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 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 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

INTRODUCTION

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

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

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

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

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

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

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

MATERIALS AND METHODS

Study Site

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

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

Pulse addition method

We conducted pulse additions using a conservative tracer (chloride, Cl^-) plus a reactive solute (ammonium, NH_4^+ or nitrate, NO_3^- conducted separately). We added the nutrient pulse by filling a 610-L cattle tank with river water and 276 kg of NaCl and 4.3 kg KNO_3 or 5.7 kg $(NH_4)_2SO_4$, depending on the release and mixing until dissolved. Before the nutrient/conservative tracer additions, we conducted a preliminary release of only conservative tracer, NaCl, and stationed crews at sites downstream (1330, 1430, 1750 and 2610m from the release point) with conductivity meters to estimate travel time and mixing, allowing us to measure the travel distance required for the solute solution to be well mixed across the channel, and to fine tune how much reactive solute we had to add. The key to mixing in the Snake River was placing the first sampling station below a large eddy created from a pool located at a river bend. Considering previous research that has shown that enrichment-type releases can saturate nutrient demand, and thus underestimate nutrient uptake (Mulholland et al. 2002, Payn et al. 2005), we aimed to raise the peak concentrations of NH_4^+ and NO_3^- during the peak of the pulse to ~50 μg/L above background concentrations. This increase was analytically detectable, but the highest concentration during the pulse was likely not high enough to saturate demand (Dodds et al. 2002, Earl et al. 2006), and only lasted for a few minutes at most. During each pulse, we collected water samples every 2 minutes at each station to characterize the peak as it passed by a station, while also measuring specific conductance. Upon return to the laboratory, we quantified NO_3^-

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

Pulse release calculations

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

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

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

RESULTS

Quantifying inorganic N uptake in the Upper Snake River

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

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

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

Snake River nitrogen uptake in context of meta-analysis

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

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

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

Although stream size is a major driver of S_w, increasing nutrient concentration also lengthens S_w (Stream Solute Workshop 1990), therefore unexplained variation in the S_w vs. Q relationship may be explained by N availability, either as background or plateau concentration (for those measured using short-term nutrient additions). For NH_4^+, Fig. 3A identifies estimates made using ^{15}N isotope additions which do not raise background NH_4^+ concentrations; these estimates fall below the regression line, being the least likely to overestimate S_w due to a saturation effect (sensu Mulholland et al. 2002). The ^{15}N tracer estimates contrast with those S_w estimates made with short-term enrichment methods where background enrichment was >50µg NH_4-N/L; these estimates fall above the regression line indicating that excess NH_4^+, particularly in smaller streams, can result in longer S_w estimates (Fig. 3A). We compared the slope of the regression of Q vs. S_w for all data (Fig. 3A) with the regression of Q vs. ^{15}N tracer data only, and although the regression was also significant for Q vs. $^{15}NH_4$ S_w (linear regression, $y = 0.69x + 0.79$, $r^2 = 0.71$, $p<0.0001$), the slope of 0.69 was significantly greater than that from the Q vs. S_w regression for all data (ANCOVA, $p<0.0001$, Fig 3A). In contrast, for NO_3^- S_w, ^{15}N tracer estimates did not influence the relationship between S_w and Q (Fig. 3B). When we compared the slope of the regression of Q vs. S_w for all data (Fig. 3B) with the regression of Q vs. ^{15}N tracer

data only, the regression was again significant for Q vs. $^{15}NO_3$ S_w (linear regression, y = 0.42x + 2.23, r^2= 0.16, p<0.0001), but the slope of 0.42 was not significantly different than the slope using all data (ANCOVA, p=0.579, Fig 3B). In summary, NO_3^- S_w does not appear to be as sensitive to variation in NO_3^- availability, which contrasts with results from the NH_4 S_w meta-analysis.

We can further explore the secondary influence of ambient concentration by examining it in the context of the residuals of the S_w vs. Q relationship for each solute. For NH_4^+, the residuals of the Q vs. S_w relationship were significantly related to background NH_4^+ concentration (r^2=0.13, p<0.0001). In contrast, this was not the case for the residuals of the Q vs. NO_3^- S_w relationship and NO_3^- concentration (p=0.316). For the meta-analysis, the range in background concentration of NH_4^+ and NO_3^- varied considerably between the two datasets; background NH_4^+ ranged from ~1-160 μg N L^{-1}, whereas the NO_3^- range was almost 40X larger (~1-6100 μg N L^{-1}). There has been some support in the literature that shows that NH_4^+ is used preferentially over NO_3^- to satisfy inorganic N demand (e.g. Dortch 1990), supporting our results indicating that background concentration of NH_4^+ was a major driver in the deviation from the Q vs. S_w relationship, but the same was not true for NO_3^- S_w.

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

We also plotted NH_4^+ S_w vs. NO_3^- S_w from the subset of studies (N=132) that quantified both solutes on the same stream (Fig. 3C). If NH_4^+ and NO_3^- were biologically used interchangeably, we would predict that the data would show a 1:1 relationship (dashed line, Fig. 3C), but in fact this is not the case (91% of the data fall on or above the 1:1 line). In particular, for the smallest streams (open boxes, Fig 3C), when NH_4^+ S_w is low (i.e. highest demand), NO_3^- S_w is longer, and it appears that NH_4^+ is meeting the inorganic N demand. For the largest systems, (closed boxes, Fig. 3C), the data (including that for the Upper Snake River) approach the 1:1 line. In streams >200 L s^{-1}, the demand for NH_4^+ compared to NO_3^- is similar. These results suggest that larger systems appear to behave distinctly different than smaller systems in regards to NH_4^+ vs. NO_3^- cycling.

DISCUSSION

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

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

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

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

Three scenarios of large river biotic demand:

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

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

To date, we know of only three rivers with Q >10000 L s^{-1} where N uptake was empirically measured using whole-system techniques comparable to measurements made in smaller systems (Fig. 1). While NH_4^+ S_w was long in all 3 rivers, despite their geographic separation, NH_4^+ S_w in the Lower Kuparuk River was more than twice as long (S_w = 5360m, Wollheim et al. 2001), compared to the NH_4^+ S_w = 2000m for both the Kansas River, KS (Dodds et al. in review) and

the Upper Snake River WY (this study)(Fig. 3A). When we account for differences in discharge among the 3 rivers (Q= 12,000–18,300 L s^{-1}), NH_4^+ demand (expressed as an uptake velocity, V_f) was also lowest in the arctic Lower Kuparuk at 3.7 mm min^{-1}, compared to the high of 9.3 mm min^{-1} in the Upper Snake River during summer (this study); the low-gradient Kansas River fell in between (V_f = 5.7 mm min^{-1}). Both the Lower Kuparuk River and the Upper Snake River have very low background inorganic N concentrations ($NH_4^+ + NO_3^-$ = 10 – 20 ugN/L), which would be expected to result in fairly high V_f estimates, yet the NH_4^+ V_f from the Upper Snake River was ~2.5 times higher than that of the arctic Lower Kuparuk River, perhaps reflecting differences in biotic activity influenced by lower (albeit summer) water temperatures (Wollheim et al. 2001). Notably, these NH_4^+ V_f from 3 rivers are comparable to those found in smaller streams both when we compare streams of varying size within a catchment (e.g. Upper Snake River vs. estimates in Hall and Tank 2003) or among small streams in general (Ensign and Doyle 2006). Data summarized from Appendix A (N= 297 data points) indicate a mean NH_4^+ V_f = 7.58 mm min^{-1} and the median NH_4^+ V_f = 3.75 mm min^{-1}. Results from this meta-analysis lend support to the idea that biological demand may remain constant or even increase with increasing river size, but clearly more systematic testing of these predictions are needed (sensu Ensign and Doyle 2006). Recent models have assumed that V_f remains constant with increasing stream size, which means that large rivers can play an important role in mitigating N export, because of the longer travel time (and thus processing time) associated with larger systems (Wollheim et al. 2006). As for NO_3^- uptake in particular, our estimate from the Upper Snake River is the only one available, despite the relevance of NO_3^- export to downstream and coastal eutrophication issues (Seitzinger et al. 2002, Bernot and Dodds 2005). Clearly, more empirical estimates are needed.

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

Our analyses suggest that NH_4^+ and NO_3^- uptake respond differently to river size (Figs. 3A & B). Our data show that NH_4^+ and NO_3^- are not interchangeable forms of N; the slopes of the relationship of each vs. Q were statistically different from each other (0.51 for NH_4^+ and 0.32 for NO_3^-). Further, S_w-NO_3^- was far longer (often orders of magnitude) than S_w-NH_4^+ measured in the same stream at the same discharge (Fig. 3C). The results from the meta-analysis of those streams that had concomitant measurements for both S_w-NO_3^- and S_w-NH_4^+ (N=132) are consistent with a smaller subset of data for 10 streams from different biomes presented by Peterson et al. (2001) showing that S_w-NO_3^- was 10X greater than S_w-NH_4^+. Interestingly, the difference between S_w-NO_3^- and S_w-NH_4^+ becomes smaller as streams get larger (Fig. 3C, $Q >$ ~200 L/s), which may suggest that either form of inorganic N may be able to meet biotic demand in rivers, while NH_4^+ is preferred in small streams. This finding is similar to that of Ensign and Doyle (2006) who found that cumulative uptake flux of NO_3^- increased with stream order while the same was not true for NH_4^+ . One reason for this may be that larger systems have increased nutrient demand as a result of the contribution of water-column processes in addition to benthic dynamics (that dominate smaller streams). Further study of this hypothesis is needed.

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

Second, $^{15}N\text{-}NH_4^+$ tracer studies have documented that in some streams nitrification can account for a large (ca. 45%) fraction of apparent NH_4^+ removal (reflected in $S_w\text{-}NH_4^+$)(Peterson et al. 2001, Simon et al. 2007). Thus some portion of the $S_w\text{-}NH_4^+$ in the meta-analysis represents NH_4^+ that was nitrified to NO_3^-, which may lead to increased NO_3^- background concentrations (e.g. Bernhardt et al. 2002) and higher variation and magnitude of $S_w\text{-}NO_3^-$ values. For NO_3^-, dissimilatory nitrate reduction to ammonium (DNRA) could generate ammonium; however, our understanding of this process is lacking, and its prevalance in streams is currently being examined (Burgin and Hamilton 2007).

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

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

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

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

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

The River Continuum Concept and nutrient cycling

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

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

Summary- large river nutrient cycling

Quantifying the potential for large rivers to process nutrients is essential to elucidate the role of large rivers in controlling nutrient export to downstream ecosystems, such as the Gulf of Mexico, reservoirs, and estuaries. Modeling efforts have suggested that large rivers are important sites of nutrient removal (e.g. Wollheim et al. 2006), but empirical estimates lag far behind, mainly as a result of the methodological difficulties in applying small-stream approaches to larger river systems. We have presented a method to quantify nutrient uptake in large rivers and we place our results in the context of a meta-analysis of previous research thereby providing a context in which to place future studies. 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 and ultimately, to manage water quality effectively.

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APPENDIX A: Studies included in the meta-analysis. Cb = background concentration, Cp= plateau concentration. Note that studies not using stable isotopes where S_w >5000m for NH_4 or NO_3 were excluded from dataset to generate Fig. 3. (Ecological Archives EXXX-XXX-XX).

APPENDIX B: Full citations for studies included in meta-analysis (Ecological Archives EXXX-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^+ ($\mu g\ L^{-1}$)	$NH_4^+ S_w$ (m)	$NH_4^+ V_f$ ($mm\ min^{-1}$)	NO_3^- ($\mu g\ L^{-1}$)	$NO_3^- S_w$ (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 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 >5000m for NH_4^+ or NO_3^- from the dataset in Appendix A. (C) NH_4^+ S_w plotted vs. 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 NH_4^+ V_f vs. 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

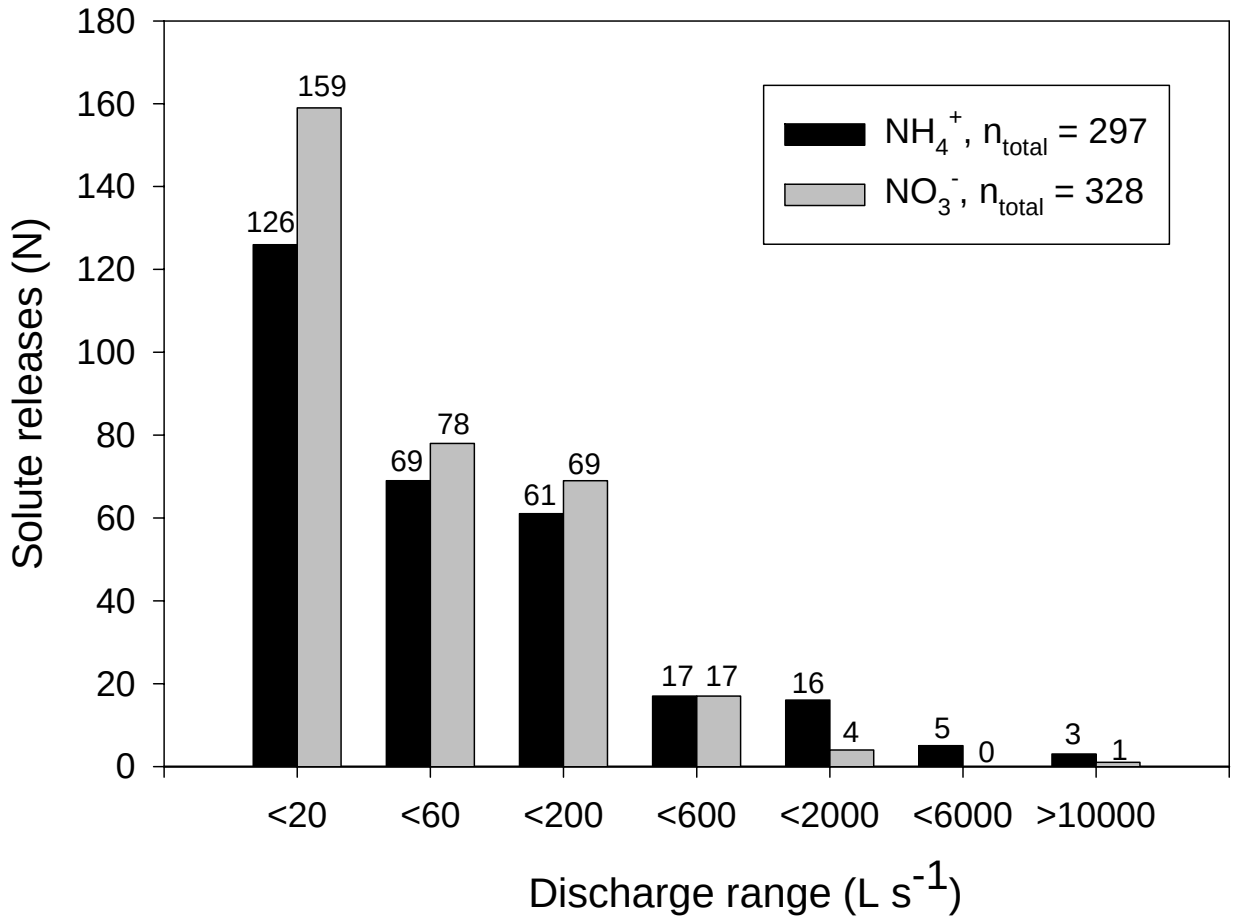

Solute releases (N)
180
160
140
120
100
80
60
40
20
0
NH_4^+, n_{total} = 297
NO_3^-, n_{total} = 328
126
159
69
78
61
69
17
17
16
4
5
0
3
1
<20
<60
<200
<600
<2000
<6000
>10000
Discharge range (L s^{-1})

Fig. 2

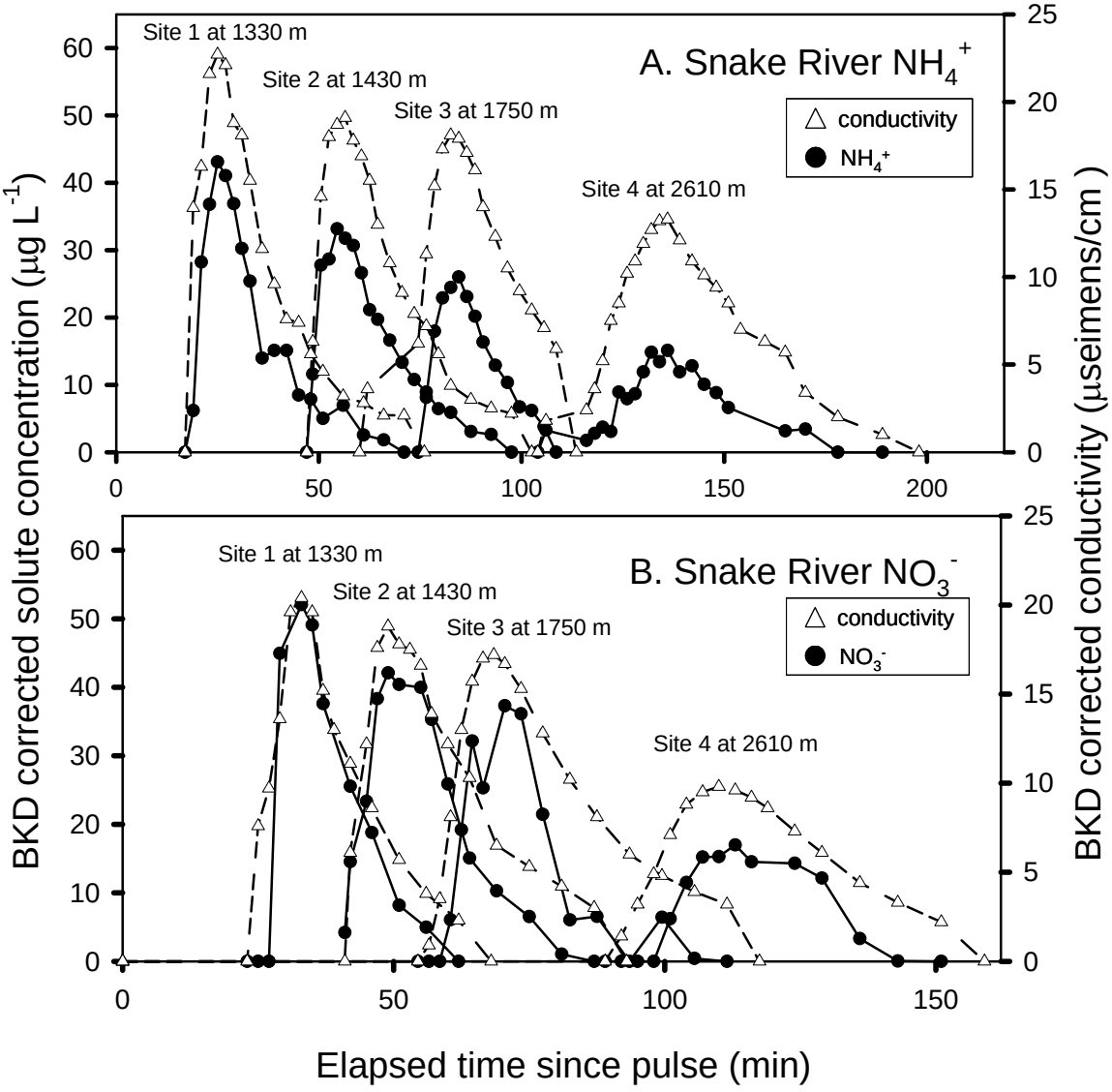

Site 1 at 1330 m
Site 2 at 1430 m
Site 3 at 1750 m
Site 4 at 2610 m
A. Snake River NH_4^+
conductivity
NH_4^+
B. Snake River NO_3^-
conductivity
NO_3^-
BKD corrected solute concentration (µg L^{-1})
BKD corrected conductivity (µseimens/cm)
Elapsed time since pulse (min)

Fig. 3

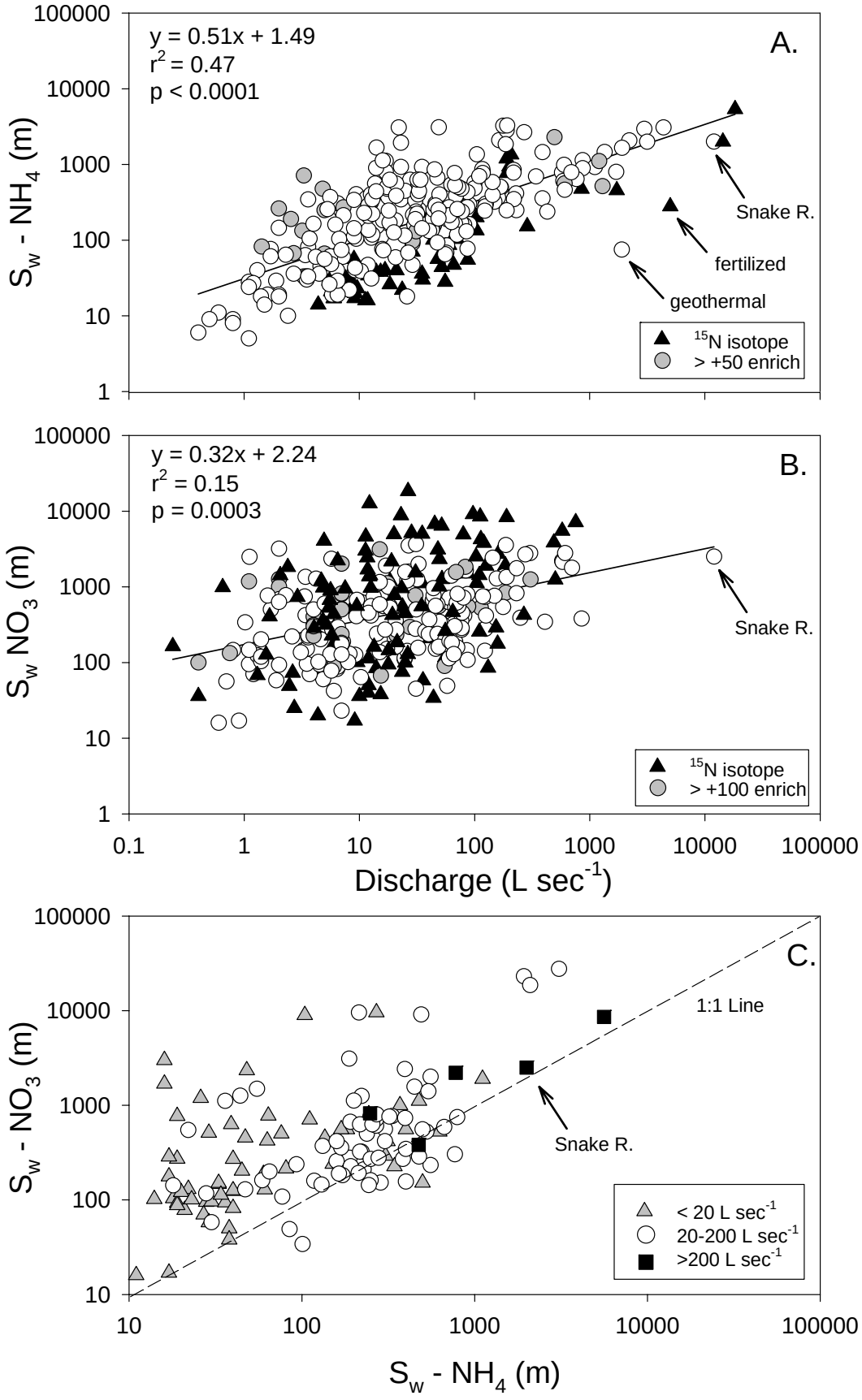
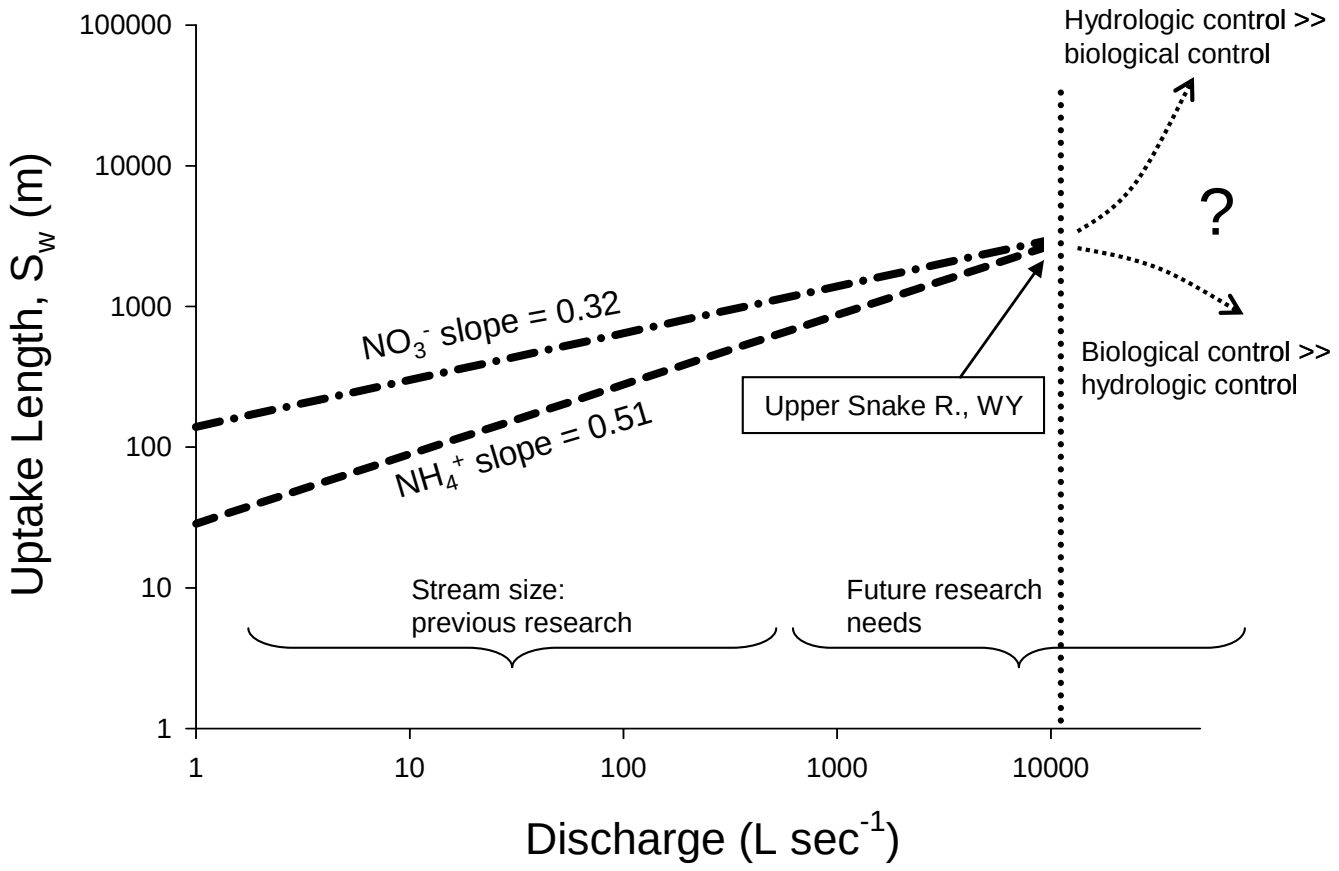

y = 0.51x + 1.49
r2 = 0.47
p < 0.0001
A.
Sw - NH4 (m)
Snake R.
fertilized
geothermal
15N isotope
> +50 enrich
y = 0.32x + 2.24
r2 = 0.15
p = 0.0003
B.
Sw NO3 (m)
Snake R.
15N isotope
> +100 enrich
Discharge (L sec-1)
C.
1:1 Line
Snake R.
< 20 L sec-1
20-200 L sec-1
>200 L sec-1
Sw - NO3 (m)
Sw - NH4 (m)

Fig. 4


Uptake Length, S_w (m)
100000
10000
1000
100
10
1
1
10
100
1000
10000
Discharge (L sec^{-1})
NO_3^- slope = 0.32
NH_4^+ slope = 0.51
Upper Snake R., WY
Hydrologic control >> biological control
?
Biological control >> hydrologic control
Stream size: previous research
Future research needs