

Review of “Photochemical aging of atmospherically reactive organic compounds involving brown carbon at the air-aqueous interface”, by Li et al. (ACP-2019-96).

General Comments

This study presents an investigation of the influence of photosensitizing species (both model species and ambient samples) on the properties of long-chain fatty acids at the surface of model seawater. Specifically, the authors couple Langmuir trough measurements of surface pressure and molecular area with PM-IRRAS compositional measurements to explore irradiation-induced changes in monolayer physical and chemical properties.

Although this is an interesting study, I have a number of major concerns regarding the manuscript in its current form that I believe should be addressed prior to publication:

First, insufficient information is provided regarding the *quantity* of photosensitizers employed, specifically in the cases of PM and SOA. It is therefore unclear whether differences in the four photosensitizer types employed arise as a result of differences in photosensitizer properties or simply differences in photosensitizer concentration.

Second, in the absence of information regarding experiment reproducibility, it is difficult to assess whether the reported results are meaningful. For example, Figure 4c does not provide error bars, and many of the spectral shifts reported are very small ($\sim 2 \text{ cm}^{-1}$)—do these results reflect variability between experiments, or real effects?

Third, the manuscript often mixes results and discussion together, and is therefore difficult to follow. I provide specific examples of this in my comments below.

Fourth, the conclusions/mechanisms in the latter half of the paper are overstated in the context of the results provided. Specifically, I believe that insufficient experimental evidence is provided for the production of hydroperoxides.

In the following sections, I outline additional specific scientific questions/issues regarding the manuscript, organized by manuscript section.

Abstract

- P1L1 Photosensitizing compounds don't *contain* brown carbon; this is confusing as written.
- P1L1 How is “low volatile” defined here? In addition, citing only energy transfer here seems unnecessarily specific.
- P1L21 OA/EA need to be defined prior to use (*i.e.* in L17).
- P1L24 I think that the experimental evidence for hydroperoxidation is weak; the abstract would be stronger, in my opinion, if it focused more closely on the results.
- P1L29 This final sentence is too vague, I think.

Introduction

- P2L4 Are these the only two fates available to phospholipids?
- P2L6 Perhaps some more recent references would be helpful here?
- P2L7 This is misleading as written—I think that it should clarify *which* component of seawater unsaturated fatty acids dominate. As is, it makes it sound as though unsaturated fatty acids are a major fraction of seawater.
- P2L11 Given that the focus of the paper is reactions at the sea surface, I think that the cooking-related references are unnecessary.
- P2L17 Is all WSOC necessarily BrC? I think that there is also non-absorbing WSOC?
- P2L20–22 I wonder if it might be useful to outline BrC sources that do not involve ammonia/ammonium.
- P2L26 I don't think that it's correct to say that photosensitizers are a *subset* of BrC, as there are photosensitizers that do not fall under the BrC umbrella.
- P2L32 I would rephrase “just a few radical reactions”—I'm not exactly sure what is being argued here.
- P3L1 I think that it might be clearer to say that IC is a *component* of BrC?
- P3L5–20 A transition between IC and HULIS is missing here. In addition, some detail regarding HULIS seems unnecessary here (*e.g.* the portions relating to combustion emissions).
- P3L32 “processing the aging”—should be reworded.

Experimental

- P4L10 What does the 90% purity level for humic acid refer to? How was it determined? Is structural information available for this humic acid standard (*i.e.* how does it compare to other HA sources, like Suwanee River humic acid / Aldrich humic acid)?
- P4L12 How were the aqueous loadings of PM_{2.5}/SOA determined? How were the reported concentrations of IC (2.5 mM) and HA (30 mg/L) chosen? Could differences between the various samples reflect different *amounts* of additives rather than differences in the properties of the various additives? Some additional information would be useful here in this context.
- P5L4 What were the NO concentrations employed? Which type of NO_x/VOC environment were the authors attempting to reproduce here, and why?

- P5L7 Would one expect different compositions for the different size fractions? Were all size fractions employed? Would one anticipate any SOA compositional biases induced by collecting under low-pressure conditions?
- P5L12 Why was chloroform employed as solvent?
- P5L15 A reference for the Wilhelmy plate method, as well as details of the method, would be useful.
- P5L18 How were the uncertainties in surface pressures (± 2 mN/m) estimated?
- P5L20 How did the illumination intensity compare to ambient conditions? How far away from the Langmuir troughs were the lamps?
- P5L26 Why was this incident angle (40 degrees) chosen for the light beam? It is my understanding that PM-IRRAS is often performed at a glancing angle? In addition, I think that some more information regarding the PM-IRRAS technique would be useful here (*i.e.* which measurements provide the PM-IRRAS signal).

Results and discussion

- P6L10 How is the light absorption relevant to the discussion of packing/phase behaviour?
- P6L12–P7L6 This section mixes results and discussion of results in a way that I find confusing. I think that it would be clearer for the reader if the isotherms were first described, and then the implications of the isotherm shapes were explained.
- Were multiple trials performed? What are the uncertainties associated with the (rather precise) values reported here (*e.g.* 46 mN/m for DOPC monolayer collapse)?
- How is it meaningful to compare collapse pressures for HA vs. IC when the two species were added in different quantities?
- Why were the collapse pressures higher for PM_{2.5}/SOA vs. IC/HA? I think that some mechanistic discussion of these differences is warranted—what is the take-home message for the reader, here?
- What does “coincided” mean, on P7L4? Is this a meaningful observation?
- P7L12 How is this collapse pressure (55 mN/m) determined, exactly? To me, it is not clear that the surface pressure is decreasing (the decrease could perhaps be noise?)
- P7L14 DPPC should read DOPC, I think.
- P7L20 Again, is there an uncertainty associated with this lift-off area?
- P7L22 What does “the same” molecular area mean? How is the lift-off area defined, exactly?

- P8L1 How is the value of 20 mN/m obtained, here? To me, the OA curve does not reach 20 mN/m.
- P8L12–25 Again, this paragraph is a mixture of numerical results and interpretation of those results. I find it extremely difficult to follow as written, and am having difficulty extracting the overarching meaning of the results. I would suggest re-writing the main points, and then explaining the significance of these main points in a manner more easily understandable to the non-expert reader.
- P9L2 It would be useful for the non-expert reader to explain (perhaps in the methods) what actually *happens* in these experiments, i.e. how does one measure an area relaxation curve, experimentally?
- P9L9 Is this a reasonable timescale for lipid oxidation? It seems quite fast to me?
- P9L12 Where is this 30% value taken from? Is it at 90 min?
- P9L12 What does a “much greater change” in the decay rate mean? It would be helpful to be more explicit here about the *direction* of this change.
- P9 Figure 4 I find Figure 4c quite unclear. What does the *difference between the curves* mean, exactly? Why was this metric chosen here? I think that the division of data between the main text and the supplementary makes this section more confusing than it needs to be. In addition, how do the differences between samples compare to sample variability between trials?
- P10L1–21 I think that this section is missing some interpretation of the results—why do these added species result in area increases for the monolayers, exactly? I think that these paragraphs would benefit from a clearer mechanistic explanation for the observed results—especially because, as I mention in my previous comment, the data are not intuitively displayed (*i.e.* much data is in the supplementary section); in the current form, I can’t quite grasp the *meaning* of the results.
- P10L30 Previously (P9L9), it was argued that the lipids underwent oxidation over the timescales of the experiments. If so, wouldn’t this oxidation be visible using PM-IRRAS?
- P10L33 How meaningful are these changes (*e.g.* 2923–2921 cm^{-1})? Would changes in “chain ordering” be expected to lead to shifts to lower wavenumbers, and why?
- P11L5 How meaningful is this change in peak height intensity ratio (1.61 to 1.82)? Were these peak height ratio changes observed for IC/HA? If not, why not? What sorts of mechanisms would be expected for each of these photosensitizers?
- P11L7 Again, how meaningful is a change from 3023 to 3020 cm^{-1} ?
- P11L12 How is the shift to lower wavenumbers related to the conformation order of the aliphatic chains? Some explanation would be helpful here.

- P12L9–P13L6 This section, in many places, says that spectral shifts are occurring due to “interactions”/“modifications”, but doesn’t clearly outline how these interactions would lead to the observed shifts. How does a shift from 967 to 942 cm⁻¹, for example, indicate modifications in DOPC monolayer packing?
- P13L7 Why do the authors think that spectral shifts for DSPC were less significant than for DOPC?
- P14–15 In my view, **Section 3.4** is not sufficiently grounded in the experimental results. How, exactly, do the results obtained support this rather complex proposed mechanism?
- P16L4–20 This material is more suitable for an introduction than a concluding section.
- P16L21 I don’t think that this statement regarding DOPC hydroperoxides is supported by the data presented in the paper, given that DOPC hydroperoxides aren’t actually measured.
- P17L11 DOPC hydroperoxide was not actually measured—in general, I think that this conclusions section does not accurately reflect the results presented in the paper.