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Comment on acp-2022-628

Anonymous Referee #3

Referee comment on "Insoluble lipid film mediates transfer of soluble saccharides from the sea to the atmosphere: the role of hydrogen bonding" by Minglan Xu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-628-RC3>, 2022

The manuscript under consideration presents a compelling model for describing the transfer of saccharides into the aerosol phase through artificial breaking waves. The authors use a combination of state-of-the-art methods to support their model: SMPS, Langmuir isotherms, PM-IRRAS, and TEM imaging all serve as a basis for exploring the interactions within a ternary system of saccharides, seawater and insoluble fatty acids. The scientific arguments are logically sequenced, and well-referenced to previous work in the discipline. Overall, I expect that this work will be well-received by the scientific community as it provides interesting insight into the transfer of organic material from the SML into the aerosol phase.

My main criticism of the work in its present form is the authors' use of PM-IRRAS to elucidate the role of hydrogen bonding between the saccharide and fatty acid layer. In particular, I would like to see stronger evidence that there was a shift in the $\nu(\text{C}=\text{O})$ frequency, as it is not abundantly clear from Figure 5 in its present form. In addition, there are some finer points of the authors' scientific arguments that could be expanded upon. I think that these should be addressed before the manuscript is accepted, as it helps to contextualize their results.

Line 35: "SSA represents **the** major source of aerosol particle populations". I think this is a complicated assertion to make. While SSA emission per annum is the greatest of all sources with respect to mass (Textor et al, 2006), the same can't be said about number: even in the Southern Ocean, where sea spray production is rampant, SSA is outnumbered by sulfate aerosols (Quinn et al, 2017). As the sentence goes on to describe effects

relating to CCN and IN, I think the statement should be softened to:

“SSA represents **a** major source of aerosol particle populations”.

Textor, C., Schulz, M., Guibert, S., Kinne, S., Balkanski, Y., Bauer, S., Berntsen, T., Berglen, T., Boucher, O., Chin, M. and Dentener, F., 2006. Analysis and quantification of the diversities of aerosol life cycles within AeroCom. *Atmospheric Chemistry and Physics*, 6(7), pp.1777-1813.

Quinn, P.K., Coffman, D.J., Johnson, J.E., Upchurch, L.M. and Bates, T.S., 2017. Small fraction of marine cloud condensation nuclei made up of sea spray aerosol. *Nature Geoscience*, 10(9), pp.674-679.

Line 152: “surface seawater was obtained by dipping an HDPE container through the seawater surface.” I think it would be misleading to describe your collection method as sampling only surface water as this manuscript often references the SML, which is <1 mm thick. There are specific glass plate sampling methods for collecting SML which would have required a glass plate. The method you described (which is fine, in principle), might be better described as having collected both “surface and near-surface seawater.”

Line 252: I think you need to provide more evidence that plunging jets are similar to breaking waves. The previous work that you cited (Christiansen et al, 2019) does not provide any data on the bubble size distribution, nor does the reference work for your apparatus (Liu et al, 2022). In particular, Prather et al (2013) only described similarities between real breaking waves and plunging sheets (which are different from plunging jets). Looking at a similar plunging jet apparatus described by Salter et al (2014) shows that the bubble size distribution produced by a plunging jet is broadly similar to the plunging sheet shown in Prather et al (2013) and Stokes et al (2013). However, note that the exponents of the power law described by Stokes et al (2013) for the plunging sheet apparatus and real waves are larger than for the plunging jet described by Salter et al (2014) (See Table

4 in Salter and Figure 4 in Stokes). Thus, I would suspect that your bubble size distribution was much broader than for true breaking waves. This ought to be discussed with slightly more nuance in the present manuscript. Larger bubbles have a smaller surface-area-to-volume ratio, which ultimately influences the relative production of film drops versus jet drops. Jet drops, whose composition is more strongly tied to the subsurface below the SML are likely depleted in OM.

Salter, M.E., Nilsson, E.D., Butcher, A. and Bilde, M., 2014. On the seawater temperature dependence of the sea spray aerosol generated by a continuous plunging jet. *Journal of Geophysical Research: Atmospheres*, 119(14), pp.9052-9072.

Stokes, M.D., Deane, G.B., Prather, K., Bertram, T.H., Ruppel, M.J., Ryder, O.S., Brady, J.M. and Zhao, D., 2013. A Marine Aerosol Reference Tank system as a breaking wave analogue for the production of foam and sea-spray aerosols. *Atmospheric Measurement Techniques*, 6(4), pp.1085-1094.

Line 287: You describe the stability of the surface layer in the presence of fatty acids, but you are constantly disrupting the surface with your plunging jet which is mixing the SML into the subsurface waters. You describe later on (Line 312) that the collapse of the 2D film is itself an irreversible process. Part of my concern with your sampling method is that it does not allow for any transient redevelopment of the SML. There is a time constant related to the development of the SML after being perturbed. In the real ocean, waves rarely ever break the same surface twice. Plunging sheet methods (Stokes et al, 2013) and wave chambers (Prather et al, 2013) allow for the redevelopment of an SML between wave-breaking events. I think it is worth discussing within your manuscript that the transfer of saccharides to the aerosol phase may actually have been limited by the continuous mixing of the SML into the subsurface.

Section 3-2: I just wanted to comment that I found this entire section well-written and illuminating.

Lines 462-465: Here you are describing a shift in the vibrational frequency as evidence of hydrogen bonding. While this is not my specific area of expertise, I am having a hard time seeing a systematic shift in the peak of $\nu(\text{C}=\text{O})$ in either Figure 5a or b. Unless I am gravely misinterpreting these plots, the peak appears to go back and forth between the dashed lines you highlighted as the saccharide concentration increased, rather than one peak systematically outweighing the others as the concentration increased. Case in point, the dominant peak for the carbonyl stretch mode $\nu(\text{C}=\text{O})$ appears to be 1732 cm^{-1} for both seawater AND your highest concentration of Glucose in Figure 5a. Perhaps you could add an inset to Figure 5 that zooms in on this band and better describes the phenomena you are observing. This is a key observation that you repeatedly use throughout the remainder of the manuscript to support evidence of hydrogen bonding between the saccharide and fatty acid. It ought to be crystal clear to the reader.

Lines 487-488: Again, I had to look quite closely to see the trifurcation of the $\nu(\text{C}=\text{O})$ peak. This is more obvious upon closer inspection than my previous comment about $\nu(\text{C}=\text{O})$, but an inset of Figure 5 that focuses on the 1500-1600 cm^{-1} region might be helpful to the reader.

Figure 6: This is a beautiful figure, but one of my concerns is that you have analyzed (and are thus comparing) particles of different sizes. There are many studies which suggest that the fraction of organic matter within the generated aerosol can be highly size-dependent for particles produced from the same bulk water composition. This complicates your comparison somewhat and ought to be discussed with more nuance in this section; particularly, as you reference Estillore et al (2017)'s finding that the core-shell morphology is highly dependent on the salt-organic ratio. I think that your qualitative argument is fine, but some additional citations and discussion of the inherent limitations of comparing different-sized particles are needed.

Line 575: "poor". I think this is a bit of a harsh way of phrasing the scope of this study. Suggest softening "poor" to "limited".

Line 582-585: While this is the general view, there is some nuance to this assertion

specifically for CCN. The hygroscopicity of a composite aerosol is generally well-modelled according to a linear mixture model based on volume fraction (Petters and Kreidenweiss, 2007). The hygroscopicity of your aerosol was likely between that of glucose ($k=0.17$; Ziemann, Kreidenweiss and Petters, 2013) and that of sea salt ($k=1-1.25$; Zieger et al, 2017). Further, you combine De Vasquez et al (2022) and (Quinn et al 2015; Hasenacz et al 2019) to conclude that the oceanic concentration of saccharides is just 0.14 mg/L, which is substantially lower than the concentrations observed here. So, how considerable of an effect is this going to have on hygroscopicity? Here is some back-of-the-envelope math:

Ocean Salinity (g/L): 35

Bulk Saccharide Concentration (g/L): 0.00014

Density of Glucose (g/cm³) \sim 1.56

Density of Salt (g/cm³) \sim 2

Enrichment factor (Zeppenfeld et al, 2021): <167000

Mass Ratio of saccharide in aerosol (g/g): $(0.00014/35)*167000 = 0.67$

Volume Ratio (L/L): $0.67*2/1.5 = 0.89$

$k = 0.89*0.17 + 0.11*1.1 = 0.27$

This is likely a lower limit of the resulting hygroscopicity of your mixed aerosol since it assumed that the enrichment factor is on the largest end of the factors reported by Zeppenfeld et al (2021). Relating this to the sc-Dd curve presented by Petters and Kreidenweiss (2007) in Figure 2, a supersaturation of just 0.1% is required to activate

>50% of your particle size distribution as CCN. Consider that 0.1% is the lower end of supersaturations experienced during cloud formation and consider that the calculation above is likely an upper limit of the abundance of the saccharide within the aerosol. Case in point, at a supersaturation of 1.0% virtually your entire particle size distribution could act as CCN. This could add a little more nuance to your discussion of climatic effects.

Ziemann, Paul J., Kreidenweis, Sonia M., and Petters, Markus D.. Quantifying the Relationship between Organic Aerosol Composition and Hygroscopicity/CCN Activity. United States: N. p., 2013. Web. doi:10.2172/1086826.

Petters, M.D. and Kreidenweis, S.M., 2007. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmospheric Chemistry and Physics*, 7(8), pp.1961-1971.

Zieger, P., Väisänen, O., Corbin, J.C., Partridge, D.G., Bastelberger, S., Mousavi-Fard, M., Rosati, B., Gysel, M., Krieger, U.K., Leck, C. and Nenes, A., 2017. Revising the hygroscopicity of inorganic sea salt particles. *Nature Communications*, 8(1), pp.1-10.