

Authors' Response to Reviews of

“Insoluble lipid film mediates the transfer of soluble saccharides from the sea to the atmosphere: the role of hydrogen bonding”

Minglan Xu, Narcisse Tsona Tchinda, Jianlong Li, Lin Du*

We thank the Referee for the constructive comments. We have addressed the comments point by point below and modified the manuscript accordingly. For clarity, the Referee's comments (RC) are reproduced in blue, authors' responses (AR) are in black and changes in the manuscript are in red color text.

Anonymous Referee #1

This manuscript presents a comprehensive study on the transfer of soluble saccharides at the sea-air interface, which affects the number concentration, chemical composition, and morphology of the resulting sea spray aerosols. I appreciate the fascinating experimental methodology of the study, and I enjoy digesting the results. The combination of Langmuir monolayer technology and infrared reflection-absorption spectroscopy helps to explain the interaction between soluble saccharides and insoluble fatty acids, and thus deduce a unique mechanism of hydrogen bonding, which is a novel technique and interesting results presentation, and certainly deserves more attention. Overall, the manuscript is well-written and most important the authors do a brilliant job in the reference list, very multidisciplinary and very updated. The authors have considered multiple views, and it is worth considering to be published in ACP after addressing some general issues.

RC: I have two questions about the abstract. Whether insoluble lipid monolayers can be absorbed at the air/water interface or simply float on the surface? Regarding hydrogen bond analysis, I think the authors are more illustrated by the changes in the infrared spectra of the carbonyl region, and it is necessary to consider whether the expression here is appropriate.

AR: To be a surfactant, a molecule must consist of distinct hydrophobic and hydrophilic portions. A common example is a fatty acid comprising a long hydrocarbon chain attached to a -COOH head group. The hydrophilic head group anchors in the water surface whilst the hydrophobic tail prefers to extend out of the water into the water/air interface. The term 'insoluble' refers to surfactants that, when placed at the water/air interface, will preferably remain there instead of dissolving in the bulk water. Therefore, this surfactant can be adsorbed at the water/air interface and studied uniquely because their concentration at the interface is known directly, from the amount added to the interface. We have modified the sentence at page 2 as:

Langmuir model was used to parameterize the adsorption and distribution of saccharide into SSA across the bubble surface, while infrared reflection-absorption spectroscopy (IRRAS) combined with Langmuir isotherms were undertaken to examine the effects of aqueous subphase soluble saccharides on the phase behavior, structure and ordering of insoluble lipid monolayers adsorbed at the air/water interface.

AR: Indeed, the interaction mechanism between fatty acids and soluble saccharides is mainly inferred by the changes of characteristic bands in the carbonyl region. We have changed the expression in the revised manuscript. We have rewritten this sentence at page 2-3:

The enhancement of the carbonyl band to the low wavenumber region implied that soluble saccharides can form new hydrogen bonds with fatty acid molecules by displacing large amounts of water near the polar head groups of fatty acids.

RC: Line 104: “A possible explanation for the SSA composition in saccharides involves”, whether or not the original meaning of expression should be the saccharides in the SSA composition, perhaps this sentence needs to be rewritten.

AR: Originally, we intended to express that a possible explanation for the origin of saccharides in SSA composition involves the affinity between soluble saccharides and insoluble surfactant monolayers adsorbed at the water/air interface, leading to co-adsorption of saccharides. The sentence has been rewritten in the revised manuscript at page 6:

A possible explanation for the origin of saccharides in SSA chemical composition involves the affinity between the bulk aqueous soluble saccharides and insoluble surfactant monolayers already adsorbed at the air/water interface, resulting in co-adsorption of the soluble saccharides (Link et al., 2019b).

RC: Line 148-149: It is best for the authors to explain why this molar ratio is used to obtain the mixed fatty acid solution in the method section, rather than in the results and discussion section below.

AR: We fully agree with the Referee that it might seem more appropriate to adjust the specific interpretation of the mixing molar ratio to the method section. Therefore, in the method section at page 8, we have added a text that explains why the mixed fatty acid solution is obtained in the indicated molar ratio:

The respective fatty acid solutions were mixed at a molar ratio of 2 MA:4 PA:3 SA to obtain a mixed lipid stock solution considering that PA and SA account for approximately two-thirds of the total saturated fatty acids in fine SSA particles, with MA being the third most abundant species (Cochran et al., 2016).

RC: In the experiment of preparing Langmuir monolayer, whether the volatilization time of 15 min is enough to make chloroform volatilize completely?

AR: Chloroform is a common spreading solvent used in Langmuir monolayer experiments (Aoki et al., 2016; Adams et al., 2016; Carter-Fenk and Allen, 2018). It can dissolve most organic compounds and can quickly evaporate when its solution is spread dropwise onto the aqueous surface. Previously, we have used stearic acid as an example to study the effect of solvent evaporation time on its π -A isotherm. Here, 5 min, 10 min, 15 min, 20 min and 30 min were selected respectively, and it was found that when waiting for 15 min, 20 min and 30 min, the π -A isotherms obtained were very close to each other, which could indicate that the volatilization time of 15 min was enough to make the solvent volatilize completely, and also proved that prolonging the waiting time would not lead to the dissolution of stearic acid molecules in the liquid phase. In addition, in the case of volatilization for 5 and 10 min, it was found that the π -A isotherms moved to the direction of larger molecular area, indicating that the solvent may not be volatilized completely.

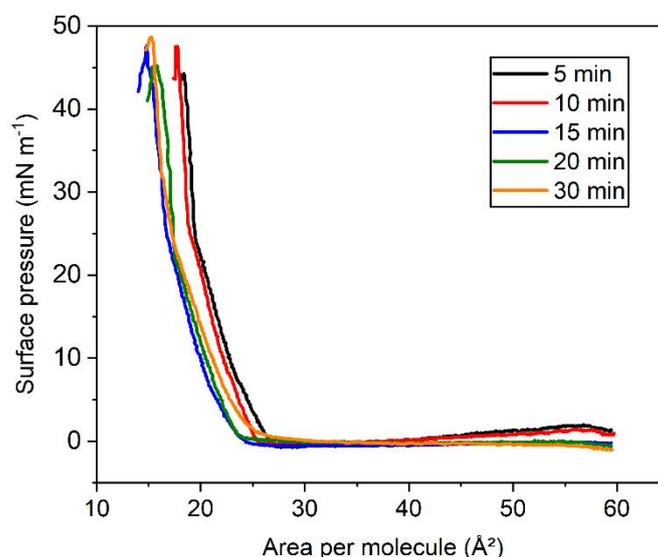


Fig R1. π -A isotherms of stearic acid on pure water subphase at different volatilization times.

RC: Line 226: Whether R and R_0 in the eq2 should be the surface covered by fatty acid monolayers and the surface of pure seawater solution?

AR: The spectra presented here are reflectance-absorbance (RA), where $RA = -\log(R/R_0)$ and R and R_0 are the reflectivity of the analyte (fatty acid) and pure aqueous solution (natural seawater), respectively. We have explained this in more detail in the revised manuscript at page 12:

The spectra presented here are reflectance-absorbance (RA) given as:

$$RA = -\log(R/R_0) \quad (2)$$

where R and R_0 are the reflectance of fatty acid monolayer and pure seawater solution surface, respectively.

RC: Section 3.1 The authors have compared the SSA produced using the sea spray aerosol generator in this study with other laboratory devices, and obtained similar consistency, but lack a comparison with the particle number size distribution of the real SSA observed in the field. In other words, whether the device can fully simulate the real SSAs?

AR: We compared the particle number size distribution of SSAs generated using the plunging-jet sea spray aerosol generator in this study with the real SSAs measured in the field observations (Xu et al., 2022; Quinn et al., 2017), as shown in Figure R2. In the submicron size range, it was observed that the size distribution of both laboratory-generated SSAs and SSAs measured in the field had a major accumulation mode in the range of 111-172 nm. The number concentration of SSAs generated in the laboratory is about 2 orders of magnitude higher than observed in the real environment. As a result, the jet sea spray generator system is capable of a wide range of measurements (e.g., size-resolved hygroscopicity and heterogeneous reactivity) that are not achievable at low number concentrations. In addition, the experiments are repeatable and provide many benefits for the study of the chemical and physical control of marine bubbles, foams and aerosols. We have supplemented the comparison with the field SSAs in the revised manuscript at page 13-14:

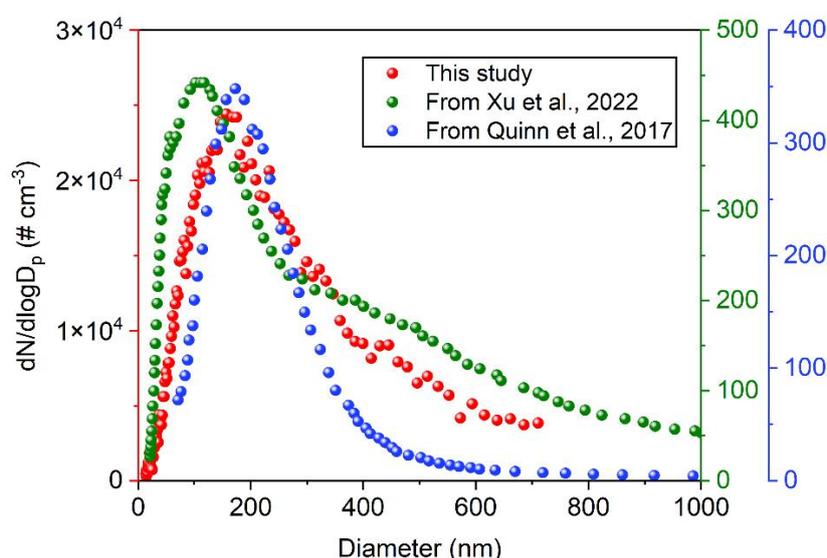


Fig R2. Comparison of particle number size distribution of SSAs generated by sea spray aerosol generator in our study with real SSA in the field measurements.

Moreover, we compared the particle size distributions of SSA generated in our laboratory with those measured in field studies (Quinn et al., 2017; Xu et al., 2022). As shown in Figure S3, it was observed that the size distribution of both

laboratory-generated SSAs and SSAs measured in the field had a major accumulation mode in the range of ~111–172 nm. However, the number concentration of SSAs produced in our experiment is about 2 orders of magnitude higher than that in the real environment. As a result, the jet sea spray generator system is capable of a wide range of measurements (e.g., size-resolved hygroscopicity and heterogeneous reactivity) that are not achievable at low number concentrations.

RC: A drawback of the presented results is the lack of quantitative information describing the SSA production, specifically the variation of SSA number concentration. A clearer presentation of measured aerosol number concentrations would be most helpful.

AR: Thank you for the very helpful comments. We agree that the results may be difficult to follow without quantitative analysis. Therefore, we have made corresponding quantitative supplements in the revised manuscript at page 15-16. For more clarity, we also added detailed information of the number concentration and mass concentration obtained by each group of experiments in the supplement (Table S1).

It was observed that glucose led to a slight increase of about 15.6% in particle number concentration, increasing the mode diameters to ~175 nm. In contrast, the natural seawater spiked with trehalose resulted in a higher total particle number concentration that increased by approximately 49.4% over a wide size range.

When the fatty acid surfactant was added to seawater alone, the number concentration decreased by about 17.2%, while the presence of glucose resulted in a decrease of about 21.6%. Moreover, fatty acids showed the highest inhibitory effect on SSA produced by trehalose-containing seawater solution, whose concentration decreased by about 49.4%.

RC: Line 261-264: An ambiguous sentence. According to the above description, the author here should be referring to the comparison of SSA particles produced by artificial seawater solution containing such organic matter, rather than SSA particles containing these substances.

AR: We have rewritten this sentence in the revised manuscript at page 14:

The results showed that the number concentration of particles produced by artificial seawater containing sodium dodecyl sulfate was significantly lower than that of particles produced by artificial seawater containing fructose. However, NaCl solution containing mannose produced SSA with lower number concentration than NaCl solution containing sodium laurate.

RC: Line 325-326: Here the decrease in the lift-off area and molecular area of the stearic acid film should be relative to the previous palmitic acid. Therefore, this sentence should be correct only if it is added with respect to palmitic acid.

AR: We have modified this sentence in the revised manuscript at page 18:

Both the lift-off area and molecular area of the stearic acid film **decreased more than those of palmitic acid film.**

RC: Line 355-360: In the Langmuir isotherms and infrared spectroscopy experiments, the authors designed concentrations about 3 orders of magnitude higher than in the real environment, and said that this high concentration is still environmentally relevant, how can it be better explained?

AR: On the one hand, the concentration of glucose and trehalose chosen in the experiment about 3 orders of magnitude higher than the marine environment is to maintain the detectability of the π -A isotherms. In addition, high concentrations remain relevant due to the evaporation process in aged sea spray aerosols (Hasenecz et al., 2020; Hasenecz et al., 2019). On the other hand, such high concentrations are close enough to remain relevant in the understanding of saccharide enrichment in the sea surface microlayer while facilitating confident interpretation of the physicochemical mechanism driving the adsorption and transfer of soluble saccharides. We have provided appropriate supplementary explanations in the revised manuscript at page 19:

At the same time, such concentrations are close enough to understand the enrichment of saccharides in sea surface microlayer and to provide a confident interpretation of the physicochemical mechanisms driving the adsorption and transfer of soluble saccharides (De Vasquez et al., 2022).

Some minor comments:

RC: Line 43: It is better to use the generic name: humic-like substances (HULIS).

AR: This was changed in the revised manuscript.

RC: Line 157: “solution” should be changed to plural “solutions”.

AR: This has been corrected in the revised manuscript.

RC: Line 272: “change”-“changes”

AR: This was changed in the revised manuscript.

RC: Line 355: There are several instances in the manuscript where “Glucose and Trehalose” should be lowercase.

AR: This was changed in the revised manuscript.

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