

Interactive comment on “The organic fraction of bubble-generated, accumulation mode Sea Spray Aerosol (SSA)” by R. L. Modini et al.

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We thank the reviewer for his/her comments. Point by point replies to the comments are provided below.

General comments

Reviewers comment 1: They also tried to compare their results of organic fractions with those of other marine locations (Keene et al. 2007 and Facchini et al. 2008). They suggest that an organic fraction in accumulation mode is remarkable lower in the Australian coastal location than in other locations previously reported. However, their experiments are not comparable to the mentioned previous experiments due to the coastal water sampling location and different bubbling method.

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Response: We believe that our measurements can be compared to the measurements of Keene and Facchini as long as the differences between the separate experiments are clearly highlighted in the paper. The coastal nature of the seawater sampled for these experiments was highlighted in many places throughout the original manuscript. In addition, based on similar comments from reviewer #1, we have further highlighted the coastal nature of the water sampled in this study in the revised manuscript. The specific additions made to the manuscript are detailed below in response to the reviewer's comment #2.

We believe that the reviewer has misunderstood some aspects of our bubbling method and that our method is actually very comparable to the bubbling arrangements employed in the Keene and Facchini studies. We argue this point in our response to the reviewer's comments #4 and #6 below. Nevertheless, we have also added a paragraph to the revised manuscript explicitly highlighting the methodological differences between this study and the 2 previous studies and discuss how these differences might affect our results. The added paragraph is detailed below in the response to the reviewer's comment #2.

Specific comments

Reviewers comment 2: Authors should highlight that the experiments of authors had clearly different water sampling conditions and particle production methods compared to Keene et al. 2007 and Facchini et al. 2008 experiments.

Response: In regards to the coastal nature of the seawater sampled during this study we have made a number of revisions to the manuscript to further highlight that this was a major difference between our study and the Keene and Facchini studies. In the abstract (P21400, L24) we have added the following sentences: "We stress that our results were obtained using coastal seawater and they can't necessarily be applied on a regional or global ocean scale. Nevertheless, considering the order of magnitude discrepancy between this and previous studies, further research with independent mea-

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surement techniques and a variety of different seawaters is required to better quantify how much organic material is present in accumulation mode SSA.”

In the implications section (section 3.3) we have revised paragraph #3 beginning on P21413, L26. The original paragraph was: “Discrepancies between the different studies could be related to not only the amount of organics present in the source waters used in each experiment, but also the composition and surface-active nature of those organics. For example Facchini et al. (2008) conducted their measurements with organic-rich Atlantic Ocean water collected during a plankton bloom. Our measurements were also conducted with organic-rich seawater, but this time collected at a coastal site significantly affected by terrestrial run-off. The difference in the composition of organics (anthropogenic or biogenic, coastal or open ocean) may affect how enriched they become in the aerosol phase.”

It has been replaced with: “Discrepancies between the different studies could be related to not only the amount of organics present in the source waters used in each experiment, but also the composition and surface-active nature of those organics. For example Facchini et al. (2008) conducted their measurements with organic-rich Atlantic Ocean water collected during a plankton bloom. The Keene et al. (2007) results were obtained using seawater collected from a Bermuda passage (Ferry Reach). Measurements indicated the water was representative of the surrounding oligotrophic open ocean surface water. Our measurements were conducted with organic-rich seawater, but this time collected at a coastal site significantly affected by terrestrial run-off. The difference in the composition of organics (anthropogenic or biogenic, coastal or open ocean) may affect how enriched they become in the aerosol phase. We are not aware of any studies that have examined the relationship between seawater type and SSA organic fraction. Therefore it is not clear what effect, if any, the use of coastal as opposed to ocean seawater had on the SSA organic fraction measured in this study.”

Finally at the end of the Conclusions section 4 (P21415, L13) we have added the following sentence: “We reiterate that our results apply to accumulation mode SSA

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generated from coastal as opposed to open ocean seawater.”

The different particle production methods used in this study compared to the Keene and Facchini studies have also been further highlighted in the revised manuscript. We have added a paragraph to the Implication section (section 3.3) that explains the methodological differences between the separate experiments and discusses how these may have affected our results. The paragraph has been added at the end of paragraph 3 (P21414, L4). It reads: “In addition to seawater type, methodological differences could have potentially contributed to some of the difference between the results of this study and the results of the Keene and Facchini studies. The two previous studies were conducted with freshly-collected seawater while in this study seawater was stored in a dark refrigerator for up to 2 weeks. The properties of seawater organics may have changed during this storage time which could have affected their transfer to the aerosol phase. However, we note that no significant differences were observed between scans completed at different times during the 2 week measurement period. Therefore any artefacts due to storage are likely to be minimal. The bubble generator employed in this study was also far smaller than those used in previous studies (see water volumes in Table 1). While this reduced the risk of external organic contamination, it also meant our generator had a high surface to volume ratio. As seawater flowed bottom-to-top in the generator organics potentially adsorbed to the walls thereby reducing the amount of organics eventually transferred to the aerosol. This potential loss mechanism was not quantified or estimated. We do not believe that these methodological differences can account for the order of magnitude difference between our measured accumulation mode SSA organic fraction and the fractions measured in the Keene and Facchini studies.”

Reviewers comment 3: -Did authors measure the particle size distribution or particle concentrations for ultrapure de-ionized water (i.e. without added salts)? This would be important information in order to see a possible effect of water itself on the GF of artificial sea water. The bubbler is not the only source of impurities.

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Response: No we did not measure the size distribution or concentration of particles generated by bubbling pure de-ionised water in the generator. We have simply assumed that the concentration of particles generated from the de-ionised water itself would be a negligible fraction of the concentration of salt particles generated from the artificial sea salt solution (something similar has been observed for nebulised solutions; (LaFranchi et al., 2003)). We note that only one peak was ever observed in the humidified size distributions of the size-classified artificial SSA particles. This indicates there were no observable impurities generated from the de-ionised water externally mixed with the artificial SSA particles and suggests that our assumption was a reasonable one.

Reviewers comment 4: -Total scan time is for VH-TDMA 1-2h (p. 21408, line 9). This time is very long compared to water residence time (Table 1.). Actually, water residence time is so short (Table 1) that the VH-TDMA practically can catch only one measurement point in the range water residence time. This also leads to main fundamental difference between Modini et al and previous experiments. The VH-TDMA is more or less on-line method whereas impactors are off-line methods and thus impactors would not suffer similar way about the short residence time of water in laboratory experiments. The very short water residence time compared to the time resolution of VH-TDMA might also hinder the detection of possible depletion of organics in the start of the experiments. On the other hand, the long total scan time might lose some composition change information during the total scan.

Response: We believe that the reviewer has misunderstood our concept of water residence time. By water residence time we mean the average time water stayed in the generator before being replaced by 'fresh' seawater from the 20 L reservoir above the generator. (It was necessary to replace seawater in the generator to ensure its organic content was not depleted over time; although our results showed this water cycling was not actually necessary). For example, at a water flow rate of 0.3 L/min through the generator, the 0.2 L volume of water in the generator will be replaced by 'fresh'

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seawater every 40 secs. The total time available to complete a VH-TDMA scan is then determined by the time required to drain the 20 L reservoir. At the flow rate of 0.3 L/min this time is equal to 66 mins 40 secs. This was the fastest water flow rate used in this study and it provided enough time to conduct a complete VH-TDMA scan.

We also point out that the time resolution of the VH-TDMA method (1-2hr) is actually significantly better than the time resolution of off-line impactor sampling. Very long sampling times are required to capture enough SSA mass on a filter to perform an accurate chemical analysis. For example the sampling time in the Facchini et al. (2008) study using impactors was approximately 10 hours.

Reviewers comment 5: In order to strengthen the authors discussion I recommend that authors show relative particle concentrations as a function of time. This kind of information could be in a table for each experiment. Additionally, time and relevant information of each experiment should be labelled.

Response: Relative particle concentrations as a function of time were not measured during the experiments. This would have required an extra particle counter which would have increased the air flow rate required for sample analysis (VH-TDMA flow rate + CPC flow rate). Bubbling flow rate was constant (0.1 L/min) so this could only be achieved by increasing the particle free make-up air flow. This would have diluted the SSA concentrations and we judged it was more important to keep SSA concentration as high as possible. Therefore relative particle concentrations as a function of time were not measured. Relevant information concerning each experiment is already detailed in Table 1.

Reviewers comment 6: -Authors report very low water flow rate compared to the other experiments shown in Table 1. They regulated water flow rate but the regulation in low flow rates was relatively small compared to uncertainties in the methods. Therefore, a possible effect of flow rate regulation on particle composition could be difficult to detect in low water flow rates. Moreover, the water flow rates were much lower than in the

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experiments of Facchini et al and Keene et al and thus the comparison is not relevant. Anyway, authors could give an estimate what type of natural conditions their water flow rate could mimic.

Response: The intention of flowing water through the bubble generator is not to mimic natural conditions. Rather the intention is to ensure that organics are not depleted from the water in the generator over time due to the production of sea spray aerosol (which can be considered as a sink for the seawater organics). Therefore the relevant variable for comparison between different bubble generators is actually the water:air (bubbling) flow ratio because this effectively defines the ratio of the source of seawater organics ('fresh' seawater) to their sink (aerosol). We specifically chose water flow rates (0.08 and 0.03 L/min) so that the water:air flow ratio was similar to the corresponding ratios in the Keene (0.8) and Facchini (0.35) experiments. In addition we also performed one experiment with a much higher water flow rate (0.3 L/min, the maximum we could achieve) so that the water:air flow ratio (3) was even higher than the Keene and Facchini studies. Therefore the comparison between our bubbling generator and the generators used by Keene and Facchini is actually very relevant. The water flow rates used in this study are only far less than the 2 previous studies because our bubbling rate is much smaller (0.1 L/min compared to 5 L/min (Keene) and 20 L/min (Facchini)). This is ultimately because we were able to perform our experiments with a much smaller scale bubble generator because the VH-TDMA method does not require the large masses of SSA required for accurate chemical analysis of impactor samples.

Reviewers comment 7: -p.21411, line 28: The ZSR approximation states that the individual components of an internally mixed particle uptake water independently of each other if the individual components do not interact with each other.

Response: Sentence beginning P21411, L28 has been changed to: "When making the ZSR approximation it is assumed that the individual components of an internally mixed particle do not interact with each other and therefore they uptake water independently."

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Reviewer comment 8: -p.21413, line 2: remove similar

Response: We believe it is appropriate to refer to the bubbling experiments of Keene and Facchini as 'similar' to our experiment (see response to reviewer comments 2 and 6 above) so have not removed the word.

Reviewer comment 9: -p.21413-21414: Please notice that organics do not always decrease the HGF (e.g., Sjögren et al. 2007). Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures" Sjögren S, Gysel M, Weingartner E, et al. JOURNAL OF AEROSOL SCIENCE ,38 , 2, 157-171,2007.

Response: We are not aware of any measurements in the literature of organic compounds that are more hygroscopic than inorganic compounds, let alone organics that are more hygroscopic than highly hygroscopic sea salt aerosol. Therefore the HGF of mixed organic-inorganic particles of a given size will always decrease with increasing organic fraction. The reference cited by the reviewer does not provide any evidence that organics do not decrease the HGF of mixed particles relative to the HGF of the inorganic portion alone. On the contrary, the data presented in that reference shows growth factors for mixed particles (ammonium sulphate-adipic acid, ammonium sulphate-humic acid sodium salt) that are below what would be expected for pure ammonium sulphate particles of the same size. In addition growth factor is shown to decrease with increasing organic fraction for mixed ammonium sulphate-adipic acid particles. We stand by our statement that an organic fraction will always decrease the HGF of SSA relative to the HGF of purely inorganic sea salt aerosol.

Reviewer comment 10: -p. 21413, line 19: : : :at a site...? Please, denife more accurately.

Response: The sentence has been modified so that the site is now more accurately defined as "a remote continental site in the arctic circle in northern Sweden."

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References: LaFranchi, B. W., Knight, M., and Petrucci, G. A.: Leaching as a source of residual particles from nebulization of deionized water, *J. Aer. Sci.*, 34, 1589-1594, 2003.

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