

Interactive comment on “Linking variations in sea spray aerosol particle hygroscopicity to composition during two microcosm experiments” by Sara D. Forestieri et al.

Anonymous Referee #2

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The paper by Forestieri et al. reports on hygroscopicity of sea spray particles generated in lab conditions during various stages of phytoplankton bloom development. Lab generated sea spray studies are being pursued by many research groups during recent years trying to uncover the mechanisms and impacts of organic matter enrichment in sea spray particles.

The hygroscopic properties of sea spray were studied by measuring scattering properties of wet versus dry particles. As it measures bulk sea spray population it is missing on the important aspect of size dependent chemical composition which is critical in uncovering organic matter enrichment processes. The results of the study are not particularly new and the authors could increase its significance by assessing radiative

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forcing impacts. It would be very interesting how the results of this study compare with the study by Vaishya et al. (2013) conducted in marine atmosphere (the study referenced, but not discussed).

The most confusing aspect of this study is that a significant change in hygroscopicity of sea spray particles is only loosely connected to chemical composition. AMS did not detect the amount of organic matter required to explaining the observed change in GF. While the authors speculate about the bounce and refractory nature of sea spray particles (providing no references) the published evidence is in favour of AMS being able to quantitatively measure sea spray e.g. (Allan et al., 2004; Ovadnevaite et al., 2012; Schmale et al., 2013) to mention a few. ATOFMS results seem to correlate with the observed GF, but ATOFMS lacks quantitative estimate as its sensitivity to sea spray is rather poor. As the mixed-in organic matter in sea spray would increase ATOFMS sensitivity, the amount of non-sea-salt particles would be biased high. Also considering ATOFMS size range and MART sea spray particle size peaking at a size where ATOFMS just starting to detect particles, it appears that ATOFMS measured only a fraction of sea spray population. As it currently stands, the data do not corroborate each other.

Other comments

Page4, Line 24. I wonder if the flow was split isokinetically (equal face velocities) between instruments sampling from MART as that could affect sampled particle sizes of individual instruments. The authors mentioned laminar conditions, but laminar conditions limit particle losses to tubing walls while isokinetic split maintains the same particle population into each sampling line.

Page 5, Line 12. Peak chlorophyll concentration was mentioned as 10ug/l in the previous paragraph.

Line 17. Was this MART reproducibility issue or else?

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Line 26. Considering 3week duration of the whole experiment a substantial degradation of organic matter (rotting) should have occurred at ambient temperatures in excess of 25C. Was bacteria growth monitored to inform on such process and if not informative, how could that be related to real world environment?

Page 6, Line 27. Were the particles dried? What RH? It seems that APS density was picked based on OM fractional contribution which suggests about 30% depending on OM density. If particles were not dried the picked density would not apply.

Page 7, Line 26. Was PM2.5 cyclone operated in dry or wet conditions which could have converted PM2.5 into PM1 or lower size cut if wet?

Page 8, Line 3. Following the paragraph above referring to minimal contribution of >2.5um particles to the total SSA population it follows that ATOFMS sampled minor fraction of particles considering its transmission efficiency. Given low ATOFMS sensitivity to sea salt particles it transpires that ATOFMS sampled fraction of a fraction of SSA population. This aspect has to be clearly articulated otherwise references to SSA chemical composition is heavily biased towards supermicron particles.

Page 9, Line 2. Is it referred to dry of wet particles? If SEMS was dried, but AMS was not then not same SSA population was measured by the two instruments making diameter match irrelevant. Wet particles entering the AMS inlet are instantly frozen due to adiabatic expansion and segregated by aerodynamic lenses based on their wet diameter. Assuming RH in the MART and subsequent sampling lines 90-100%, wet particle diameter was 2-3 times larger than dry SEMS particles. NR-OM mass was therefore limited to 186-280nm instead of 560nm. The drying issue appears quite central throughout the manuscript, so I suggest it clarifying at the beginning and using notations d(dry), d(wet) were appropriate. If AMS sampled wet particles that would explain the missing mass discussed few lines below.

Line 8. AMS is typically calibrated with dry NH4NO3 particles. Why would SS particles bounce more than the calibration particles as AMS chemical species mass is calculated

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on nitrate equivalent basis?

Page 11, Line 20. Many lab and ambient studies reported chemical composition dependence on particle size which would make GF size dependent too. This study reports size independent (averaged) GF which is rather misleading and, therefore, the issue should be clearly stated.

Line 28. The discrepancy can be partly due to shallow cut-off function of PM_{2.5} cyclon. Another source of discrepancy can be due to losses of wet particles and corresponding losses in dryers as in general wet particles are lossier. Again the drying of the particle is very unclear throughout the study and difficult to interpret.

Page 12, Line 6. Wiedensohler et al. (2012) reported that in general sizing errors of different instruments can be objectively up to 10%.

Page 13, Line 13. 2.2 at 85% or 90%? Also on page 10, GF(85%) of NaCl was referred to as 2.1.

Line 27. Is it possible that the relative abundance of Fe-rich particles was due to higher sensitivity of ATOFMS to Fe-rich versus SSA?

Page 14, Line 23. This is only true if ATOFMS and CRD size ranges were exactly the same which was not the case as ATOFMS cannot reliably detect 100nm particles, especially SSA.

Page 16, Line 13. Page 10 referred to 2.1 GF(85%). Why GF=1 is expected as the minimum combined value? Any reference to backup? Marine gels and micelles have been reported to process some water despite being generally hydrophobic (Ellison et al., 1999; Chakraborty and Zachariah, 2007). Fatty acid is only one of the many possible compounds and necessarily entirely hydrophobic.

Line 20. It has been demonstrated in numerous studies that OM fraction in sea spray is size dependent. Should the GF value of 1.39 be interpreted as a bulk average of highly enriched and poorly enriched SS particles?

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Page 17, Line 20. There is an issue regarding size dependent chemical composition. As scattering is dominated by larger submicron sizes and the smaller submicron particles tend to be more enriched in OM, averaged GF of this study missing out on the important aspect of size dependent chemical composition.

Line 24. How this volume fraction compared with AMS chemical composition? Did AMS record any substantial organics as 0.33-0.52 volume fraction would suggest? Figures show that AMS OM fraction was 0.05.

Page 18, Line 5. "which was 5 times higher". Much higher chl was probably due to higher temperature than the ocean (what was the T range?) and plentiful nutrients.

Page 19, Line 3. Consider different size ranges sampled if AMS was not dried.

Table 1. AMS size range is missing.

Allan, J. D., Bower, K. N., Coe, H., Boudries, H., Jayne, J. T., Canagaratna, M. R., Millet, D. B., Goldstein, A. H., Quinn, P. K., Weber, R. J., and Worsnop, D. R.: Sub-micron aerosol composition at Trinidad Head, California, during ITCT 2K2: Its relationship with gas phase volatile organic carbon and assessment of instrument performance, *J. Geophys. Res.-Atmos.*, 109, 10.1029/2003jd004208, 2004. Chakraborty, P., and Zachariah, M. R.: "Effective" negative surface tension: A property of coated nanoaerosols relevant to the atmosphere, *Journal of Physical Chemistry A*, 111, 5459-5464, 10.1021/jp070226p, 2007. Ellison, G. B., Tuck, A. F., and Vaida, V.: Atmospheric processing of organic aerosols, *Journal of Geophysical Research: Atmospheres*, 104, 11633-11641, 10.1029/1999JD900073, 1999. Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G., Worsnop, D. R., and O'Dowd, C.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, *J. Geophys. Res.-Atmos.*, 117, 10.1029/2011jd017379, 2012. Schmale, J., Schneider, J., Nemitz, E., Tang, Y. S., Dragosits, U., Blackall, T. D., Trathan, P. N., Phillips, G. J., Sutton, M., and Braban, C. F.: Sub-Antarctic marine aerosol: dominant contributions from biogenic sources, *Atmos. Chem. Phys.*, 13,

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8669-8694, 10.5194/acp-13-8669-2013, 2013. Vaishya, A., Ovadnevaite, J., Bialek, J., Jennings, S. G., Ceburnis, D., and O'Dowd, C. D.: Bistable effect of organic enrichment on sea spray radiative properties, *Geophys. Res. Lett.*, 40, 6395-6398, 10.1002/2013gl058452, 2013. Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjaraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Gruning, C., Faloon, K., Beddows, D., Harrison, R. M., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H. G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Loschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, *Atmospheric Measurement Techniques*, 5, 657-685, 10.5194/amt-5-657-2012, 2012.

[Interactive comment on Atmos. Chem. Phys. Discuss.](#), doi:10.5194/acp-2016-36, 2016.

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