

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

R. L. Modini et al.

r.modini@student.qut.edu.au

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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: The main critic to the manuscript is that coastal water have been used to perform the experiment. Although rich in organics and chlorophyll, coastal waters, particularly if highly influenced by river run-off (and probably by anthropic activity), represent a different system than open ocean waters. The organic matter volume contribution to sea spray obtained in the experiment is not representative of high biologically active open ocean regions and the data cannot be extended to the regional

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or global scale. The authors highlight the coastal origin of the collected water in the manuscript, nevertheless, the limits of the experiment should be stressed more strongly in the abstract and in the conclusions.

Response: We have modified the abstract and conclusions according to the reviewers comment. In the abstract we have added the following sentence (P21400, L24): “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 measurement techniques and a variety of different seawaters is required to better quantify how much organic material is present in accumulation mode SSA.”

At the end of the conclusion (P21415, L13) we have added the following sentence: “We reiterate that our results apply to accumulation mode SSA generated from coastal as opposed to open ocean seawater.”

In relation to this comment we have also modified paragraph #3 in the Implication section 3.3 (P21413, L26) to further highlight the fact that this study was conducted with coastal seawater, while previous studies were conducted with representative open ocean seawater. The old 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

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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.”

Specific comments

Reviewers comment 2: P21403 – L2: in their comment about the difference between Facchini et al. (2008) and Keene et al (2007) the authors should consider that the difference is mainly due a different operative definition of soluble and insoluble organic matter. The results could be more similar than expected if measurements would have been done with comparable methods.

Response: We have modified the sentence (P21403, L2) to: “While both studies had different operative definitions of solubility, this consideration still implies that the results of these separate experiments do not agree as well as they first appear to.”

We still contend that the Keene and Facchini studies do not agree as well as they first appear to. From what we can gather following the references cited in Facchini et al. (2008), both studies measure soluble organic matter by extracting filter samples into water and measuring the organic carbon content of the extract with a liquid TOC analyser (there are differences in the type of filters used and extraction method). The Facchini study, in addition, measures total carbon content using evolved gas analysis

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(EGA) technique. Insoluble organic carbon content is then obtained by subtracting the soluble organic carbon from total carbon. The result is that insoluble organic carbon dominates the total (~94%). If this is also true for the particles analysed in the Keene study then their reported organic fractions underestimate the true fractions, because their method doesn't pick up the insoluble organic carbon which was only observed by the EGA analysis in the Facchini study. Consequently the 2 studies do not actually agree very well.

Reviewers comment 3: P21405 – L24: the authors should report the particle residence time in the thermodenuder. This information is important to understand how reasonable is the assumption of complete organic matter removal by the thermodenuder. Several papers in the literature report data about thermal behavior of particulate organic matter and many of them evidence the presence of refractory, thermo-stable, material.

Response: The particle residence time in the thermodenuder of 0.3 secs is now reported on P21405, L26. In regards to the possibility of non-volatile organics we have heated the particles to a high enough temperature (583°C) at a residence time of 0.3 secs to initiate the evaporation of NaCl. Thus, if we assume that the organic fraction of SSA is more volatile than the inorganic fraction than we are volatilising the entire SSA organic fraction by heating the particles to 583°C. We believe this is a reasonable assumption. It is stated clearly on page 21406, line 26.

Reviewers comment 4: P21403 – L1: a figure with a scheme of the experimental setup would help the comprehension.

Response: A new figure (new Fig. 1) consisting of a schematic diagram of the bubble generator has been added to the revised manuscript.

Reviewers comment 5: P21403 – L2: the presented configuration suggests a high surface/volume ratio of the bubbles generator, do the authors have any estimate of the fraction of water insoluble, surface active, organic matter that can be loss by adsorption to the tube walls? This issue should be addressed because determinant for the final

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organic content of the sea spray aerosol. P21405 – L18: have the authors any evidence that sea water stored for days, although refrigerated in the dark, maintain its properties unchanged, especially on the organic matter content and properties point of view? One of the main differences between this experiment and those performed by Keene et al. (2007) and Facchini et al. (2008) lays on the fact that in this case not-freshly-collected sea water have been used for the sea spray generation. This issue should be better addressed.

Response: These comments both point to methodological aspects of our study and their comparison to the Keene et al. (2007) and Facchini et al. (2008) studies. We have inserted a new paragraph into the implications section 3.3 that raises the reviewer's points and discusses how they might influence our low measured organic fraction. The paragraph has been added at the end of paragraph 3 (P21414, L4). It is: "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."

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Reviewers comment 6: P21409 – L21: the difference between the "A" and "N" curves is not constant from 200_C on, the average value of the organic fraction volume contribution should be presented with the actual standard deviation and not with the $\pm 6\%$ estimate derived from the V/V_0 measurement error.

Response: The standard deviation of the differences between the "A" and "N" points is only 2%, well below the 6% theoretical uncertainty (twice the V/V_0 measurement error). We have erred on the side of caution in choosing to report our (absolute) error estimate for organic volume fraction as the larger theoretical uncertainty value. This produces an error range which encompasses all but 2 of the "A" and "N" points. Thus we believe this to be a suitable, though probably overestimated error for organic volume fraction.

In accordance with the reviewers comments the sentence on P21409, L21 has been replaced with: "This average difference was 8%. The standard deviation of the difference was 2% and the theoretical uncertainty was 6% (twice the V/V_0 measurement error). We take the larger value of $\pm 6\%$ as the absolute error in the measured organic volume fraction of 8%."

Reviewers comment 7: P21410 – L22: a more quantitative approach would be appreciated in the comparison between the three curves. As done for the previous plot, the authors should quantify the V/V_0 difference (with uncertainty) between the three curves and check its statistical significance, although it is acceptable the comment that the differences cannot be attributed only to the particle organic fraction content.

Response: A more quantitative approach has been taken and the paragraph in question (P21410, L22: Section 3.1.3) has been modified according to the reviewers comments.

The old paragraph was: "Figure 3 displays the N0.0838, N0.0871 and N0.08173 volatility curves. It appears that volatility increased with decreasing particle size. For example at 464°C, 81% of N0.08173, 79% of N0.0871 and 76% of N0.0838 particle volume remained. However these volatility differences could be due to differences in particle size

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as well as composition. Therefore we cannot quantify solely from this data how the organic fraction of our natural SSA particles depended on particle size. Nevertheless, because the differences in the volatility curves of all three particle sizes were so small and all three curves had the same general shape, we can still conclude that the organic fraction of natural SSA particles did not vary significantly (in amount and composition) with particle diameter in the range 38–173 nm.”

It has been replaced with: “Figure 4 displays the 38 nm (N0.0838), 71 nm (N0.0871) and 173 nm (N0.08173) volatility curves. It appears that volatility increased slightly with decreasing particle size. In the temperature range 200–500°C where it is expected that the organic fraction of the particles has evaporated the average difference (± 1 standard deviation) between the 173 nm and 38 nm curves is $6\pm 3\%$. The average difference between the 173 nm and 71 nm curves and the 71 nm and 38 nm curves in the same range is $2\pm 2\%$ and $3\pm 2\%$, respectively. However, these volatility differences could be due to differences in particle size as well as composition (organic fraction). Therefore these values do not represent the difference in organic volume fraction for the different particles sizes. Rather they overestimate these fractions by an unknown amount equal to the percentage change in V/V_0 due to the change in initial particle size. Taking this into account and the fact that the theoretical uncertainty in the calculation of organic volume fraction is 6%, we conclude that the organic fraction of natural SSA particles did not vary significantly with particle mobility diameter in the range 38–173 nm.”

Reviewers comment 8: P21411 – L23: the authors comment “At temperatures above 206_C the artificial and natural HGF90% curves agreed almost completely within experimental variation” is not fully convincing. Have the authors checked for statistic significance of the differences between the “Art” and “Nat” SSA HGF90% curves in the two ranges before and after 200_C?

Response: The sentence is meant to reflect that for most data points the standard deviations of the measurements overlapped at temperatures above 206°C, and as such the difference between the two curves in this range is not statistically significant.

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Technical comments

Reviewers comment 9: P21403 – L12: “to act AS CCN”

Response: Change has been made.

Reviewers comment 10: Figure 4: the use of a darker color for the green curve would probably help in reading the plot.

Response: Curve colour changed to violet.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21399, 2009.

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