EGUsphere, referee comment RC2
https://doi.org/10.5194/egusphere-2022-613-RC2, 2022

Comment on egusphere-2022-613

Anonymous Referee #2

Referee comment on "Hyporheic Zone Respiration is Jointly Constrained by Organic Carbon Concentration and Molecular Richness" by James C. Stegen et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-613-RC2, 2022

Does the paper address relevant scientific questions within the scope of BG?

Yes – it reaffirms the importance of organic carbon (OC) concentration as a major control on hyporheic zone respiration and offers suggestions for further relevant research and suggests a possible role of Organic matter molecular richness on hyporheic zone respiration.

Does the paper present novel concepts, ideas, tools, or data?

Mostly – more effort could have been made to fully analyse the data available in order to achieve the stated goals.

Are substantial conclusions reached?

Yes

Are the scientific methods and assumptions valid and clearly outlined?

Yes, but effort can be made to further validate assumptions/methods

Are the results sufficient to support the interpretations and conclusions?

Yes, the authors clearly state the importance of organic carbon (OC) concentration (as found by other authors) as a major control on hyporheic zone respiration, and that OM richness may have an influence on hyporheic zone respiration

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

Yes

Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

Yes, but more credit should be given to the contributors of the WHONDRS dataset as the work presented here is an analysis of data collected and analysed by a wide range of contributors

Does the title clearly reflect the contents of the paper?

The title overstates the findings with respect to the authors findings in terms of molecular richness- The authors themselves state in the Abstract *"we found that organic carbon (OC) concentration imposes a primary constraint over hyporheic zone respiration, with additional* ***potential*** *influences of OM richness."* May I suggest to avoid any possible misunderstanding, that the title be adjusted to reflect the quoted text. Also further discussed below with respect to the use of respiration maxima.

Does the abstract provide a concise and complete summary?

Yes

Is the overall presentation well structured and clear?

Yes

Is the language fluent and precise?

Yes

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

Yes

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

Yes, see detailed comments

Are the number and quality of references appropriate?

Yes

Is the amount and quality of supplementary material appropriate?

Yes, but more effort could be made to potentially analyse the data in more detail, possibly leading to further significant scientific findings and conclusions.

Detailed comments

The authors aim to test and advance a proposed hypothesis from Lehmann et al. (2020) and seek to test this hypothesis of the presence of a negative relationship between respiration rates and OM molecular richness in the hyporheic zone on a continental scale using data collected from the WHONDRS consortium. The hyporheic zone is chosen due to its higher levels of hydrologic connectivity which may diminish influences of spatial isolation such as an OM stabilization mechanism. The authors research rejects the hypothesis of any direct relationship between respiration rate and OM richness, both using the full dataset of sample respiration rates and maximum respiration rates across the OM richness. The authors confirm previous findings that OC concentration could impose a primary constraint over maximum respiration rates, with OM richness acting as a potential additional (but less important) constraint. The authors use maximum respiration rates to show that the combined influences of OM richness and OC concentration are realized as a non-linear constraint space, with the vast majority of measured respiration rates falling well below the constraint boundary. They further suggest research into additional factors which act as controls over respiration, which drive respiration below its potential maximum. The significant relationship between OM richness / NPOC and respiration rate is only valid for the respiration maxima and not for all the data collected, this seriously limits this continental scale study to a very small dataset. I would be interested to know the model results for the entire dataset of Respiration rate vs OM richness / NPOC (similar to the other models done) shown in Figure 4. I believe the title again does not reflect this important detail of the study findings and could lead to misunderstandings. Maybe a title along the lines of **"Maximum respiration rates in the subsurface of rivers is predominantly constrained by organic carbon concentration, modulated by molecular richness"** may be more representative.

L9-10: I would be cautious with the phrasing here to avoid a misinterpretation – What is the definition of the hyporheic zone referred to ? To my knowledge most definitions, including those of authors cited in the current manuscript (eg. Krause et al. 2011) define the hyporheic zone as a zone of mixing of shallow groundwater and surface water. Not all sections of the river bed subsurface exhibit surface and groundwater mixing.

L15-17 / 25-26: Since the hyporheic zone is specifically mentioned, is the data used from WHONDRS exclusively from the hyporheic zone (HZ)?

L24-25: What are the potential "other variables" that the results indicate are secondary influences on Hyporheic zone respiration (other than OM concentration) ? Could the authors hypothesise based on literature which exists on the topic? Maybe lability, presence/ density of double/triple bonds, ring structures ?

L31-33: I would stress here not only contaminant removal, but more relevant to the paper, increased CO_2 evasion (respiration) and DOM alteration within the HZ. Several papers exist on the topic eg. Nature Comms. and Scientific Reports

L41-46: I would argue that the classification of the molecular diversity in terms of structural complexity (eg. presence and number of ring structures, C:H, C:O ratios, N containing molecular formulae potentially indicating proteins, etc) and not simply number of unique organic molecules (after all the authors present FTICR-MS data) is also important for this. I would be interested which effect the different fractions of DOM molecules have on respiration. Have the authors explored DOM diversity in the level? I think it would be very interesting to identify groups of molecules that lead to higher respiration rates versus other groups.

L50-56: I am not convinced that all the data used from WHONDRS is actually from the hyporheic zone, can you confirm that it is ?

L100 – 101: This seems counter intuitive to me. You inverted ratios that were less than 1 ? Please explain further

L 106-118: Is the use of a Michaelis-Menten function and the half saturation truly more justifiable than the use of a least squares approach with a pre-determined limit on the tolerated difference between the "replicate" Field and Incubation NPOC samples (maybe 20%) that would justify removal. Please explain.

L126-130: Would FTICR-MSnot yield information on molecular formulae, C:H, C:N, C:O ratios and thus indicate apparent lability ? This may give further useful information.

L161-165: Just for clarity, was the maximum respiration rate in each bin plotted against the corresponding 1/NPOC value for that respiration rate or against an average of the bin ?

L177-179: A skewed distribution is a possible indicator of another key controlling factor that was not taken into account by the model / study, correct?

L185-188: While the hypothesis sounds reasonable, I am not completely convinced by the data presented in the current graph. There are only three (out of ten) points making up the negative slope on the right of the graph showing a decrease in respiration rate with OM richness above 4000 unique peaks. The point representing the highest OM richness corresponds to almost double the respiration rate of the point representing the bin before it. Maybe using the maxima from 15 or 20 bins would make the relationship clearer ?

L201 – 209 : Given the authors analysis of the results, is the title of the paper truly justified ? Is it possibly a bit of an overstatement of the role of OM richness ? Should the title reflect more the statements in L 211 – 212?

Figure 1: It seems that the samples were biased toward rivers in lower altitudes and flatter terrain (possibly lower gradient rivers?), as well as away from the central section of the USA. Could this have excluded some important environments/factors that are important for a "continental scale" model ? Also, what does the map look like showing the spatial distribution of final data point locations that were analysed for the model ?

Figure 4/5: The full dataset is shown here. Why wasn't a model for the full dataset calculated and results shown as comparison as done previously in Fig. 3 ?