

We have revised our manuscript according to the suggestions of the Referee's comments and the responses to the comments are as following. For clarity, the Referee's comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red color text.

Anonymous Referee #2

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.

»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...".)

Response:

We have deleted the discussion about the comparison of the photosensitizing efficiency of the four photosensitizers at different concentrations. The change of relative area of DOPC monolayer in the artificial seawater containing IC was the greatest. The photosensitizing reaction of unsaturated lipids involving PM_{2.5} sample and SOA sample indicated that such reaction may occur in the ambient environment. We have modified the statement on Page 13 and 18:

"According to Fig. 5(e), the shifts in these CH₂ and CH₃ bands induced by IC were the most dramatic among the four samples in the photosensitized reaction of organic aerosol surface."

"In addition, the largest increase of the relative area of the DOPC monolayer was observed in the presence of IC, as compared to the laboratory generated SOA sample and field collected PM_{2.5} sample."

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?

Response:

The concentration of 30 mg/L humic acid is commonly used in the photochemical experiment (*Environ. Sci. Technol.*, **2015**, 49, 13199-13205; *Sci. Rep.*, **2015**, 5, 12741). In the previous studies, larger than or equal to 30 mg/L humic acid were added directly into the artificial seawater to mimic the presence of the dissolved organic matter in the sea surface microlayer (*Sci. Rep.*, **2015**, 5, 12741; *Geophys. Res. Lett.*, **2017**, 44, 1079–1087). In this investigation, the concentration of humic acid in fresh sea spray is close to the real seawater.

These dissolved organic matters are present in different and varying concentrations in seawater and aerosols. The concentrations of IC commonly used in the experiment varied from 0.25 mM to 0.6 M (*Environ. Sci. Technol.*, **2018**, 52, 7680–7688; *Faraday Discuss.*, **2013**, 165, 123–134; *C. R. Chimie*, **2014**, 17, 801–807). IC can also be chosen as seed particle in some chamber simulation (*Environ. Sci. Technol.*, **2014**, 48, 6, 3218–3227). The concentration of IC used in our experiment is lower than its saturated concentration. The surface activity of organic film gives rise to a concentrating effect at the interface. Therefore, the chromophoric dissolved organic matters are more concentrated in the surface of sea microlayer than in the bulk seawater. These organic compounds may be present in the aerosol at much higher concentrations than in either the seawater or air bulk phases. In term of photosensitizing efficiency, the impact of a photosensitizer is dependent on its concentration. We have deleted the discussion about the comparison of their photosensitizing efficiency at different concentrations.

The aqueous mass concentrations (mg-PM/L-solution) of the PM_{2.5} and SOA samples in ASW are not given: these need to be included.

Response:

In the revised manuscript, we have given the aqueous mass concentration of PM_{2.5} and SOA samples, and added some description about this issue on Page 5-6:

“All the filters were dissolved into 40 mL ultrapure water with ultrasonic agitation. Sonication was performed in an ultrasonic bath with a frequency of 40 kHz and the power of 80 W. The sonication time was 15 min. Subsequently, the suspension was centrifuged at 1780 g for 40 min. The supernatant, which contains the water-soluble fraction including water-soluble organic compounds (WSOC) and inorganic ions, was re-collected by freeze-drying. The insoluble fraction separated from soluble fraction was also freeze-dried. The mass ratio of insoluble to soluble fraction is 0.91:1. Then, 3.3 mg of freeze-dried soluble sample was dissolved in 1000 mL artificial seawater. The concentration of PM_{2.5} sample in the artificial seawater is 3.3 mg/L.”

“Then, the SOA samples collected on the aluminium foil pieces were dissolved in ultrapure water by sonicating for 1 min in an ultrasonic bath. The extract water solution was concentrated by rotary evaporation. The residue was dried under high purity nitrogen stream. Then, the SOA sample was transferred to the artificial seawater with the concentration of 0.66 mg/L.”

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.

Response:

UV–vis spectra were acquired on a UV–vis spectrophotometer (P9, Shanghai Mapada) using 1 cm quartz cuvettes. The absorption spectra of the aqueous solutions for 0.006 g/L IC, 0.006 g/L humic acid, 0.01 g/L PM_{2.5} and 0.01 g/L SOA were recorded. In order to compare the light-absorbing properties of four samples, we also calculate MAC and average MAC (<MAC>) values over the wavelengths range from $\lambda_1 = 200$ nm to $\lambda_n = 700$ nm). We have added the UV-vis spectra measurements in the experimental section on Page 6:

“The UV–vis absorption spectra of the four photosensitizers were measured using a UV-vis spectrophotometer (P9, Shanghai Mapada, China). Spectra were collected using quartz cuvettes with internal path length of 1.0 cm. Aqueous solutions of 0.006 g/L IC, 0.006 g/L humic acid, 0.01 g/L PM_{2.5} sample and 0.01 g/L SOA sample were used.

The IC aqueous solution displays a major absorption band at 288 nm which is in an agreement with previous studies (Tinel et al., 2014; Berke et al., 2019). The maximum absorption of SOA sample was at 286 nm, as can be seen from the absorption spectrum shown in Fig. S1 in the supplement. Similar to the previous studies, HA and PM_{2.5} samples’ absorptions have the main feature around 200 nm with a clearly visible hump between 250 and 300 nm (Kristensen et al., 2015). We calculate the mass-absorption coefficients (MAC) (cm²/g) of the four samples by the following equation:

$$\text{MAC}(\lambda) = \frac{A(\lambda) \times \ln 10}{b \times C_m}, \quad (1)$$

where A is the absorption, b is the length of the cuvette (1 cm), and C_m is the concentration of the dissolved reaction products (g/mL).

In order to compare the light-absorbing properties of the four samples, we estimated the light-absorbing properties of aerosols by the average MAC (<MAC>) over the wavelengths range from $\lambda_1 = 200$ nm to $\lambda_n = 700$ nm) (Jiang et al., 2019).

$$\langle \text{MAC} \rangle = \frac{\sum_{i=1}^n \text{MAC}(\lambda_i)}{n}, \quad (2)$$

HA sample with <MAC>_{200–700 nm} of 64460 cm²/g is also more absorbing than IC sample (<MAC>_{200–700 nm} = 41267 cm²/g), SOA sample (<MAC>_{200–700 nm} = 32867 cm²/g) and PM_{2.5} sample (<MAC>_{200–700 nm} = 16048 cm²/g).”

****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) 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.

Response:

To lower the content of reactive species in the atmosphere adjacent to the film, the trough was placed in a sealed box in some experiments. The DOPC monolayers in the artificial seawater displayed a trend for decreasing area, probably owing to loss of material to the subphase (*Langmuir*, **2016**, 32, 3766–3773; *Biophys. J.*, **2010**, 98, 50–52). At a relative area of approximately 0.18, the barriers could not move anymore and the experiment was terminated.

Indeed, it may be a possible explanation for the increase of relative area that the photosensitizer could reduce the loss of DOPC by making products which slow DOPC oxidation by gas-phase oxidants. However, the existence of new bands at approximately 3000 cm^{-1} suggested that DOPC and photosensitizers under irradiation can produce some unsaturated organic compounds. According to the mechanism of photosensitizing reaction, DOPC hydroperoxides are the primary products (*Langmuir*, **2007**, 23, 1307–1314; *Biophys. J.*, **2009**, 97, 1362–1370; *Colloid Surface B*, **2018**, 171, 682–689). Additionally, no other new bands but the shifts of bands for DOPC were measured by IRRAS. Though IRRAS spectra are quite indistinct in the range of $3500\text{--}4000\text{ cm}^{-1}$ for OH stretching vibration, the unsaturated products measured by IRRAS can still be assigned as DOPC hydroperoxide.

The irradiation experiments also can be performed in a completely sealed container that was purged with nitrogen to protect unsaturated lipids from oxidation. Such experiments may not accord with the ambient environment. Moreover, DOPC needs to be exposed to oxygen in the photosensitizing reaction. Therefore, the irradiation in a sealed container was not considered in the experiment.

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.

Response:

The new band corresponding to CH stretching vibration of HC=CH group was measured by IRRAS, while other bands were changed little. Accordingly, the structure of photochemical product must be similar to DOPC. The photosensitizing reaction mechanism of unsaturated lipids proposed here was generally accepted (*Langmuir*, **2016**, 32, 3766–3773; *Langmuir*, **2007**, 23, 1307–1314; *Biophys. J.*, **2009**, 97, 1362–1370; *Colloid Surface B*, **2018**, 171, 682–689). Based on the increase of relative area and the detected products, we tentatively assigned the unsaturated products measured

by IRRAS as primary oxidation products——DOPC hydroperoxide.

****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.

Response:

Figure 6 for DSPC monolayer has been moved to the supplement. We have shortened this section significantly on Page 13:

“The molecular-level interactions of photosensitizers with DOPC and DSPC monolayers can be analysed by surface sensitive PM-IRRAS. In the dark experiment on pure artificial seawater (**Fig. 5(a)**) the bands at 2922 and 2853 cm^{-1} were assigned to antisymmetric ($\nu_{\text{as}}(\text{CH}_2)$) and symmetric methylene ($-\text{CH}_2-$) stretching ($\nu_{\text{s}}(\text{CH}_2)$) modes, respectively. The antisymmetric ($\nu_{\text{as}}(\text{CH}_3)$) and symmetric methyl stretching ($\nu_{\text{s}}(\text{CH}_3)$) vibrations were observed at 2959 and 2882 cm^{-1} , respectively. The observation of the CH_3 bands indicated the *gauche* defects in the alkyl chain (Li et al., 2017a). The CH stretching in the $\text{HC}=\text{CH}$ group at 3023 cm^{-1} was relatively weak. In the absence of photosensitizers, there were no significant changes of the IRRAS spectra for DOPC monolayer after 90 minutes of irradiation. For the DOPC monolayer on the artificial seawater containing IC molecules, the bands of $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ stretching were observed at 2923 and 2854 cm^{-1} , respectively. After 90 minutes of irradiation, the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ bands were shifted to lower wavenumbers at 2921 and 2842 cm^{-1} , respectively. The shifts in CH_2 and CH_3 bands to lower wavenumbers indicate that the *gauche* rotamers in DOPC monolayer were decreased after 90 minutes of irradiation. Therefore, the conformation order of the aliphatic chains in DOPC monolayer was increased. According to **Fig. 5(e)**, the shifts in these CH_2 and CH_3 bands induced by IC were the most dramatic among the four samples in the photosensitized reaction of organic aerosol surface. The peak height intensity ratio between the antisymmetric CH_2 stretching (I_{as}) and symmetric CH_2 stretching (I_{s}) is usually used to assess the order of the organic monolayer packing (Aoki et al., 2016; Huang et al., 1982). In the case of IC in the subphase, the peak height intensity ratio between I_{as} and I_{s} in the DOPC monolayer increased from 1.61 to 1.82 due to irradiation. The increase of peak height ratio also occurred in the presence of HA. It indicated the order of the monolayer chains was increased. With respect to DOPC mixed with the $\text{PM}_{2.5}$ sample (**Fig. 5(b)**), the ratio between I_{as} and I_{s} increased from 1.48 to 1.73 under irradiation. The band of $\nu(\text{HC}=\text{CH})$ at 3023 cm^{-1} was shifted to 3020 cm^{-1} under the irradiation of the DOPC monolayer mixed with IC. It indicated that the aliphatic chains became more ordered under irradiation. The existence of the $\nu(\text{HC}=\text{CH})$ band in the irradiation experiment suggested that the aliphatic chain of DOPC molecules does not break at the initial position of the double bond. The new weak bands at 3001, 3007 and 3009 cm^{-1} that appeared after irradiation was also assigned to $\nu(\text{HC}=\text{CH})$ stretching. This band implied the formation of unsaturated products in the photosensitized reaction. The antisymmetric P=O stretching ($\nu_{\text{as}}(\text{PO}_2^-)$) band and the symmetric stretching

($\nu_s(\text{PO}_2^-)$) band for DOPC monolayer on pure artificial seawater (**Fig. 5(c)**) were located at 1227 and 1073 cm^{-1} , respectively. The bands of asymmetric carbonyl ester stretching ($\nu_{\text{as}}(\text{CO-O-C})$) at 1187 cm^{-1} shifted to 1161 and 1167 cm^{-1} for the DOPC monolayer mixed with IC and HA, respectively. For the DOPC monolayer on the artificial seawater containing SOA sample, the $\nu_{\text{as}}(\text{PO}_2^-)$ band at 1236 cm^{-1} and $\nu_s(\text{PO}_2^-)$ band at 1084 cm^{-1} (**Fig. 5(d)**) were shifted to 1231 and 1062 cm^{-1} , respectively. The shifts in the P=O stretching vibrations suggested that hydrogen bonding between phosphate groups and surrounding water molecules appeared to be affected by irradiation. The band at 1059 cm^{-1} assigned to $\nu_s(\text{C-O-PO}_2^-)$ vibration was shifted to 1070 cm^{-1} for the DOPC monolayer on the artificial seawater containing PM_{2.5} sample. These shifts in phosphate bands indicated that the interaction between photosensitizer and DOPC molecules induced the dehydration of phosphate groups (Arrondo et al., 1984). In the presence of the SOA sample in the subphase, the antisymmetric stretching of the choline group $\nu_{\text{as}}(\text{CN}^+(\text{CH}_3)_3)$ band of irradiated DOPC monolayer was shifted from 967 to 942 cm^{-1} , which indicated that photosensitizer molecules affected the hydration of DOPC head groups.

The spectral shifts induced by the photosensitizer and irradiation were more obvious for DOPC monolayers than for the DSPC ones. With respect to the DSPC monolayer on the artificial seawater, the antisymmetric CH₂ stretching and symmetric CH₂ stretching (**Fig. S6(a)**) were 2919 and 2851 cm^{-1} , respectively. The CH₂ bands in the DSPC monolayers were more intense relative to the DOPC monolayer, thus shifting to lower wavenumbers. This can be attributed to the formation of more a compressed and packed DSPC monolayer relative to DOPC. Lower wavenumbers of CH₂ bands are indicative of highly ordered conformation with *all-trans* characteristics (Simon-Kutscher et al., 1996; Christoforou et al., 2012; Snyder et al., 1978). Minimal wavenumber shifts of P=O, C-O-PO₂⁻ and CN⁺(CH₃)₃ stretching vibrations were observed under irradiation in **Fig. S6(b)**. According to the comparison with the IRRAS spectra of DSPC monolayer in dark condition, no new bands of products were observed from the irradiated DSPC film. This result suggested that the DSPC films were less affected by irradiation.”

****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?

Response:

We have moved this material to the introduction section and modified the atmospheric implication section on Page 17-18:

“In this work, photosensitizers like IC and HA in aqueous core of aerosol can take part

in the oxidation of unsaturated lipid film coated on the aerosol in the presence of UV light. There was significant organic aerosol aging. The results such as relative area increase and new IRRAS bands of the unsaturated products also indicate that chamber generated SOA samples and authentic PM_{2.5} samples were involved in the photosensitizing reaction of DOPC monolayer. The introduction of authentic PM_{2.5} sample in this simulated experiment suggested that such process of organic aerosol aging may be occurred in the atmosphere.

The hydrophobic characteristics of organic film were changed greatly in the process of organic aerosol aging. According to the mechanism of photosensitizing reaction, the possible products—DOPC hydroperoxides were more water-soluble. They appear to dissolve into bulk artificial seawater and partition into the hydrophilic core of organic aqueous aerosols. Subsequently, the processes of hygroscopic growth of aerosol and cloud condensation nuclei activation are impacted. If the organic film on the aerosol surface is either destabilized under irradiation or it is metastable due to the loss of ordering and packing, the organic aerosol will become more permeable to water. As a result, the hygroscopicity of the aerosol particle and the overall size of droplet can increase (Ruehl and Wilson, 2014). Consequently, the atmospheric lifetime of unsaturated species on the aerosol surface can decrease. Volatility is generally inversely correlated with O:C ratio (Aiken et al., 2008). The photochemical reaction at the air-aqueous interface under the condition of BrC is an efficient and common pathway to oxidize organic films toward low volatile organic compounds (O:C ratio of 0.25 to 1) (Jimenez et al., 2009). Moreover, the photosensitized reaction of organic aqueous aerosol likely depends on the film-forming species, given the different reactivities of saturated and unsaturated phospholipids.”

»Other points page 4, line 19: Sonication is a poor choice to remove PM from filters because it can oxidize organics. What was the power of the ultrasonic bath? How long were samples sonicated?

Response:

It has been an increased interest in the use of ultrasound to destroy organic pollutants. Long time sonication with methanol or water may generate OH radicals to oxidize organics (*J. Phys. Chem.*, **1983**, 87, 1369–1377). The filter sample was extracted by sonication with 40 mL ultrapure water for 15 min. The rated frequency of ultrasound is 40 kHz. Higher frequency ultrasound can increase the number of free radicals in the system.

We have added some explanation of sonication on Page 5:

“All the filters were dissolved into 40 mL ultrapure water with ultrasonic agitation. Sonication was performed in an ultrasonic bath with a frequency of 40 kHz and the power of 80 W. The sonication time was 15 min.”

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?

Response:

Temperature, relative humidity (RH), O₃, NO, and NO_x were continuously monitored. H₂O₂ was used as OH radical precursor and was introduced into the chamber by passing pure zero air over 20 μL H₂O₂ (Sigma-Aldrich, 30 wt% in H₂O) solution. The concentration of H₂O₂ was estimated to be 4324 ppb. RH was about 20 % throughout the experiments. The concentration of OH radicals in the chamber cannot be explicitly determined due to lack of appropriate device. The concentration of limonene was determined by gas chromatograph equipped with flame ionization detector (GC-FID) (Agilent Technologies, GC-FID 7890B). The chromatographic separation was achieved by using a DB-624 capillary column (Agilent Technologies, 30 m length × 1.8 μm film thickness × 0.32 mm i.d.). The GC oven temperature was heated at a rate of 2 °C/min from 180 °C to 186 °C. At this temperature, the peaks for each reference would not overlap with the reactant. The relative concentrations of each compound were determined from peak areas. The chamber was flushed using zero air three times after each experiment. The reaction was allowed to proceed for 4 hours before SOA particles were collected. At that time, the concentration of limonene could not be detected. The initial concentration of NO_x and limonene were 206 ppb and 684 ppb, respectively. The SOA mass was 0.22 mg. The aluminium foil pieces collected from each stage were all combined to get one PM extract. The experimental conditions of chamber were also listed in Table S1 in the supplement.

We have added more details on Page 5:

“A customized diffusion dryer was added after aerosol generator to make sure that the (NH₄)₂SO₄ aerosols were in solid phase in chamber. Relative humidity was about 20% throughout the experiments, which is lower than the crystallization RH (35%) of (NH₄)₂SO₄ (Ng et al., 2007). The seed particle was kept at solid phase. The total gas volume in the chamber was recorded with mass flow meters (D80-8C/ZM, Beijing Sevenstar, China). Limonene (99%, tci) was injected into the chamber by a micro syringe and was evaporated into a stream of purified air. Then, an aqueous H₂O₂ solution (30 wt %) was injected to the chamber and served as the OH precursor in these experiments. The concentration of H₂O₂ was estimated to be 4324 ppb. NO was introduced into the chamber by a gas-tight syringe. Typically, 684 ppb limonene and 5×10⁴ cm⁻³ (NH₄)₂SO₄ seed aerosols were employed. The concentration of limonene was determined by gas chromatograph equipped with flame ionization detector (GC-FID) (Agilent Technologies, GC-FID 7890B). The SOA formation of limonene photooxidation experiments was performed under high-NO_x condition (Sarrafzadeh et al., 2016). The initial concentration of NO_x and NO detected by NO-NO₂-NO_x analyzer (Model 42C, Thermo Electron Corporation, USA) were 206 ppb and 164 ppb, respectively. The reaction was allowed to proceed for 4 hours before SOA particles were collected. At that time, the concentration of limonene could not be detected. The initial concentrations of reactants in the chamber were also listed in Table S1 in the supplement.”

page 6. It would be very helpful to give a short description of how a π -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 π -A isotherm would help.

Response:

Langmuir films are formed when surfactants are spread at the air–water interface. Surfactants are amphiphilic molecules with hydrophobic tails and hydrophilic heads. Since their tails of surfactants are hydrophobic, their exposure to air is favored over that to water. Similarly, since the heads are hydrophilic, the head–water interaction is more favorable than air–water interaction. The overall effect of such packing is reduction in the surface energy. When surfactant concentration is less than the minimum surface concentration of collapse, the surfactant molecules can arrange a monolayer on the surface of water.

Surface pressure–area isotherms show phase transition-like behaviour of the Langmuir films. In the gas phase, there is minimal pressure increase for a decrease in area. The first transition from gas phase to liquid phase occurs at the lift-off area. There is a proportional increase in surface pressure with decreasing area. Moving into the solid region of monolayer is accompanied by another sharp transition to a more severe area dependent pressure. This trend continues up to a point where the molecules are packed closely and have very little space to move. Applying an increasing pressure at this point causes the monolayer to become unstable and destroy the monolayer. The surface pressure during the monolayer collapse may remain approximately constant (in a process near the equilibrium) or may decay abruptly (out of equilibrium - when the surface pressure was over-increased because lateral compression was too fast for monomolecular rearrangements).

We have added some description of surface pressure-area isotherm and the inserts in Figure 2 to show the phase behaviours on Page 8:

“The monolayers usually composed of amphiphilic molecules with a hydrophilic head and a hydrophobic tail are assembled vertically at the air–water interface. Surface pressure–area (π -A) isotherms show phase transition behaviours of organic films. Owing to the amphiphilic characteristics of phospholipids, the head groups of DOPC and DSPC molecules prefer to be in the solution while their tails stretch into the air. The π -A isotherms recorded for DOPC and DSPC monolayers on artificial seawater with and without photosensitizers are shown in **Fig. 2(a)** and **(b)**, respectively. When the surface area of the DOPC monolayer was larger than $125 \text{ \AA}^2/\text{molecule}$, the distance between the DOPC molecules was quite large and the intermolecular force was quite weak. The surface pressure of a DOPC monolayer on artificial seawater started to increase from $125 \text{ \AA}^2/\text{molecule}$, where the DOPC monolayer surface state underwent a transition from the gas to the liquid-condensed phase. After the first phase transition, there is a proportional increase in surface pressure with decreasing area. This caused condensation and ordering at the interface, increasing the surface pressure of the organic monolayer. This trend continued up to a point where the DOPC molecules were

packed closely and have very little space to move. Finally, the DOPC monolayer collapsed at 46 mN/m (Pereira et al., 2018). Applying an increasing pressure at the collapse pressure caused the monolayer to become unstable and destroy the monolayer. The packing and phase behaviours of DOPC monolayer at different pressures were also shown in the inserts in **Fig. 2(a)**.”

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

Response:

We have modified the sentence on Page 11:

“The relative area of the DOPC monolayer on pure artificial seawater was reduced to 30% after 90 min 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..”).

Response:

The decay rate of the DOPC monolayer in the artificial seawater containing photosensitizers was slower than that on the subphase of pure artificial seawater. The presence of photosensitizing molecules in the subphases decreased the loss of the molecular area for the DOPC monolayer. To avoid misunderstanding, we have modified the sentence on Page 11:

“It is evident that the presence of photosensitizing molecules in the subphases decreased the loss of the molecular area for the DOPC monolayer.”

»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.

Response:

We have modified the statement on Page 1:

“The oleic acid (OA) monolayer possessing a *cis* double bond in an alkyl chain is more expanded than elaidic acid (EA) monolayers on artificial seawater that contain a photosensitizer.”

“Instead, the photochemical reaction initiated by the excited photosensitizer and molecular oxygen can generate new unsaturated products in the DOPC monolayers, accompanied by an increase in the molecular area.”

“The results of PM_{2.5} and SOA samples will contribute to our understanding of the processing of organic aerosol aging that alters the aerosol composition.”

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

Response:

We have corrected the sentence on Page 2:

“Therefore, photosensitizers can contribute to organic aerosol aging and growth when generating a triplet excited state that can oxidize hydrocarbon upon absorbing light.”

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?

Response:

The trough was surrounded by three UV fluorescent lamps (UVA range, Philips TUV TL-Mini 8W, 31 cm length, 2.6 cm o.d.). The light spectrum of the UV fluorescent lamps ranged from 300 to 420 nm with peak intensity at 365 nm, which was similar to the irradiation of solar UV band. We have modified the sentence on Page 7:

“The trough was illuminated by three UV fluorescent lights (Philips TUV TL-Mini 8 W) with peak intensity at 365 nm. The lamps were located above the Langmuir trough at a distance of 20 mm.”

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

Response:

We have modified the structures of lipids in Figure 1.

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

Response:

Gas phase and liquid phase are corresponding to the different phase behaviours of lipid monolayer. We have added some inserts in Figure 2 to show different phase behaviours of lipid monolayer on Page 9.

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

Response:

We have corrected the sentence and added the inserts in Figure 2 to show the different behaviours of DOPC monolayer on Page 9:

“The π -A isotherms of the DOPC monolayer on artificial seawater mixed with SOA sample and IC overlaps in the liquid-condensed phase.”

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

Response:

We have corrected the sentence as suggested.

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

Response:

We have modified the sentence on Page 9:

“The introduction of HA into the subphase also had a profound effect on the shape of π -A isotherms for DSPC monolayers.”