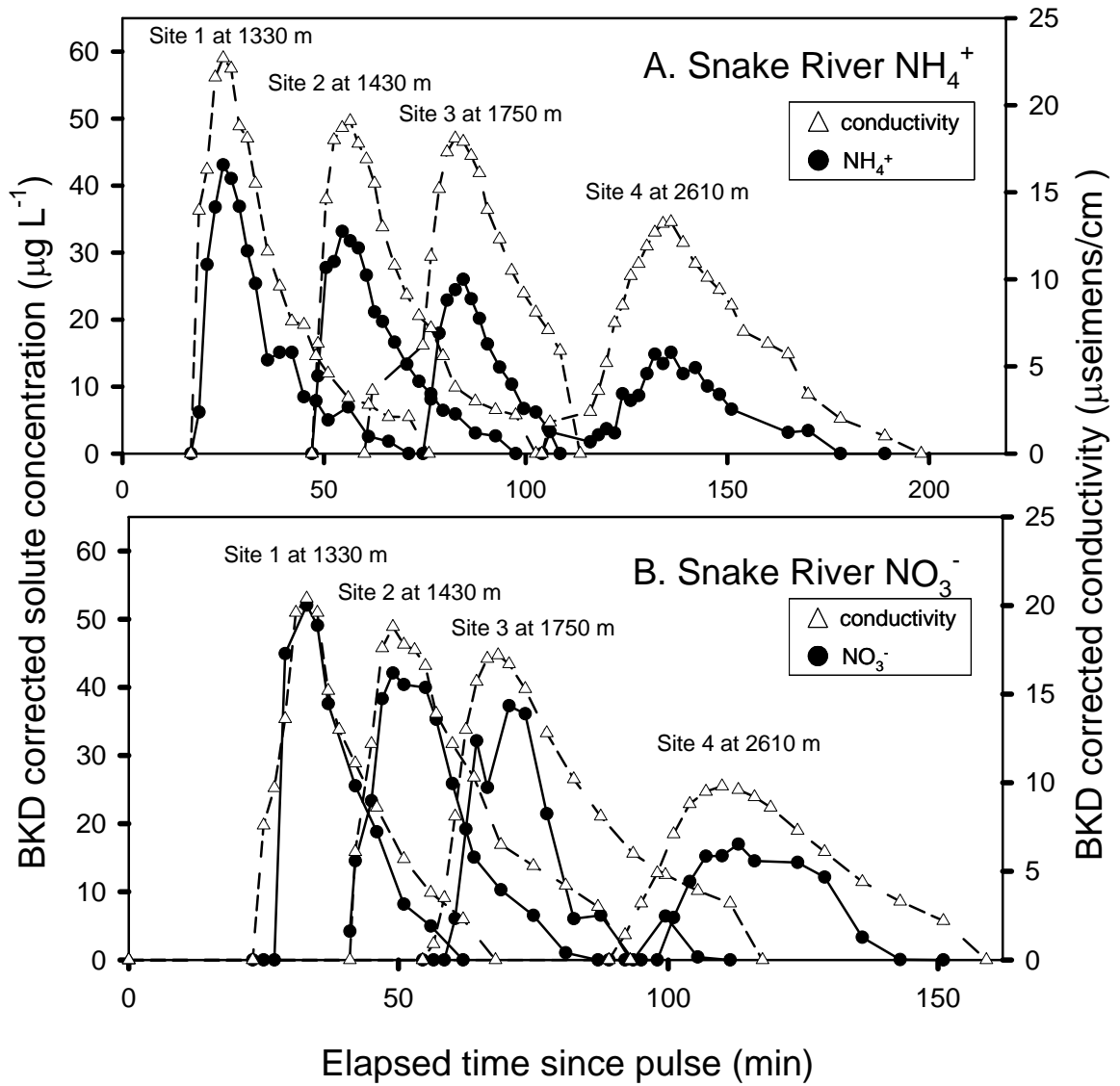


Fig. 3

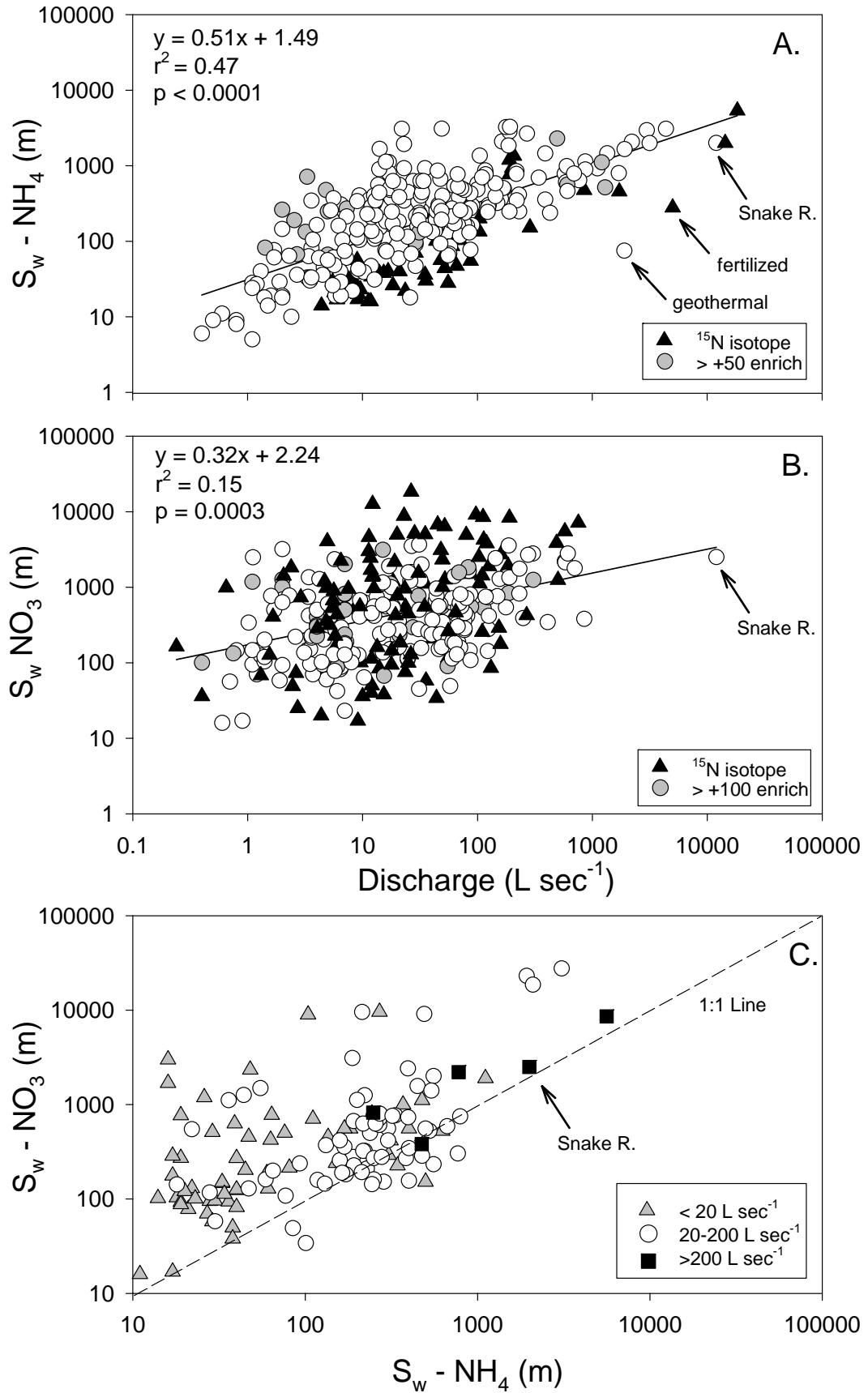


Fig. 4

