

Biogeosciences Discuss., author comment AC3
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Reply on RC2

Aleksandar I. Goranov et al.

Author comment on "Microbial labilization and diversification of pyrogenic dissolved organic matter" by Aleksandar I. Goranov et al., Biogeosciences Discuss.,
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I agree that radical oxygenation is a potential source of the molecular diversity of DOM, but I still think that the 3.3 section of this paper (Radical oxygenation as a potential source of molecular diversity) is an overinterpretation of the FT-ICR-MS results. I have read the references cited by the authors, in studies of Waggoner et al., lignin-derived organic matter (OM) was treated by hydroxyl radicals originating from Fenton reactions, and the new produced molecular formula, including condensed aromatic compounds, alicyclic compounds and oxidized compounds, were observed using FT-ICR-MS. It is no doubt that the new products were produced due to the reactions between hydroxyl radicals and initial OM. Studies suggest that oxidized products can be produced by radical oxygenation of DOM. However, this does not mean that the presence of oxidized molecules is necessarily the result of radical oxygenation. On the other hand, the authors cannot sure that formula $C_cH_hO_{o+1}$ is just from the oxygenation of $C_cH_hO_o$ but not from other precursors or other pathway. On the base of above appoints, although the authors observed the presence of oxidized products of pyDOM, the evidence to support radical oxygenation of pyDOM in this study is very limited. Therefore, I recommend the author to provide direct evidence of the presences of ROS especially hydroxyl radical in the system. If so, this would be an excellent work.

We thank the referee for their continued interest in our manuscript. As we described in our first comment, we agree with the referee that we cannot confidently say that these $C_cH_hO_{o+1}$ molecules are from radical oxygenation and we have provided an alternative explanation. We only discuss that the FT-ICR-MS data suggests oxygenation pathways. NMR data published in our companion paper (Goranov et al., 2020) also strongly suggests oxygenation reactions - we observe degradation of olefins (Vinyllic-C) and an increase in oxygenated functional groups (Oxygenated-C). Olefins are particularly labile towards oxidation and are easily oxygenated, as discussed in length by Goranov et al. (2020).

Unfortunately, we cannot directly prove radical processes at this time though we completely recognize the need for it. The bio-incubations of this study were performed and samples were analyzed in December 2018 – April 2019, and neither Bostick (leader of

sample preparation and bio-incubations) nor Goranov (leader of instrumental analyses) are at the institutions where this work was performed. Thus, performing additional experiments with radical quenchers and radical monitoring using radical quantification via HPLC methodologies is not possible at the time. An experiment performing the same incubations with radical quenchers and radical quantification is also beyond the scope of the current manuscript. The main goal of the present work was to analytically (structurally/molecularly) characterize pyDOM following bio-transformation and provide possible insights regarding its bio-reactivity. Experiments with radical quenchers and radical quantification are the logical continuation following this study and we hope future work in the field of pyrogenic organic matter pursues work with focus on radicals. For the current manuscript, we will have to acknowledge the limitations of our experiment and clearly state that the proposed oxygenation pathway is only a speculation that needs to be robustly tested in future studies.

Referenfes

Goranov, A.I., Wozniak, A.S., Bostick, K.W., Zimmerman, A.R., Mitra, S. and Hatcher, P.G. (2020) Photochemistry after fire: Structural transformations of pyrogenic dissolved organic matter elucidated by advanced analytical techniques. Geochimica et Cosmochimica Acta 290, 271-292.