Physical and stoichiometric controls on stream respiration in a headwater stream

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Note from the Editor:

Dear authors,

I have consulted once more reviewer #1 who presented more substantial criticism in the last review round. This reviewer is now in general satisfied yet points out that you have obviously decided not to include a revision on the Damköhler analysis. It is ok in my opinion to not reach full agreement among authors and reviewers, yet this should be based on solid argumentation and - in Biogeosciences - scientific debate that will be made public. In this respect, I am missing an answer to this particular point of criticism about the Damköhler analysis.

Please provide a justification for the approach you took in your Damköhler analysis. Provide a clear answer to reviewer #1´s main point of critique about Da analysis that was presented in the last review round. This may also include additional statements of justification or statements about appropriate caution with interpretation in the methods and discussion sections, respectively.

I consider this a hopefully last round of minor revision before I can recommend the paper for publication. Please upload an answer letter and revised manuscript that let me clearly recognize your reactions to the reviewer´s critique.

Regards, Gabriel Singer

Previous note from Reviewer # 1

The authors define "reach-scale" metric as any metric derived from reach-scale observations. This is fine, but it's important to note that the two reach-scale metrics being compared in their Da analysis are fundamentally different. Their reaction timescale (inverse of Eq. 5) is a LUMPED metric that reports the combined influence of transport and reaction processes. In contrast, the transient storage timescale is inferred from a model fit of an average LOCAL process (i.e., retention during a single immobilization in the transient storage zone). That is true even if the model fit is based on reach scale experimental data. I therefore don't think the two metrics should be used for a Da analysis because they are not independent. The reaction rate inferred from Eq 5 is inherently correlated with the transient storage timescale. See, for example, Eqs 10-12 from Runkel (2007).

Our response to previous note from Reviewer # 1

The authors define "reach-scale" metric as any metric derived from reach-scale observations.

We agree.

This is fine, but it's important to note that the two reach-scale metrics being compared in their Da analysis are fundamentally different.

We agree. One characterizes conservative transport (i.e., the transient storage timescale). The other characterizes reactive transport (i.e., the transformation timescale).

Their reaction timescale (inverse of Eq. 5) is a LUMPED metric that reports the combined influence of transport and reaction processes.

We agree.

In contrast, the transient storage timescale is inferred from a model fit of an average LOCAL process (i.e., retention during a single immobilization in the transient storage zone). That is true even if the model fit is based on reach scale experimental data.

We disagree with the use of "in contrast" in the statement above. Both reaction and transient storage timescales are inferred from model fits of the same transient storage model and use reach-scale effective parameters such as dispersion coefficients, velocities, etc. Therefore, both timescales describe lumped metrics characterizing reach-scale processes, i.e., the finest resolution our data allow. For this reason, we also disagree with the use of "local" in the statement above, as no part of our work focuses on riffle, side cavity, or pool-specific (i.e., local scale) aspects occurring at a sub-reach scale, as has been done in other studies.

I therefore don't think the two metrics should be used for a Da analysis because they are not independent. The reaction rate inferred from Eq 5 is inherently correlated with the transient storage timescale. See, for example, Eqs 10-12 from Runkel (2007).

To the reviewer's point, multiple researchers have found that the parameters of the transient storage model and other typically used hydrologic models have identifiability, sensitivity, and equifinality issues (Kelleher et al., 2013; Knapp and Kelleher, 2021). These issues result from having more unknowns than the data can constrain, i.e., more parameters to calibrate than the number of equations available (Vrugt et al., 2002). Therefore, model parameters are not entirely independent, and analytical solutions cannot be derived. In response to these long-standing issues, numerous improved algorithms for parameter identification have emerged, such as the Differential Evolution Adaptive Metropolis (DREAM [ZS]) algorithm used in our work (Vrugt et al., 2009). Still, we argue that by estimating transient storage and reaction timescales from conservative and reactive tracer data, we can learn how flow dynamics and our nutrient additions converged to create different types of ecosystem functioning, i.e., reaction- vs. transport-limited conditions. This Damköhler number-based approach has been used extensively, as described in our Introduction and Discussion sections.

Concerning the interdependencies between reactions and transient storage parameters shown in the work by Runkel (2007), we highlight that his equations show that the net uptake (or transformation) of solutes depends on multiple quantities, including discharge, channel *geometry, biological supply, and demand, and the coupling of fast- and slow-moving compartments (and dispersion, which was not included in his equation 12 to simplify the analysis). Therefore, rather than ignoring or veering away from such interdependencies, the primary value of our work is precisely our explicit attempt to carefully monitor (discharge and the coupling of fast- and slow-moving compartments) or control (nutrient supply) key quantities to understand their influence on nutrient uptake better, using consistent methods.*

After this review request, we have clarified in multiple sections (abstract, introduction, results and discussion, and conclusions) along the manuscript that our analysis focuses on reach-scale metrics. We hope these changes will close any previous misunderstandings.

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