

Interactive comment on “Sea spray aerosol organic enrichment, water uptake and surface tension effects” by Luke T. Cravigan et al.

Anonymous Referee #1

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The authors present observations of particle evaporation and sub-saturated hygroscopic growth for particles produced from bubbling air through seawater that was collected from a number of locations around New Zealand. They compare these observations with concurrent measurements of the particle composition and with the seawater composition. They use their evaporation measurements to infer organic content of the sampled particles. Among other findings, they observe the particles to have hygroscopic growth factors greater than expected given the large inferred organic content for some of the samples. They attribute this to surface tension depression. I have a number of questions and suggestions for clarification, and have some concerns about their interpretation of the sub-saturated hygroscopic growth. This paper should ultimately be publishable, but I think there are a number of aspects that require clarification first.

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P1/L9: I suggest “the Aitkin mode” be specified as a size range.

P1/L16: The particle size should be stated.

P2/L1: The influence of surface partitioning is quite small on sub-saturated hygroscopic growth. The impact of surface partitioning, and surface tension depression, becomes much more important at very high RH, near 100%. If the authors want to highlight this as a reason for their observations, they need to perform calculations within the main text that illustrate the importance of this effect. Simply stating that surface partitioning can explain the results is insufficient. The discussion on Page 20, which is in reference to various CCN measurements and not sub-saturated hygroscopic growth measurements, is not directly relevant. There needs to be a clear discussion of the impact at the conditions of the measurements. I suggest this sentence be deleted unless it can be backed up with appropriate calculations. The details regarding the compressed film model and how it was used (Page 24) are not sufficiently clear to allow a reader to understand what specifically was done.

P3/L7: I suggest it would be better to refer to the OVF values determined from hygroscopicity measurements as “derived” rather than “observed.”

P3/L11: I suggest “volatilizable” is more appropriate than “volatile” to describe the organic material in SSA. As the material exists in the condensed phase, it is not exactly “volatile.”

P3/L13: As the location is given for the Modini paper, it seems appropriate to give it for the Quinn paper as well.

P3/L15: I do not see how the Modini paper here concluded that there was not a non-volatile organic fraction. Modini et al. characterized only the volatility and hygroscopicity. They did not characterize organic components. Thus, they would not be able to directly address the question of non-volatile, residual organic compounds.

P3/L20: As fatty acids tend to have long hydrocarbon tails, their presence is not nec-

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essarily consistent with a large hydroxyl fraction, as stated. This is noted in the next sentence. I suggest these are better aligned.

P4/L13: I do not follow how the studies cited in this sentence are “chamber” studies. I don’t think any of these are actually chamber studies. Also, suppressed relative to what? Relative to ZSR? This would then conflict with the first part of the sentence. This could be clearer.

P4/L16: It would be useful if the authors would more clearly distinguish between sub-saturated and super-saturated measurements here, as these can be quite different in their response to added organics.

P4/L14: Technically, the Ovadnevaite paper is not on SSA. It is on secondary particles in the marine environment. These should be distinguished, as the composition is very different.

Introduction in General: As the composition of the organic material may (and likely does) vary with particle size, it might be helpful if the authors were to be as explicit as possible in stating the size range of the measurements when they refer to different studies. For example, are the measurements the total submicron? For just smaller particles? The authors might also consider adding further discussion regarding what the literature suggests about variability in the OA chemical composition with size.

P6: Particle generation: What concerns do the authors have regarding the representativeness of their size distributions obtained from their particle generation method, and how this might influence particle composition? The observed particle distributions (Fig. 4) differ notably from measurements of sea spray particles from breaking waves (e.g. Prather et al., PNAS, 2013) or estimated from multi-mode fitting of ambient distributions (e.g. Quinn et al., Nat Geosci., 2017; Saliba et al., PNAS, 2019). Differences in size distribution can be indicative of differences in composition. This issue needs to be explicitly discussed, including discussion of potential biases that might result.

Fig. S2: These are not exactly “volatility profiles” as stated in the main text, but instead a comparison of the volatile fraction for sea spray versus sea salt. A volatility profile would be a graph of volatile fraction or fraction remaining versus temperature.

P7/L15: The Vaattovaara et al. (2005) paper indicates that there is negligible growth for 10 nm inorganic particles, but that growth of larger particles in ethanol vapour is not negligible. Furrhter, that paper did not consider sodium chloride. Has it been demonstrated that this method works for particles more representative of those sampled here, that is do sodium chloride (or sea salt) particles not grow? This would be helpful to place uncertainty bounds on the authors measurements. If this has not been demonstrated, how do the authors derive an uncertainty?

Methods: There is a general lack of discussion of uncertainties. Such discussion would be welcome (aka is really needed).

P8/L17: The TDMA_{inv} method does not account for multiply charged particles. Are these a concern? Based on the size distributions shown, I would think they would be.

P8/L22: I do not find it clear how the volatility of hydrates is accounted for, nor how consideration of the hydrate proportion yields the organic fraction. If much of the organic fraction is truly non-volatile, wouldn't this method fail? Or if organic material chars to become non-volatile? Also, wouldn't this method fail if organics also evaporate between 200C and 400C? Organic volatility tends to be a continuum. Thus, one might not expect a bimodal distribution, as assumed here. How do the authors justify this assumption regarding organic volatility? It may be reasonable, but requires justification. (Note: if something is non-volatile, then it doesn't evaporate. Thus, the “non-volatile” organics indicated here are not non-volatile, but very low volatility. I strongly suggest the authors adopt a more precise language.)

Eqn. 2 relationship to OVF_{tot}: I think that these relationships could be stated more clearly. It is not clear, at least to me, why the total OVF would be 1-f (P9/L3). If the OVF_{SV} = 0, then in Eqn. 2 the value of f is by definition unity. The OVF_{tot}

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would then be $1 - 1 = 0$. But, this wouldn't account for evaporation above 400C. So it is unclear to me how this works. It is similarly unclear how the authors end up with OVF_tot values up to 0.9 (Fig. 6) when the max VF values in Fig. S2 reach only 0.23. Perhaps I am misunderstanding, but I find the discussion here to be unclear, making it difficult to really understand how the OVF_tot values were determined. I suggest revision is needed. I strongly encourage the authors to include graphs of VF (or VFR) versus temperature so that the reader can clearly see what must be a step change after ~400C indicative of evaporation of "non-volatile" components. There must be huge differences between the samples with OVF_tot = 0.9 and those with small values. It would be useful to the reader to see these.

P15/L5: The authors need to provide much more detail here regarding how they apportion things to the different modes. There must ultimately be full consistency with all the measurements. How do they decide how much of the volatile and "non-volatile" material goes between the three modes that overlap? Does this add up appropriately to, hypothetically, reproduce the observations? It is also not clear whether the authors assumptions allow for any salts in modes 1-3, or whether these are limited to mode 4. As written, they only indicate salts in mode 4. If this is the case, then the assumptions here are inconsistent with the VF observations. There must be a salt component at 50 nm, based on their interpretation, and thus there must be some salt in either Mode 1, 2, or 3. Additionally, the authors point the reader to Section 3.4 to justify their split, but it is not evident after reading Section 3.4 exactly how they made this determination. They need to be more explicit here and (i) fully justify their choices while (ii) demonstrating the internal consistency. As best I can tell from the range of sizes considered, the authors do not have an independent constraint on the composition of Mode 4 since it contributes negligibly to the number concentration below 150 nm, although will have a large influence on the overall mass.

OVF correlations: What does the slope of OVF versus some seawater metric (e.g. concentration of alkanes) mean? These are reported, but the meaning is not clear as

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the OVF is a fraction of the total PM. Also, shouldn't these slopes have units?

P15/L10: An assumption of an organic density of 1.1 g/cm³ seems at odds with the determination that species such as saccharides dominated the composition (based on the large hydroxyl fraction). Can this be further justified? Citation of Modini is insufficient, as that paper simply assumed 1.1 g/cm³ based on Keene et al. (2007) and thus is not an independent determination. Then, Keene et al. (2007) do not actually determine this, but state it is estimated based on Schkolnik et al. (2006). The title of Schkolnik et al. (2006) is "Constraining the density and complex refractive index of elemental and organic carbon in biomass burning aerosol using optical and chemical measurements" and this is an AGU abstract, not a published paper. Thus, the assumption of 1.1 g/cm³ does not seem justified by the literature references.

Eqn. 5: It would be helpful if the OMF here (and throughout) were labeled as OMF_PM1 to make clear that it is for the bulk PM1 measurement.

P11/L22: it would be helpful to have clarification on what is meant by "organic-salt mixtures" and how this differs from a ZSR model of an organic with a salt.

P11/L32: The compressed film model dynamically partitions material between the bulk and surface dependent on the specified parameters. What does it mean to say that all of the organics were partitioned to the surface here? Was this constrained somehow?

P11/L27: Is this speciation applied within the context of the compressed film model? If so, how were all these different components specified? What was assumed to occur for the organic components that did not partition to the surface? Are they dissolved in the bulk?

P12/L1: How was this decided for the SSA distribution? Where do these parameters come from?

P12/L11: The authors state "Significant correlations were observed between Chl a and total high molecular weight proteins and polyunsaturated fatty acids ($R^2 = 0.51$, p-value

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< 0.01).” Can it then be assumed that there is a weak correlation between Chl-a and things that are not mentioned as being correlated, in particular the saturated fatty acids that the authors note dominate the total?

P12/L19: It seems inconsistent to say that the Chl-a was highest in Bloom 1 with a value of 0.84 while the range is given earlier as up to 1.53.

P13/L5: it is perhaps more appropriate to indicate these as “SSA size distributions produced from natural sea water” rather than as “natural SSA size distributions” given that the reported distributions look quite different than what has been estimated for ambient SSA.

P13/L5: The authors note that the SSA size distributions produced from natural sea water are narrower than those produced from sea salt and suggest this is consistent with addition of surfactant material, citing Fuentes (2013) and Modini (2010). However, they authors might also note that the size distributions from Forestieri (2018) were nominally the same between sea salt and real seawater and from Zabori et al. (2012) were nominally the same for NaCl water and after spiking with succinic acid, although they did observe a notable difference for real Arctic ocean water.

P14/L3: This statement does not seem correct. The size distributions here peak at smaller, or similar modal diameters compared to a number of other studies. For example, the authors compare with Prather et al. (2013). The SSA from sintered glass filters in Prather et al. peak around 80 nm, consistent with the observations here, although the literature distribution is narrower. However, the SSA distribution produced from wave breaking had a modal diameter much larger. Also, the modal diameters estimated from multi-mode fitting in e.g. Saliba et al. (2019) are much larger in general.

P17/L15: For consistency with the discussion of Ca and Mg EFs, the authors should report the Cl/Na ratios for their lab sea salt experiments in addition to the reported values for seawater.

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P19/L14: Where does this factor of 1.5 come from? It seems like it comes from the tartaric acid experiment in Vaattovaara, but it is not clear. Has the variability in this value to different organic species been explored beyond Vaattovaara, in particular saccharides? Is 1.5 reasonable? What is the uncertainty?

P19/L17: What does it mean that the ethanol GFs did not correlate with the other estimates of organic volume fraction? This seems quite important in the context of the OVF interpretation, and is worth some discussion beyond just saying that perhaps the organics that contributed to growth were a subset of those that evaporated. Why would this be the case? Is this consistent with the estimates of the composition?

P19/L23: I am squinting at Table S2 and Fig. 5 and failing to see clearly how the difference in OVF or OMF from deep to mixed layer is statistically significant, or even real. I suggest this be removed unless the authors can justify it further. They note the limited number of samples, but even within these few samples there seems to be sufficient variability to not make this a robust conclusion.

Fig. 9: Which OVF is shown here? The total, I assume.

Fig. 10: Should indicate the particle size.

P24/L11: The word “observed” would better be “required” or “determined.” Also, while below the “threshold” indicated to have notable surface tension effects, is this small value reasonable from a physical standpoint? I think that the value they note, $< 10 \text{ cm}^3/\text{mol}$, corresponds to an unreasonably small molecular weight. Additionally, the authors might note that the Forestieri et al. (2018) work focused on CCN while the current work focuses on sub-saturated conditions. As noted above, the hygroscopic response to surface tension depression in different RH regimes can be quite different. In general, greater distinction between sub-saturated and super-saturated measurements is needed throughout the paper.

P24/L16: Which OCEANFILMS model? 1 or 2?

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P24/L8: It would be very helpful to the reader if the authors showed the calculated HGF as a function of the assumed critical area and molar volume. As this would likely need to be done for different OVF cases, the authors might consider a low, medium, and high case based on their Fig. 9. It is challenging to see how the compressed film model can resolve the observation-model (ZSR) discrepancy in Fig. 9. If I am understanding what the authors are saying, they are able to do so by tuning of the compressed film parameters. I will be honest and say that from what I understand of the model I don't really believe that the compressed film model can resolve the model-measurement gap here for sub-saturated conditions. There is quite a bit of literature on the relationship between sub- and super-saturated hygroscopicity that the authors might consider (c.f. Wex et al. (2009) and citations therein and that follow). Finally, as noted above already, further details regarding the partitioning of the different components in the context of the compressed film model is needed. What happens to the components that do not go to the surface? What hygroscopicity is assumed?

Fig. 14: I think this should state that this is for the compressed film model where all organics can partition to the surface, not that they are. Their partitioning is dynamic in the model. Same for Fig. 15.

P27/L7: The authors mention this 30 mN/m surface tension depression as being consistent with various SSA proxies, citing Forestieri et al. (2018). However, that paper, as well as Nguyen et al. (2017), show that the fatty acids have negligible impact on activation because the surface tension is dynamic. This aspect, that the surface tension is an evolving property, seems to be lost in the current discussion.

If the DOI for the data set is now known, it should be provided.

Grammar note:

P1/L10: "comprised of" should be "composed of".

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