1 Comment on "Solute specific scaling of inorganic nitrogen and phosphorus uptake in

- 2 streams" by Hall et al. (2013).
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12 Abstract

13 Hall et al. (2013) presented a synthesis on 969 nutrient tracer experiments conducted primarily in headwater streams (generally $< 4^{\text{th}}$ order streams), with discharges < 200 L/s for 14 15 ~90% of the experiments, and used a scaling method to test the hypothesis that nutrient demand is 16 constant with increasing stream size (i.e., along a river continuum). In this comment, we present a 17 reanalysis of a subset of the data used by Hall et al. (2013) and propose that their correlations 18 between nutrient uptake lengths of ecologically important solutes and specific discharge are 19 inadvertently spurious. Therefore, the conclusions derived from such correlations are debatable. 20 We conclude the comment highlighting some of the uncertainties associated with using modeling 21 frameworks for scaling nutrient uptake in stream ecosystems.

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23 Estimating uptake lengths: Transport model used by Hall et al. (2013)

24 Hall et al. (2013) analyzed a dataset of in-stream nutrient uptake experiments performed 25 using plateau tracer injections. The basis of these experiments and estimation of nutrient uptake 26 metrics come from the advection-dispersion equation (equation 1), with the addition of a first-27 order uptake rate coefficient (Stream Solute Workshop, 1990; Runkel, 2007):

$$\frac{dc}{dt} = -u\frac{dC}{dx} + D\frac{d^2C}{dx^2} - K_c c, \qquad (1)$$

where $c \left[M L^{-3} \right]$ is the concentration of the reactive solute at a cross-section located downstream 29 of the solute injection site; $u [LT^{-1}]$ the mean flow velocity; $D [LT^{-2}]$ the dispersion coefficient; 30 K_c [T⁻¹] the first-order rate coefficient representing nutrient uptake; x [L] longitudinal distance; 31 32 and t [T] time. Assuming that dispersion is negligible at plateau concentrations (i.e., when 33 dc/dt = 0, equation (1) can be solved for downstream solute concentration:

$$c = c_o$$

 $\exp(-(K_c/u) x)$, (2)

where $c_0 [M L^{-3}]$ represents the initial (or upstream) concentration. The form of this solution 35 motivated the introduction of the uptake length metric, $S_w = u/K_c$, which is a representation of 36 37 the average distance traveled by a nutrient molecule in inorganic phase prior to uptake (Ensign 38 and Doyle, 2006). Due to experimental simplicity, equation (2) has guided data collection efforts 39 on nutrient cycling where an experimentalist estimates S_w by measuring the plateau concentrations upstream (c_{up}) and downstream (c_{dn}) of a study reach of length L: 40

41 $S_w = u/K_c = L/\ln\left(C_{up}/C_{dn}\right).$ (3)

Note that equations (1-3) support estimates of S_w , given stream conditions satisfy model 42 43 assumptions, i.e., stream reaches with constant discharge and where dispersion and transient 44 storage do not play important roles (Runkel, 2007). The uptake length derived from equations (145 3) is equivalent to S_w^I in Runkel (2007), who derived four different uptake lengths 46 ($S_w^I, S_w^{II}, S_w^{III}, S_w^{IV}$) from solute transport models with increased complexity (i.e., adding transient 47 storage, lateral inflows and dispersion). Following Runkel (2007), uptake lengths can be 48 generally represented by a velocity term and an uptake term.

49 It is important to keep in mind that S_w is an abstract variable represented by model 50 parameters that cannot be simultaneously measured. Since u and K_c are likely to be highly 51 variable along a stream reach, measurements of longitudinal decline in tracer concentrations 52 (c_{up}, c_{dn}) and stream length (L) offer a more tractable approach to estimating S_w through the use 53 of equation 3. While the use of equation 3 circumvents errors associated with estimating u and 54 K_c at the reach scale, the estimation of S_w using c_{up} , c_{dn} , and L must be numerically equivalent to 55 u/K_c at the reach scale. As is the case with any abstract variable derived from a mathematical 56 model, using S_w to infer stream processes entails acknowledging the quantitative role of the 57 model parameters u and K_c from where it was derived.

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59 Critique to the scaling approach used by Hall et al. (2013)

60 The analysis presented by Hall et al. (2013) was based on plateau experiments conducted in 61 multiple stream ecosystems, where S_w was estimated for each experiment using equation (3). Hall 62 et al. correlated nutrient uptake length, S_w (L), with specific discharge, Q/w (L² T⁻¹), to test the 63 hypothesis that nutrient uptake demand is constant across stream orders.

$$S_w \propto (Q/w)^a, \tag{4}$$

$$v_f = \frac{Q/w}{S_w},\tag{5}$$

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69 where Q (L³T⁻¹) is stream discharge, w (L) is stream width, a is a scaling exponent and v_f (L T⁻¹) 70 is the nutrient uptake demand (or nutrient uptake velocity, as it has been traditionally called).

In their hypothesis testing, the existence of a constant nutrient uptake demand (constant v_f) was implied by a scaling exponent a = 1 (isometric scaling), whereas a scaling exponent $a \neq 1$ (allometric scaling) would imply the reverse. Note that in this context, the existence of a constant nutrient uptake demand would be useful to scale and predict nutrient uptake in stream ecosystems.

76 In Table 1 we present the different forms that S_w vs. Q/w from Hall et al. (2013) would take 77 if such relationship was estimated for two general types of natural channel geometries.

Table 1. The relationship S_w vs. Q/w for natural channel geometries.

Quantity or relationship	Rectangular channel	Non-rectangular channel
Q	$u \cdot A$	$u \cdot A$
S_w	u/K_c	u/K_c
Q/w	$u \cdot h$	$u \cdot (f(w,h)/w)$
S_w vs. Q/w	u/K_c vs. $u \cdot h$	u/K_c vs. $u \cdot (f(w,h)/w)$

81 Note that each side of S_w vs. Q/w shares the common (hidden) variable u. Therefore, an 82 increase in u (e.g., with stream order or increasing discharge) would increase both sides of the 83 proportion, likely forcing a strong correlation between the variables. This would happen 84 regardless of whether u is measured in the field or not because S_w is an abstract quantity derived 85 from u and K_c (cf. equations 2-3) and, by definition, $Q = u \cdot A$. The fact that Hall et al. (2013) used only estimates of S_w , and field measurements of Q and w to seek a mechanistic relationship 86 87 from S_w vs. Q/w (cf. equation (4)) does not change the induced correlation created by having the 88 factor u playing a key quantitative role on both sides of the relationship. Since the form of S_w is 89 dependent on the transport model presented in equations (1-2), the only way to negate the role of 90 u in S_w (note that it cannot be negated in Q/w) is to select a completely different transport model 91 and perform a completely different set of field experiments. Also, under the ideal scenario in 92 which we could actually measure S_w in streams (i.e., if S_w was not an abstract variable), the 93 regression S_w vs. Q/w would mainly support the development of conceptual models for S_w , 94 which already exist.

95 We propose that if a meaningful, significant correlation exists between S_w and Q/w, there 96 should be a significant correlation between the underlying parameters (i.e., $1/K_c$ vs. h in 97 rectangular channels or $1/K_c$ vs. f(w, h)/w in other types of natural channels). However, if there 98 is not a corresponding correlation in both of these cases, then the correlation between S_w and 99 Q/w would be falsely influenced by the presence of u in both products. Benson (1965) and 100 Kenney (1982) demonstrated that spurious correlations can result from the use of ratios or 101 products that share a common factor and are more likely when working with complex variables 102 and dimensional analysis. The relationship from Hall et al. (2013) that we deem spurious is 103 analogous to that of Model II presented by Benson (1965) for the spurious correlation of products sharing a common factor (i.e., $X_1 \cdot X_2$ vs. $X_3 \cdot X_2$; where $X_1 = 1/K_c$, $X_2 = u$, $X_3 = h$ or 104 105 $X_3 = f(w, h)/w$, cf. Table 2 in Benson (1965)). As shown by Benson (1965), the correlation of 106 complex variables (i.e., S_w and Q/w) is dependent on the coefficients of correlation and variation 107 of the three original component variables. Due to the presence of a common factor in the scaling 108 relationship proposed by Hall et al. (2013), we hypothesize that it is a spurious correlation (u109 influences both S_w and Q/w) that may be mechanistically irrelevant for scaling in-stream nutrient 110 uptake.

111 We tested our hypothesis using the dataset published by Tank et al. (2008), another meta-112 analysis of nutrient addition experiments which was included in the Hall et al. (2013) meta-113 analysis. This dataset was chosen because it reports values for S_w , Q, w, and h for nutrient 114 experiments with NH_4 and NO_3 (SRP not included), even though these values were not reported 115 for all the studies (n=143 for NH₄, n=210 for NO₃). Note that since we do not know the particular 116 geometry for each channel where the tracer experiments were conducted (i.e., we do not know 117 f(w,h), we assumed a rectangular channel geometry (i.e., A = f(w,h) = wh), which is the 118 same assumption made by Hall et al. (2013) while defining their equations for uptake length and 119 uptake velocity (cf. equations 1-2 in Hall et al (2013)). The dataset published by Hall et al. (2013) 120 does not include values of h, hence we were not able to use it for our analysis. While the 121 assumption of having rectangular channels might be seen as an overgeneralization, it is the only 122 one that allows us to see trends given the scarce information available on the channel geometries 123 of the headwater streams where the experiments were conducted. Furthermore, the transport 124 model implicitly used by Hall et al. (2013) assumes uniform flow (i.e., dh/dx = 0, dw/dx = 0), which supports our assumption of using a prismatic channel for testing our spurious correlationhypothesis.

We proposed a null condition in which we removed the common variable u from the scaling relationship and compared the correlation with that of the original scaling relationship (i.e., we compared $1/K_c$ vs. h and S_w vs. Q/w). We calculated mean stream velocity as $u = Q/(w \cdot h)$. This allowed us to produce values for the relationship $1/K_c$ vs. h, by dividing S_w and Q/w by u(cf. Table 1). By doing so, we were able to evaluate the scaling relationship with and without the common term u to compare the coefficient of determination, r^2 , for both relationships. Results of this analysis are shown for NH₄ and NO₃ in Figures 1 and 2.

134 Our results show that $1/K_c$ vs. h are weakly correlated $(r_{(NH4)}^2=0.029, p_{(NH4)}=0.042;$ $r_{(NO_3)}^2 = 0.036$, $p_{(NO_3)} = 0.0057$). However, the correlation S_w vs. Q/w is higher $(r_{(NH_4)}^2 = 0.161)$, 135 $p_{\text{(NH4)}} < 0.00001; r_{\text{(NO3)}}^2 = 0.151, p_{\text{(NO3)}} < 0.00001), \text{ i.e., } r^2 \text{ is improved by 452\% and 317\% for NH_4}$ 136 137 and NO₃, respectively. These findings suggest that the correlation S_w vs. Q/w is spurious because 138 it is driven by the shared velocity (u) term, rather than by an inherent correlation between the 139 inverse of the nutrient uptake rate constant $(1/K_c)$ and stream depth (h). The correlations shown in Figures 1 and 2 are comparable to those reported by Hall et al. (2013). However, we note that 140 141 the r^2 values do not match because of different datasets (we were limited by the number of studies 142 reporting all parameters S_w , Q, w, h), and our aggregation of reference and altered streams. 143 Regardless, our analysis suggests that the inclusion of the parameter u falsely improves the 144 correlation of the investigated relationships.

145 The mechanism producing spurious correlation in the dataset by Hall et al. (2013) can be 146 viewed more clearly using three arbitrary and uncorrelated variables to represent the relationship 147 between $X_1 \cdot X_2$ and $X_3 \cdot X_2$. We gathered mean daily values for specific conductance $(X_1, \mu S/cm)$ in the Potomac River (DC) (USGS, 2008a), turbidity (X₂, FNU) in the Little Arkansas River (KS) 148 149 (USGS, 2008b), and temperature $(X_3, °C)$ in the Rio Grande (NM) (USGS, 2008c) for the year 150 2008. First, we isolated the common factor X_2 and plotted X_1 versus X_3 , as shown in Figure 3 (r^2 151 = 0.020, p = 0.012). As expected, there was no statistically significant correlation between these 152 water quality parameters. However, when we incorporated the turbidity (X_2) from a remote location by plotting $X_1 \cdot X_2$ vs. $X_3 \cdot X_2$ (n=313), we found a positive correlation (Figure 4) with a 153 drastic improvement in r^2 ($r^2 = 0.846$, p < 0.00001). Despite the evident correlation in this 154 155 relationship, the result is mechanistically irrelevant. Analogous to this case example where the 156 correlation is driven by X_2 (turbidity), the correlation S_w vs. Q/w seems to be driven by u (recall 157 $S_w = u / K_c$ and $Q/w = u \cdot h$ or $Q/w = u \cdot (f(w, h)/w)$). Thus, our findings suggest that the 158 results produced by Hall et al. (2013) regarding the isometric scaling (a=1) of NH₄, and 159 allometric scaling (a>1) of NO₃ and SRP, resulted from an unintentional spurious correlation of 160 S_w vs. Q/w.

161 In addition to scaling nutrient uptake length with specific discharge, Hall et al. (2013) also 162 provide a method for scaling nutrient uptake with stream length using several parameters 163 including the scaling exponent a obtained from the analysis of the scaling relationship shown in 164 equation (2). Our findings have implications for these results as well. While Hall et al. (2013) 165 commented that their results for scaling uptake with stream length was most influenced by b (hydraulic geometry exponent), their analysis still relies on the spurious correlation S_w vs. Q/w166 167 not only for parameter a, but also for their subsequent derivations (cf. equations 3-10 in Hall et 168 al. (2013)). Therefore, we also find those results debatable.

171 Concluding remarks

172 The majority of nutrient addition experiments have been performed in headwater streams 173 because they are more experimentally tractable (Tank et al., 2008). Consequently, the dearth of 174 empirical evidence of nutrient processing in large rivers limits our understanding of the role of 175 these rivers in nutrient processing at the catchment scale. While empirical and theoretical 176 advances are being made toward performing nutrient addition experiments in large rivers (Tank et 177 al., 2008; Covino et al., 2010), the need to understand and quantify nutrient export from these 178 systems has driven the development and use of scaling relationships. This motivated the work by 179 Hall et al. (2013) and their results after correlating S_w vs. Q/w for a large dataset of field nutrient 180 experiments suggest that uptake demand (v_f) for NH₄ is relatively constant across stream orders, 181 whereas that for soluble reactive phosphorous (SRP) and NO₃ declines with increasing specific 182 discharge. Here, we demonstrated that these conclusions are subject to debate due to 183 unintentional spurious correlations present in their scaling relationships.

184 We also suggest that S_w should be used with extreme caution to scale nutrient uptake 185 because, even though its magnitude can be directly estimated from relatively simple field 186 measurements, its mechanistic interpretation strongly depends on the type of model assumed to 187 describe the real-world system (cf. Table 1 in Runkel (2007)). This is because the same estimate 188 of the magnitude of S_w may be arbitrarily used to co-estimate or constrain the magnitude of 189 parameters describing different (arbitrary) sets of processes (see Cases I-IV in Runkel (2007)). 190 Finally, when a model describing a given set of processes is chosen to interpret how nutrient 191 uptake scales along a river continuum, the main assumption is that such processes operate 192 analogously along the continuum. For example, if the model of advection-decay chosen by Hall et 193 al. (2013) to interpret S_w across stream orders were correct, our analysis presented in Figures 1 194 and 2 would suggest that headwater streams tend to have higher nutrient uptake rate coefficients, 195 which might be mechanistically supported by their higher ratio of benthic area to cross-sectional 196 area. However, this (biased) analysis would not provide insight into how mass-transfer processes 197 between the main-channel and transient storage zones may control nutrient uptake and retention 198 along the river continuum. Paradoxically, increasing the complexity of the transport models used 199 to derive S_w (e.g., Cases II-IV in Runkel (2007)) does not necessarily improve the mechanistic understanding gained on how nutrient uptake scales along the river continuum because such 200 201 models are poorly constrained (González-Pinzón et al., 2013), i.e., the number of parameters 202 introduce more degrees of freedom than the data collected (from field and remote measurements) 203 can constrain.

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Figure 1 – NH₄ scaling relationship with and without shared velocity term. The original relationship is represented by S_w vs. Q/w and the null condition by $1/K_c$ vs. h.



269 relationship is represented by S_w vs. Q/w and the null condition by $1/K_c$ vs. h.



