

Interactive comment on “Photomineralization and photomethanification of dissolved organic matter in Saguenay River surface water” by Y. Zhang and H. Xie

Anonymous Referee #1

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Zhang and Xie have reported on photochemical production of climatically important gases CO₂ and CH₄ in DOM from the Saguenay River, a major tributary to the St Lawrence River in Canada. The manuscript showed photodegradation results using filtered water exposed in a solar simulator. Results of loss to CDOM absorption at 330 nm (a_{330}) were presented along with production rates of CO₂ (as DOC loss) and CH₄. I liked this manuscript a lot because it was very clearly written in a logical manner and easy to follow. Plus the authors did some nice extrapolations of their work to present and past ocean carbon cycling.

Some general points that I think need clarifying as very minor revisions.

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1) The DOC loss could partially be due to CO photoproduction yet this was not discussed. I think the authors need to correct their estimates (or provide bounds) considering some loss as CO.

2) p14312 L12: Might it be better to just describe this as an oxygen gradient (supersaturated, saturated, depleted) after describing how the oxygen conditions were achieved. I know there is the problem of some reoxygenation during sample transfer and I think the authors do a good job of making that caveat clear, but reference to O₂-, air-, N₂-purging is cumbersome.

3) P14313: "TDOM" often is used for terrigenous (terrestrial) DOM so its use to describe transparent CDOM is confusing. Also, perhaps misleading. For example, is this meant to convey transparency at 330 nm or transparency at all wavelengths, even deep into the UV? If the former, this certainly is not correct as molecules may lack charge transfer for absorption bands in the mid UV but absorb strongly at say 254 nm. If the latter, the discussion as written was purely speculative. One way forward is to perhaps show how slope values (S or SR) change during photodegradation. If slope changes all line up together over the first 50 hours of exposure (re: Fig 3) and then diverge, you may get a bit more insight to the differences between oxygen conditions.

4) The role of lignin in explaining these results could be better emphasized. The methoxy (-OCH₃) groups in dissolved lignin are good candidates for CO, CO₂, and CH₄. P14314, L17-21: Makes sense if the aldehydes in lignin are being oxidized to acids.

5) The CH₃ radical may be a key intermediate in low O₂ settings. I wondered, too, if nitrate photolysis is important in these photochemical pathways?

Specific comments p14310, L8: "moisturized" – better word choice here; not worried about methane's complexion! :)

p14315, L15: "different" not "differed"

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p14321, L9: This result has been observed in CDOM photobleaching; may wish to explore this result a bit more. Photomethanification tracks more closely with photobleaching than does photooxidation? Perhaps photomethanification is more of a primary photochemical process. No photodecarboxylation required, for example.

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