

Interactive comment on “Photochemical aging of atmospherically reactive organic compounds involving brown carbon at the air-aqueous interface” by Siyang Li et al.

Anonymous Referee #2

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Li and co-authors examined the packing of surfactants at the air-water interface, how this varies with different surfactants, and how it changes with irradiation in the presence of four types of photosensitizers. They also examined how irradiation changes the properties of the films. While there are some components here that are interesting, the environmental implications of the work are not always clear. For example, how can the pi-A isotherm figures help us understand something about atmospheric particles? I am also concerned that the interpretation of the irradiation data for DOPC, which was the focus of the illumination experiments, is confounded by the fast dark reaction of this unsaturated phospholipid. Overall, I would consider this manuscript to straddle the border of reject/major revisions.

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»Major points

****Photosensitizer issues**** The paper makes many comparisons between the relative effects of the four sensitizers (IC, humic acids, limonene SOA, and ambient PM). But these effects likely depend on the concentrations of the sensitizers, which were different (and apparently arbitrary) for the four sensitizers. Based on this, it seems that the sensitizer comparisons are meaningless. (For example, see line 13-14 in the Conclusions: “. . . IC was the most efficient photosensitizer to increase the relative area of the DOPC monolayer. . .”.)

Also, the concentrations of photosensitizers seem quite high: how do they compare to atmospherically relevant amounts in airborne particles with typical liquid water contents? The IC concentration (2.5 mM) seems especially high since it appears to be of intermediate volatility and would primarily partition to the gas phase in an aerosol. This raises a question: is the impact of a photosensitizer proportional to its concentration? For example, in Fig. 3, is the influence of IC on the pi-A isotherms proportional to IC concentration?

The aqueous mass concentrations (mg-PM/L-solution) of the PM2.5 and SOA samples in ASW are not given: these need to be included.

It would be helpful to show a figure with UV/Vis spectra of the four sensitizers at the concentrations used in the experiments. At least this would allow the reader to understand the differences in the rate of light absorption in the four cases, as this would influence the formation of singlet oxygen.

****Irradiation issues**** Fig. 4. DOPC in artificial seawater (ASW) has a short half-life, approximately 70 min, both in the dark and under irradiation (Fig. S1). The authors attribute this rapid DOPC loss to reactions with gas-phase oxidants. Compared to the ASW base case, the loss of “relative area” is slowed in irradiated samples containing a photosensitizer, which the authors attribute to formation of hydroperoxides, but they have not analyzed for this functional group. Fundamentally, the relative area (A/A_0)

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measure of Fig. 4 is very crude and the interpretation of the results is very poorly constrained. For example, it seems possible that the photosensitizer could reduce the loss of DOPC by making products that slow DOPC oxidation by gas-phase oxidants. Or a larger product other than hydroperoxides could be made by the interaction of sensitizer and DOPC. The authors need better evidence for their interpretation; this should start by doing the irradiation in a sealed container so that gas-phase oxidants are not rapidly destroying DOPC.

What is the most important point from these results? If it is that hydroperoxides are formed, then peroxides should be analyzed. If it is that the DOPC products have larger molecular areas than DOPC, then the rapid background loss of relative area needs to be stopped.

****Section 3.3. PM-IRRAS results**** This section of text, currently 3 pages, is too long, is very dry and is too focused on the details of various band assignments. Similarly, Figures 5 and 6 generally show only very subtle differences between some of the bands after irradiation. Much of this section could be moved to the supplemental material so that the main text contains a 1-page summary that focuses on the most important results.

****Section 3.5. Atmospheric implication**** This section should focus less on a review of what others have done and more on the implications of the current work. What do the current results tell us that we didn't know before? The second sentence of this section states that salt particles are covered with a film of surfactants, but as I understand it, this is still a topic of debate. Similarly, I believe there is debate about whether an organic film on particles is an effective barrier to mass transport, e.g., of water vapor, as this section states. Given that the photosensitizer concentrations were very high in the current work, can a timescale for oxidation under atmospheric conditions be estimated?

»Other points page 4, line 19: Sonication is a poor choice to remove PM from filters

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because it can oxidize organics. What was the power of the ultrasonic bath? How long were samples sonicated?

page 5, top: Need more details on the chamber experimental conditions, including a supplemental table describing different chamber experiments. What were concentrations of H₂O₂ and NO in the chamber? How long was the reaction allowed to proceed before particles were collected? What was the concentration of limonene that was reacted? What was SOA mass collected? Were DLPI stages combined to get one PM extract per chamber experiment?

page 6. It would be very helpful to give a short description of how a pi-A isotherm can be interpreted. I imagine most readers, like myself, are not familiar with reading these types of figures. What information does the isotherm reveal? What is a lift-off area? What is a collapse? How are these determined from the isotherm? Why are these quantities important? Amending Figure 1 to show a molecular picture of the various stages in the pi-A isotherm would help.

page 9, line 12. Indicate that this is 30% after 90 min of irradiation.

lines 12 – 14: “There was evidently..” This statement is contrary to the data: the addition of photosensitizer appears to decrease the decay of the DOPC monolayer. This sentence is then contradicted by the next sentence (“The presence of . . .”).

»Minor points page 1, lines 20-22: Define OA and EA. Also, the sentence is unclear. What is the comparison? line 24: Since there is no direct experimental evidence for hydroperoxidation in the current work, this statement should be qualified. line 28: “the processing of organic aerosol aging” does not “control” aerosol composition.

page 2, l.28: This is poorly worded: the triplet state is not susceptible to oxidation by a hydrocarbon.

page 5, line 20: Is TUV the model number of the lights? If not, what is model number? What was the photon flux in the sample?

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Figure 1: The structures are very small and difficult to discern, especially the double bonds.

page 6, line 17: This sentence is not precise enough: the entire DOPC molecule didn't go from gas phase to aqueous phase.

page 7, line 5: "in both the liquid and condensed phase". How is "condensed" phase different from "liquid" phase?

line 14: "for the DPPC monolayer". Shouldn't this be DOPC?

line 17: "The introduction of photosensitizers...had a profound effect...". This is only true for HA, not for IC.

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