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Biogeosciences Discussions

Interactive comment on "Controls of longitudinal variation in δ^{13}C-DIC in rivers: A global meta-analysis" *by* K. A. Roach et al.

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Dear Anonymous Reviewer 2,

We have made extensive revisions to our manuscript "Controls of longitudinal variation in δ13C-DIC in rivers: A global meta-analysis." The excellent suggestions allowed us to critically review the manuscript, and as a result the paper is much improved. We have increased the number of studies from our meta-analysis from 26 to 31. We also changed one of the covariates in our GAMMs from DIC concentration to bicarbonate (HCO3-) concentration. We did this because we originally used DIC as a proxy for weathering, following Bade et al. (2004), however we realized that substituting DIC for HCO3- would increase the number of data points included in the GAMMs from 889 to 2,087, resulting in much better geographic coverage. We particularly appreciate the

suggestions on the paper's organization, including adding working hypotheses in the Introduction section and dividing the Discussion sections into sub-sections. Below are detailed comments justifying how the manuscript was revised. We are ready to submit our revised manuscript and data-base upon request by the editor. We hope that you will find the revised manuscript suitable for publication in Biogeosciences.

Sincerely, Katherine A. Roach on behalf of the authors

Reviewer comment: This paper summarizes current knowledge on factors determining δ13C of DIC in stream water. As shown in many previous studies, the mechanism is highly complicated and the variables are usually inter-correlated. Furthermore, the effects are sometimes nonlinear and this seems to be why the authors adopted the GAMM. I'm not confident that this approach is valid because the mechanism lies on multi-scale (both in space and time), showing a hierarchical structure. In this viewpoint, structural equation modelling or path analysis may be better approach to deal with this type of analysis. If the authors can show a certain advantage of GAMM over a hierarchical approach, it should be explained in text. Another problem is that the authors did not quantitatively show the uncertainty in their results. I think the parameters are too many to explain the observed range in δ13C-DIC. Dissolved atmospheric CO2 and carbonate bedrocks in particular show overlapping δ13C values (ca. âĹij 0 permil) in general. Therefore, it is usually difficult to estimate relative contributions of these isotopically similar endmembers to stream water DIC. The use of another isotope (e.g., 14C) may be one of the solutions for this "too many sources problem". For example, Ishikawa et al. (2015) Radiocarbon measured δ13C and Δ14C of DIC and tried to estimate their sources. Although there are not many Δ14C-DIC data available yet compared with δ13C-DIC, Δ14C-DIC may be useful for understanding potential controls of spatiotemporal variations in carbon isotopic compositions of DIC. Overall, I acknowledge the authors' effort for collecting the literature data, but the manuscript is not ready for immediate publication. Since this study is potentially important for the biogeochemical science, the authors should revise the manuscript especially focusing on my comments below.

Author comment: Our GAMMs are multi-level hierarchical models, with three levels of spatial structure (site, watershed, and river). We did not use a temporally hierarchical model because the data from the literature survey did not allow for this type of analysis. We added an additional sentence in the Methods section of the manuscript explaining that our GAMMs are hierarchical models that represent an improvement over previous analyses of δ13C-DIC using correlations and multiple regressions (e.g., Bade et al., 2004) because they account for the multiscale structure (sites, rivers, watersheds) of the data and allow for nonlinear relationships.

The uncertainty in the GAMM fits is reflected in the 95% confidence intervals for the smooths that are shown by the dashed lines in Figures 4 and 6. This is explained in the figure legends. As we explain in the Methods section, for each of the GAMMs, we iteratively removed variables if the 95% confidence intervals for the smooth function included zero throughout the range of measured values. Additionally, the p values provided in Tables 1 and 2 provide an indication of the usefulness of individual predictors in the GAMMs.

We realize that dissolved atmospheric CO2 and carbonate bedrock both have high δ13C-DIC values. We attempted to make this clearer by adding an additional hypothesis in the Introduction section explaining that "We anticipated that $\Delta\delta$13C-DIC and δ13C-DIC values would increase with HCO3- concentration, consistent with carbon derived from carbonate rock weathering." In addition, we added the following sentence to the Discussion section: "Because dissolved atmospheric CO2 and DIC derived from carbonate rock weathering have similar δ13C values, the use of Δ14C as an additional tracer would result in more effective differentiation between these sources (e.g., Raymond et al., 2004; Ishikawa et al., 2015)." We agree that it would have been interesting to include Δ14C-DIC as a covariate in the GAMMs, however this variable was only measured for four of the thirty-one studies from our meta-analysis.

Ishikawa, N.F., Tayasu, I., Yamane, M., Yokoyama, Y., Sakai, S., and Ohkouchi, N. Sources of dissolved inorganic carbon in two small streams with different bedrock geology: insights from carbon isotopes, Radiocarbon, 57, 439–448, 2015.

Raymond, P.A., Bauer, J.E., Caraco, N.F., Cole, J.J., Longworth, B., and Petsch, S.T. Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers, Mar. Chem., 92, 353–366, 2004.

Reviewer comment: L.36: “altered” should be replaced with “determined”

Author comment: We changed the sentence "The δ13C signature of DIC (δ13C-DIC) in the water column can be altered by the addition of DIC with a distinctive δ13C signature and by processes that affect the relative abundance of 13C:12C (fractionation)" to "The δ13C signature of DIC (δ13C-DIC) in the water column can be modified by the addition of DIC with a distinctive δ13C value and by processes that affect the relative abundance of 13C:12C (fractionation)." We use "modify" here in the conventional sense: to change somewhat the form of qualities of; alter partially; amend.

Reviewer comment: L.53-54: “At isotopic and CO32-” Meaningless sentence so delete

Author comment: We don’t agree that the sentence "At isotopic equilibrium with the atmosphere, CO2 (aq) has a lower δ13C signature relative to HCO3- and CO32-" is meaningless. We simply meant that when pH is low and the DIC pool is dominated by CO2, DIC at isotopic equilibrium with the atmosphere has a lower δ13C signature than when pH is high and the DIC pool is dominated by HCO3- or CO32-. However we attempted to clarify this sentence by revising it to "δ13C-DIC values at isotopic equilibrium with the atmosphere (δ13C-DICequilibrium) are low in streams with acidic surface water (dominant in CO2; approximately -10‰ to -2‰ relative to values in streams with neutral to basic pH (dominant in HCO3-; approximately -2‰ to 2‰."

Reviewer comment: L.55: “DIC(aq)” should be replaced with “DIC”

Author comment: We replaced DIC(aq) with DIC.

Reviewer comment: L.60: “For example δ13C-DIC” You forget to say groundwater DIC is generally 13Cdepleted

Author comment: We revised the sentence "Groundwater is supersaturated in CO2 (aq) from soil respiration and decomposition of organic matter, and its input lowers δ13C-DIC" to "Groundwater has DIC that is depleted in 13C (low δ13C values) from soil respiration and its input lowers instream δ13C-DIC."

Reviewer comment: L.70: “δ13C signature of DIC at isotopic equilibrium with the atmosphere” You already defined “δ13C-DICequilibrium” above so call it hereafter

Author comment: We moved the definition δ13C-DICequilibrium to the second paragraph of the Introduction section.

Reviewer comment: L.103: Can you show working hypotheses of this study at the last paragraph of the Introduction? Then explain why you focused on each of the variables and how you expected the results

Author comment: We revised the last paragraph of the Introduction section and now explain our expectations for relationships between $\Delta\delta$13C-DIC and/or δ13C-DIC and pCO2, elevation, HCO3- concentrations, and Strahler order. We explained that "We originally expected that if δ13C-DIC was mainly under biotic control, we would find a negative relationship between pCO2 and $\Delta\delta$13C-DIC. We expected to find low $\Delta\delta$13C-DIC values in high-elevation streams because of significant CO2 outgassing in these systems. We anticipated that $\Delta\delta$13C-DIC and δ13C-DIC values would increase with HCO3- concentration, consistent with carbon derived from carbonate rock weathering. Finally, we expected that δ13C-DIC values would be positively related to river size, as measured by Strahler order, because of a decrease in groundwater inputs and an increase in CO2 loss to the atmosphere and algal primary production with increasing river size."

Reviewer comment: Results section should be re-organized because many topics are

scattered and not in order

Author comment: We believe the Results section is ordered logically. We first provide information on the full range in observed values of δ13C-DIC and δ13C-DICequilibrium. We then discuss results from the GAMM of $\Delta\delta$13C-DIC, including the explanatory variables retained, the deviance explained, and relationship between $\Delta\delta$13C-DIC and each of the explanatory variables. We then discuss results from the GAMM of δ13C-DIC, including the explanatory variables retained, the deviance explained, and the relationships between δ13C-DIC and each of the explanatory variables.

Reviewer comment: L.229: “Again, nonlinear” This result is already reported

Author comment: This paragraph explains GAMM results for δ13C-DIC, and the previous paragraphs explains GAMM results for $\Delta\delta$13C-DIC (deviations between δ13C-DIC and δ13C-DICequilibrium).

Reviewer comment: L. 209-211 Discussion section is relatively long so should be divided by several subsections

Author comment: We have divided the Discussion section into three subsections: "Processes influencing $\Delta\delta$13C-DIC and δ13C-DIC", "Seasonal shifts in $\Delta\delta$13C-DIC and δ13C-DIC", and "Longitudinal shifts in processes controlling δ13C-DIC."

Reviewer comment: L.237: Start with main finding, not objective, of this study

Author comment: We revised the first sentence of the Discussion section from "Our main objective was to investigate controls and spatial and temporal patterns of δ13C-DIC in rivers throughout the world" to "Overall, our analysis indicates that processes that add DIC to the water column such as respiration of terrestrial organic matter have a greater influence on δ13C-DIC than processes that remove DIC."

Reviewer comment: L.254: “low surface:volume ratio” Needs more explanation. I expect high elevation (headwater?) streams are shallow in depth and narrow in width

Author comment: We changed "the high gradient and low surface:volume ratio in these ecosystems increases water turbulence and promotes CO2 outgassing" to "the high gradient and shallow depth of these ecosystems increases water turbulence and promotes CO2 outgassing."

Reviewer comment: L.261: “likely low” Remove “likely”. Do you mean “near zero”?

L.266: “values also were low” Do you mean high DIC concentration is due to large proportion of carbonate dissolution?

Author comment: We revised these minor issues during manuscript revision.

Reviewer comment: L.268-270: “$\Delta\delta$13C-DIC δ13C signature” A gap in logic. Carbonate (e.g., limestone bedrock) has higher δ13C value than atmospheric CO2. Weathering (dissolution) of carbonates provides high δ13C into water column. But note that dissolved atmospheric CO2 typically shows a similar δ13C value with that of carbonates

Author comment: We changed this sentence during manuscript revision. In addition, we added the following sentence addressing this issue to the Discussion section: "Because dissolved atmospheric CO2 and DIC derived from carbonate rock weathering have similar δ13C values, the use of Δ14C as an additional tracer would result in more effective differentiation between these two DIC sources (e.g., Raymond et al., 2004; Ishikawa et al., 2015)."

Reviewer comment: L.277-281: “Although algal by algae” Unclear. The second sentence does not connect well with the first sentence

Author comment: We revised these two sentences to increase clarity.

Reviewer comment: L.288-289: “The cycling δ13C-DIC” This is a principal of your analysis and should be appeared earlier in discussion

L.289 “, thus” this statement is already mentioned just before this clause. Redundant

L.294-295: “Most lotic the atmosphere” This is already mentioned above

L.295: “Therefore” Given CO2 in most streams is supersaturated, CO2 output should rise above input. You already mentioned that streams are source but not sink of CO2

L.300: “Our results also” Redundant. Is this because of carbonate?

L.303: “buffering capacity” What is this? Unclear

Author comment: We revised these minor issues.

Reviewer comment: P.323: The authors do not directly answer the question here: why seasonal shift in δ13C-DIC in high latitude is observed?

Author comment: In the Discussion section we summarized what probably caused the seasonal shifts in $\Delta\delta$13C-DIC and δ13C-DIC in rivers in temperate regions with seasonal snow cover: "Ice cover also has been documented to increase pCO2 in the water column of rivers, and should be responsible for the seasonal shifts in $\Delta\delta$13C-DIC and δ13C-DIC values in rivers at high latitudes in the northern hemisphere."

Reviewer comment: L.336: “Mayorga et al. (2005)” Another important contribution of this paper was that they measured radiocarbon (Δ14C) of DIC as well as other organic carbon fractions. I strongly recommend the authors also mention Δ14C because it can separate sources (e.g., dissolved atmospheric CO2 and carbonate bedrocks) that cannot be separated by δ13C. See also Raymond et al. (2004) Marine Chemistry and references therein

Author comment: In the Discussion section we will stated that "Mayorga et al. (2005) analyzed δ13C and Δ14C (radiocarbon) of DIC, dissolved organic carbon, and multiple particulate organic carbon fractions in Amazonian rivers and concluded that high pCO2 was sustained by in situ respiration of terrestrial plants." In addition we added the following sentence in the Discussion section: "Because dissolved atmospheric CO2 and DIC derived from carbonate rock weathering have similar δ13C values, the use of Δ14C as an additional tracer would result in more effective differentiation between these two

DIC sources (e.g., Raymond et al., 2004; Ishikawa et al., 2015)."

Reviewer comment: L.336-339: “Terrestrial C4 low-water periods” But C4 plants have higher δ13C values than C3, don’t they?

Author comment: We clarified our reasoning for low δ13C-DIC values in tropical rivers by stating that "Most tropical rivers are highly weathered and thus their waters tend to be more dilute in dissolved materials than temperate rivers (Gaillardet, 1997). Whereas δ13C-DIC in temperate rivers may be more strongly influenced by carbonate weathering, δ13C-DIC in tropical rivers may be more influenced by respiration of organic matter of terrestrial origin."

Reviewer comment: L.337: “terrestrial C3” Remove “terrestrial”. Redundant

Author comment: We revised the manuscript to focus on the importance of respiration of organic matter of terrestrial origin (rather than focusing on C4 grasses and C3 plants separately) to δ13C-DIC in tropical rivers.

Reviewer comment: Fig. 3: Are panels A and B same? They look very similar

Author comment: As explained in the figure legend, Figure 3A shows the relationship between fitted values and $\Delta\delta$13C-DIC and Figure 3B shows the relationship between fitted values and δ13C-DIC.

Reviewer comment: Figs. 4, 7, and their legends: Please explain how you calculated y axis (Contribution of covariate to smooth for $\Delta\delta$13C-DIC or δ13C-DIC)

Author comment: The y axis represents the additive contribution of each covariate to the value of the dependent variable. It is the contribution made to the fitted value for that smooth function at a given value of the covariate. We added a sentence to the figure legends of Figures 4 and 6 explaining that "The y-axis represents the additive contribution of each covariate to the value of $\Delta\delta$13C-DIC" (Figure 4) and "The y-axis represents the additive contribution of each covariate to the value of δ13C-DIC" (Figure 6).

Reviewer comment: Fig. 6: Seasonal pattern seems to be different between northern and southern hemispheres. Why? Just because of number of data?

Author comment: In the Discussion section we clarified why we believe there were different seasonal patterns in $\Delta\delta$13C-DIC and δ13C-DIC between rivers at high latitudes and rivers at low latitudes by revising "Sample size was low in temperate regions of the southern hemisphere. A greater number of sites sampled from these rivers may result in a seasonal trend that is similar to the pattern observed in the northern hemisphere" to "In the southern hemisphere between 40° and 60°, data were sparse in space and time (Fig. 5). More complete sampling from these rivers may result in a seasonal pattern similar to the pattern observed in the northern hemisphere."

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