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September 2, 2015

Dear Editor Dr. Katja Fennel

Please find enclosed our revised manuscript "Comment on "Solute specific scaling of inorganic nitrogen and phosphorus uptake in streams" by Hall et al. (2013).". We are very pleased to see that our comment has already generated a very productive discussion within the biogeosciences community. As you have seen, we have replied in a timely manner to the comments submitted by the reviewers and other registered peers.

We have addressed and incorporated the revisions outlined in our responses on the discussion forum. In the final version of our manuscript, we also addressed the recent comments by Hall et al. We have reorganized the comment by sections and have added new text, new equations and a new table in an effort to make our points clearer to the broader scientific community.

Regarding your specific request about addressing Hall et al.'s point that "the covariate was not used on both sides of the regression, and their statement: "We would lose the ability to deduce mechanism, or test the functional form of relationships if we assume that unmeasured covariates negate the utility of the regression approach", we have added the text below, which is preceded by a new section demonstrating the derivation of the uptake length metric.

"In Table 1 we present the different forms that  $S_w$  vs. Q/w from Hall et al. (2013) would take 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
A	$w \cdot h$	f(w,h)
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. $u \cdot (f(w,h)/w)$

Note that each side of  $S_w$  vs. Q/w shares the common (hidden) variable u. Therefore, an increase in u (e.g., with stream order or increasing discharge) would increase both sides of the proportion, likely forcing a strong correlation between the variables. This would happen regardless of whether u is measured in the field or not because  $S_w$  is an abstract quantity derived 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 from  $S_w$  vs. Q/w (cf. equation (4)) does not change the induced correlation created by having the factor u playing a key quantitative role on both sides of the relationship. Since the form of  $S_w$  is dependent on the transport model presented in equations (1-2), the only way to negate the role of u in  $S_w$  (note that it cannot be negated in Q/w) is to select a completely different transport model and perform a completely different set of field experiments. Also, under the ideal scenario in which we could actually measure  $S_w$  in streams (i.e., if  $S_w$  was not an abstract variable), the regression  $S_w$  vs. Q/w would mainly support the development of conceptual models for  $S_w$ , which already exist."

We look forward to receiving your final decision and we want to thank you for all your hard work.

Sincerely,

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THANKS.

4 5 6 Comment on "Solute specific scaling of inorganic nitrogen and phosphorus uptake in streams" by Hall et al. (2013).

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**Keywords:** nutrient uptake, scaling, spurious correlations, streams, solute transport.

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## Abstract

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

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

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

$$\frac{dc}{dt} = -u\frac{dC}{dx} + D\frac{d^2C}{dx^2} - K_c c_2$$
where  $c$  [M L<sup>-3</sup>] is the concentration of the reactive solute at a cross-section located downstream

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

$$c = c_0 \exp(-(K_c/u) x), \tag{2}$$

where  $c_o$  [M L<sup>3</sup>] represents the initial (or upstream) concentration. The form of this solution motivated the introduction of the uptake length metric,  $S_w = u/K_c$ , which is a representation of the average distance traveled by a nutrient molecule in inorganic phase prior to uptake (Ensign and Doyle, 2006). Due to experimental simplicity, equation (2) has guided data collection efforts 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:

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

Note that equations (1-3) support estimates of  $S_w$ , given stream conditions satisfy model assumptions, i.e., stream reaches with constant discharge and where dispersion and transient storage do not play important roles (Runkel, 2007). The uptake length derived from equations (1-

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97 98 99 3) is equivalent to  $S_w^I$  in Runkel (2007), who derived four different uptake lengths  $(S_w^I, S_w^{II}, S_w^{III}, S_w^{III})$  from solute transport models with increased complexity (i.e., adding transient storage, lateral inflows and dispersion). Following Runkel (2007), uptake lengths can be generally represented by a velocity term and an uptake term.

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

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

The analysis presented by Hall et al. (2013) was based on plateau experiments conducted in multiple stream ecosystems, where  $S_w$  was estimated for each experiment using equation (3). Hall et al. correlated nutrient uptake length,  $S_w$  (L), with specific discharge, Q/w (L<sup>2</sup> T<sup>-1</sup>), to test the hypothesis that nutrient uptake demand is constant across stream orders.

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

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

where  $Q(L^3T^{-1})$  is stream discharge, w(L) is stream width, a is a scaling exponent and  $v_f(LT^{-1})$  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.

In Table 1 we present the different forms that  $S_w$  vs. Q/w from Hall et al. (2013) would take 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.

Rectangular channel	Non-rectangular channel
$w \cdot h$	f(w,h)
$u \cdot A$	$u \cdot A$
$u/K_c$	$u/K_c$
$u \cdot h$	$u \cdot (f(w,h)/w)$
$u/K_{c}$ vs. $u \cdot h$	$u/K_{c}$ vs. $u \cdot (f(w,h)/w)$
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Note that each side of  $S_w$  vs. Q/w shares the common (hidden) variable u. Therefore, an increase in u (e.g., with stream order or increasing discharge) would increase both sides of the proportion, likely forcing a strong correlation between the variables. This would happen regardless of whether u is measured in the field or not because  $S_w$  is an abstract quantity derived 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 from  $S_w$  vs. Q/w (cf. equation (4)) does not change the induced correlation created by having the factor u playing a key quantitative role on both sides of the relationship. Since the form of  $S_w$  is dependent on the transport model presented in equations (1-2), the only way to negate the role of u in  $S_w$  (note that it cannot be negated in Q/w) is to select a completely different transport model and perform a completely different set of field experiments. Also, under the ideal scenario in which we could actually measure  $S_w$  in streams (i.e., if  $S_w$  was not an abstract variable), the regression  $S_w$  vs. Q/w would mainly support the development of conceptual models for  $S_{w,s}$  which already exist.

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We propose that if a meaningful, significant correlation exists between  $S_w$  and Q/w, there should be a significant correlation between the underlying parameters (i.e.,  $1/K_c$  vs. h in rectangular channels or  $1/K_c$  vs. f(w, h)/w in other types of natural channels). However, if there is not a corresponding correlation in both of these cases, then the correlation between  $S_w$  and Q/w would be falsely influenced by the presence of u in both products. Benson (1965) and Kenney (1982) demonstrated that spurious correlations can result from the use of ratios or products that share a common factor and are more likely when working with complex variables and dimensional analysis. The relationship from Hall et al. (2013) that we deem spurious is 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  $X_1 = 1/K_c$ ,  $X_2 = u$ ,  $X_{3v} = h$  or  $X_3 = f(w, h)/w_1$  cf. Table 2 in Benson (1965)). As shown by Benson (1965), the correlation of complex variables (i.e.,  $S_w$  and Q/w) is dependent on the coefficients of correlation and variation of the three original component variables. Due to the presence of a common factor in the scaling relationship proposed by Hall et al. (2013), we hypothesize that it is a spurious correlation (u influences both  $S_w$  and Q/w) that may be mechanistically irrelevant for scaling in-stream nutrient uptake.

We tested our hypothesis using the dataset published by Tank et al. (2008), another metaanalysis of nutrient addition experiments which was included in the Hall et al. (2013) metaanalysis. This dataset was chosen because it reports values for  $S_w$ , Q, w, and h for nutrient
experiments with NH<sub>4</sub> and NO<sub>3</sub> (SRP not included), even though these values were not reported
for all the studies (n=143 for NH<sub>4</sub>, n=210 for NO<sub>3</sub>). Note that since we do not know the particular
geometry for each channel where the tracer experiments were conducted (i.e., we do not know f(w,h)), we assumed a rectangular channel geometry (i.e., A = f(w,h) = wh), which is the
same assumption made by Hall et al. (2013) while defining their equations for uptake length and
uptake velocity (cf. equations 1-2 in Hall et al (2013)). The dataset published by Hall et al. (2013)
does not include values of h, hence we were not able to use it for our analysis. While the
assumption of having rectangular channels might be seen as an overgeneralization, it is the only
one that allows us to see trends given the scarce information available on the channel geometries
of the headwater streams where the experiments were conducted. Furthermore, the transport
model implicitly used by Hall et al. (2013) assumes uniform flow (i.e., dh/dx = 0, dw/dx = 0),

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which supports our assumption of using a prismatic channel for testing our spurious correlation hypothesis.

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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 NH<sub>4</sub> and NO<sub>3</sub> in Figures 1 and 2.

Our results show that  $1/K_c$  vs. h are weakly correlated ( $r^2_{(NH4)}$ =0.029,  $p_{(NH4)}$ =0.042;  $r^2_{(NO3)}$ =0.036,  $p_{(NO3)}$ =0.0057). However, the <u>correlation</u>  $S_w$  vs. Q/w is higher ( $r^2_{(NH4)}$ =0.161,  $p_{(NH4)}$ <0.00001;  $r^2_{(NO3)}$ =0.151,  $p_{(NO3)}$ <0.00001), i.e.,  $r^2$  is improved by 452% and 317% for NH<sub>4</sub> and NO<sub>3</sub>, respectively. These findings suggest that the correlation  $S_w$  vs. Q/w is spurious because it is driven by the shared velocity (u) term, rather than by an inherent correlation between the 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 the  $r^2$  values do not match because of different datasets (we were limited by the number of studies reporting all parameters  $S_w$ , Q, w, h), and our aggregation of reference and altered streams. Regardless, our analysis <u>suggests</u> that the inclusion of the parameter u falsely improves the correlation of the investigated relationships.

The mechanism producing spurious correlation in the dataset by Hall et al. (2013) can be viewed more clearly using three arbitrary and uncorrelated variables to represent the relationship between  $X_1 \cdot X_2$  and  $X_3 \cdot X_2$ . We gathered mean daily values for specific conductance  $(X_1, \mu \text{S/cm})$ in the Potomac River (DC) (USGS, 2008a), turbidity (X2, FNU) in the Little Arkansas River (KS) (USGS, 2008b), and temperature (X3, °C) in the Rio Grande (NM) (USGS, 2008c) for the year 2008. First, we <u>isolated</u> the common factor  $X_2$  and <u>plotted</u>  $X_1$  versus  $X_3$ , as shown in Figure 3 ( $r^2$ = 0.020, p = 0.012). As expected, there was no statistically significant correlation between these 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 <u>found</u> a positive correlation (Figure 4) with a drastic improvement in  $r^2$  ( $r^2 = 0.846$ , p < 0.00001). Despite the evident correlation in this relationship, the result is mechanistically irrelevant. Analogous to this case example where the correlation is driven by  $X_2$  (turbidity), the correlation  $S_w$  vs. Q/w seems to be driven by u (recall  $S_w = u / K_c$  and  $Q/w = u \cdot h \cdot or \cdot Q/w = u \cdot (f(w,h)/w)$ . Thus, our findings suggest that the results produced by Hall et al. (2013) regarding the isometric scaling (a=1) of NH<sub>4</sub>, and allometric scaling (a>1) of NO<sub>3</sub> and SRP, resulted from an unintentional spurious correlation of  $S_w$  vs. Q/w.

In addition to scaling nutrient uptake length with specific discharge, Hall et al. (2013) also provide a method for scaling nutrient uptake with stream length using several parameters including the scaling exponent a obtained from the analysis of the scaling relationship shown in equation (2). Our findings have implications for these results as well. While Hall et al. (2013) 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/w not only for parameter a, but also for their subsequent derivations (cf. equations 3-10 in Hall et al. (2013)). Therefore, we also find those results debatable.

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## Concluding remarks

The majority of nutrient addition experiments have been performed in headwater streams because they are more experimentally tractable (Tank et al., 2008). Consequently, the dearth of empirical evidence of nutrient processing in large rivers limits our understanding of the role of these rivers in nutrient processing at the catchment scale. While empirical and theoretical advances are being made toward performing nutrient addition experiments in large rivers (Tank et al., 2008; Covino et al., 2010), the need to understand and quantify nutrient export from these systems has driven the development and use of scaling relationships. This motivated the work by Hall et al. (2013) and their results after correlating  $S_w$  vs. Q/w for a large dataset of field nutrient experiments suggest that uptake demand  $(v_f)$  for NH<sub>4</sub> is relatively constant across stream orders, whereas that for soluble reactive phosphorous (SRP) and NO<sub>3</sub> declines with increasing specific discharge. Here, we demonstrated that these conclusions are subject to debate due to unintentional spurious correlations present in their scaling relationships.

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

## Acknowledgments

We want to thank Gabriel Huerta and Tim Covino for providing feedback on earlier versions of this manuscript. This work was funded by NSF grant HRD-1345169.

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## Ricardo Gonzalez-Pi..., 9/2/2015 3:06 PM

**Deleted:** Kirchner, J. W. 2009. Catchments as simple dynamical systems: Catchment characterization, rainfall-runoff modeling, and doing hydrology backward. Water Resources Research 45:W02429.



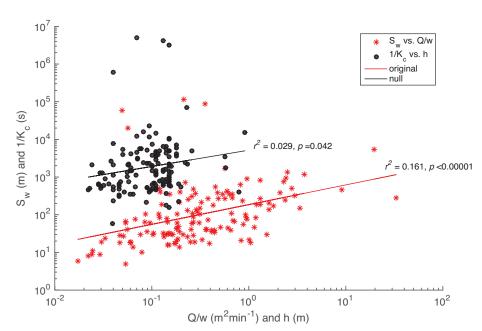


Figure 1 – NH<sub>4</sub> scaling relationship with and without shared velocity term. The original relationship is represented by  $S_w$  vs. Q/w and the null condition by  $1/K_c$  vs. h.

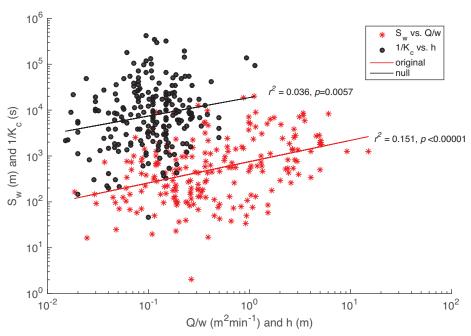


Figure  $2-NO_3$  scaling relationship with and without shared velocity term. The original relationship is represented by  $S_w$  vs. Q/w and the null condition by  $1/K_c$  vs. h.

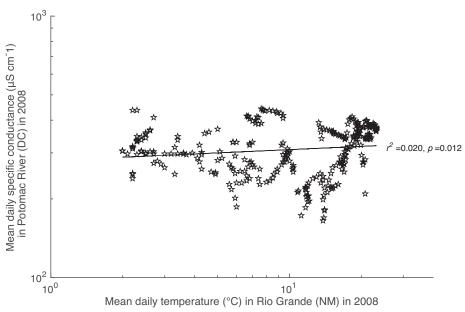


Figure 3 – Synthetic data correlation, type  $X_1$  vs.  $X_3$ , without common parameter,  $X_2$ . There is a weak correlation between these water quality parameters.

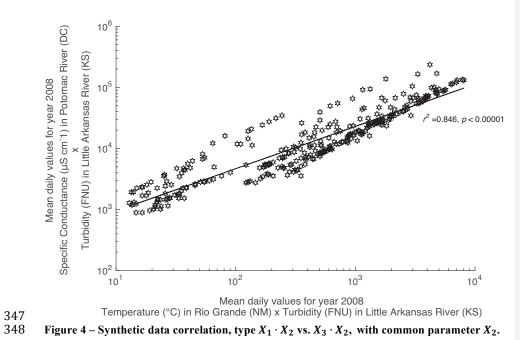


Figure 4 – Synthetic data correlation, type  $X_1 \cdot X_2$  vs.  $X_3 \cdot X_2$ , with common parameter  $X_2$ . This spurious correlation results simply because  $X_2$  is common to both quantities.

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