



EGUsphere, referee comment RC2
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Comment on egusphere-2022-194

Anonymous Referee #2

Referee comment on "Potential bioavailability of representative pyrogenic organic matter compounds in comparison to natural dissolved organic matter pools" by Emily B. Graham et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-194-RC2>, 2022

General comments

In this manuscript Graham et al. investigate the bioavailability of pyrogenic organic matter (PyOM) using a substrate-explicit model, which is then compared to that of natural dissolved organic matter and water-extracted particulate organic matter. The current understanding of the impact of PyOM in freshwaters remains mainly speculative. On this note, the manuscript addresses an important topic in riverine biogeochemistry that would be of interest to the scientific community. The manuscript is also very well-written and easy to follow. I would recommend its publication after major revisions.

Specific comments

■

Based on the compounds selected as representation of PyOM, I wonder if there is any information in the literature regarding their experimental bioavailability. The same applies to DOM and POM. The authors could expand a bit more in the introduction to further clarify the contribution of the study they are presenting.

■

The rationale behind the experimental design is not completely clear and could not be adequate to test the proposed hypothesis. PyOM derived compounds mainly exhibit high K_{ow} values that indicate their low solubility in water. In fact, some of the compounds included in Table S1 were determined after solvent extraction or CuO oxidation according to the references cited therein. However, these PyOM representative compounds were then compared to natural water-soluble organic matter (dissolved and particulate). Regardless, the authors report similar bioavailability

parameters across phases, raising concerns about the model selection. This is because of the range of compounds with totally different chemical and physical properties that are being compared. I wonder why the list of PyOM derived compounds was not filtered to include just water-soluble compounds or the list of natural organic matter (dissolved and particulate) expanded to incorporate non-water-soluble compounds. These could represent an important overlooked fraction of natural organic matter, especially in the case of sediments. Also important is to include compounds that are detected beyond the 200-900 m/z analytical window or that escape the SPE procedure. I would recommend expanding the databases based on previously published literature and re-running the models. It would be interesting to see if similar results are obtained after expanding the composition of natural organic matter.

■

It is interesting that the authors included sediment water-extracted organic matter. This is usually not the rule in organic matter related studies in rivers, but definitely something that should be acknowledged more often.

■

In the supplemental material, the authors mentioned that samples were normalised based on the concentration of dissolved organic carbon before SPE extraction. Given that the extraction efficiency of SPE cartridges is not constant, please add more information about how the organic matter extracts were normalised before FT-ICR-MS analysis or during data processing.

■

Please include information regarding quality controls used during FT-ICR-MS analysis.

■

I would strongly suggest using the ranges proposed by Laszakovits & MacKay (2022) to assign compound classes via van Krevelen diagrams (DOI: 10.1021/jasms.1c00230). Please update.

■

Please include the F-value of the results of the statistical analysis, when appropriate, in the main body or as supplemental material.

■

I would recommend that the authors include a statement in the *Conclusions* addressing their previously proposed hypothesis.

■

The authors stated the limitations of this approach well enough (e.g., lines 226-229).

This is important considering the implications and future work.

Technical corrections

line 53: please convert to Tg or Gg or an appropriate standard unit.

line 103: please use an appropriate notation (instead of p (PyOM-sediment)).

line 300: Is the dataset in Garayburu-Caruso et al. (2020a) the most comprehensive assessment of DOM in rivers to date?

line 331: please include the references for the R software as well as for each package.