

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 #1

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General comment:

The paper by Forestieri et al. presents results from two microcosm experiments on the properties of sea spray aerosols, focusing on their hygroscopic and optical properties, as a function of the seawater composition. The seawater composition was artificially modified in the microcosms by the addition of nutrients. The authors infer an average hygroscopic growth factor (HGF) for the whole sea spray aerosol population, from the measurement of the aerosol extinction enhancement due to the uptake of water vapour at 85% humidity. Results show a decrease of the HGF by 10 to 19% relative to pure inorganic sea salt. The authors then infer an average chemical composition from the HGF with the hypothesis that the organic fraction is hydrophobic. No linear

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link between the increase of Chl-a levels and the change in aerosol chemical composition (organic content, mainly) was observed. The study of the impact of the presence of organic matter in primary sea spray on its optical properties through the effect of a decreased water uptake has never been investigated in the past to my knowledge. Whether this has an important impact or not is important. In this view this is a very valuable study. However, the measurement methodology rely on several hypothesis and approximations that could be better justified (see detailed comments), and the article is more focusing on inferring the organic fraction of primary organic aerosol than on evaluating this impact, which could be more emphasised (the impact on scattering is only mentioned in the conclusion as a range from 10 to 35% for 85% humidities). I would have expected a time series of the extinction (wet and dry) in order to directly evaluate the impact of a phytoplanktonic bloom on the optical properties of sea salt aerosol. I recommend publication after major revisions.

Detailed comments

Page 4, lines 6-7 : “SSA particles sampled from the MARTs are primary, since the average residence time in the MARTs is much shorter than the time scale required for secondary processing of SSA particles (e.g. heterogeneous gas-phase reactions) (Lee et al., 2015).” What is the residence time in the microcosm headspace, what are briefly the results from Lee et al. 2015 to support this hypothesis ? How can the absence of any photochemical reactions producing condensing organic matter be excluded?

Page 5 lines 13_18 : “The same seawater as used in the indoor MART was added to a separate MART and sampled immediately after collection and before nutrient addition. However, the resulting particle size distribution from this MART differed substantially from those measured from the indoor MART, with a much greater contribution of large particles. Thus, the measurements from this separate MART are not directly comparable to the measurements from the indoor MART and are not considered further” Is there any explanation for this ? Could it be that the same difference in original size distribution (before enrichment) was observed in the outdoor experiment ?

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Page 6, line 10 : "Group 1 sampled for 1.5 h, group 2 sampled for 2 h, and Group 3 for sampled 1 h each day that sampling was conducted" Was sampling always performed in this order ? Can there be a bias due to the position of the sampling period during the day ? Has this been tested ?

Page 6, line 25 : "The SEMS and APS distributions were merged using the SEMS distribution up to 1 μm and the (dp,m equivalent) APS distribution at larger diameters." How did the two instrument compare on their common size range ? Why was the APS preferred over the APS on the 1-1.9 micron size range ?

Page 7, line 2 : "Light absorption by the SSA particles was negligible, and thus extinction is equal to scattering, i.e. $b_{\text{ext}} = b_{\text{sca}}$." Was this assumption validated ? Can Brown carbon contribute the SSA absorption ?

Page 9, lines 16-17 : "Unlike $f(\text{RH})$, GF values are independent of the dry particle size, and thus only depend on composition" This is only true for larger particles, the smaller the particles the highest the kelvin effect is. Maybe it is useful to argue that this hypothesis is true for the sizes of particles relevant here.

Pages 9 and 10 : calculation of GF(RH) : the underlying hypothesis for such a iterative calculation is that the chemical composition of the aerosol is homogeneous over the whole range of sizes (independent of the particle diameter). Figure S6 does not show this. How does this impact the results ?

Page 10, lines 10-21 : "The measured GF(85%) for NaCl was 2.09 +/- 0.03 and for (NH₄)₂SO₄ was 1.59 +/- 0.05, which compare very well with literature values of ~2.1 for NaCl (Cruz and Pandis, 2000; Laskina et al., 2015; Hansson et al., 1998) and ~1.55 for ammonium sulfate (Laskina et al., 2015; Wise et al., 2003)." The literature values should be reported for a given aerosol size (or size range).

Page 12 , lines 13_14 : "Uncertainty in the assumed RI value for the dry particles may explain a small fraction (<5%) of the difference." How was this assessed ? Has

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the chemical analysis of the aerosol been used to estimate the real RI? All hypothesis for possible discrepancies addressed in this paragraph should be detailed in the methodology section (or at least in the supplementary material). An overall uncertainty on the HGF retrievals procedure should be calculated and compared to the measured HGF variability and consequent Org frac variability, so the reader can be convinced that the measured time variations are real. The uncertainty on the calculation method should be less than the 10 to 19% decrease in HGF for the results of the paper to be significant.

Page 12, lines 21-24 : "We have tested the sensitivity of the retrieval method to an 8% increase in the particle diameters. The retrieved GF values are increased by a marginal amount (0.015-0.03) when the diameters are increased, and thus such potential sizing uncertainty does not affect the main conclusions presented here" Does this mean that a particle diameter increase of 8% was actually applied to the data set ?

Page 17, lines 10-12 : "By using a campaign-average scaling factor, it is implicitly assumed that the actual variations in $f_{\text{SS},0.75\mu\text{m}}$ are captured by $f_{\text{SS},\text{avg}}$, which seems reasonable given the general constancy of the size distributions over the course of each of the microcosm experiments, c.f. Fig. 2." Why would the relative stability of the size distribution shown on fig 2 insure that the non-sea salt content of the aerosol (shown to increase in the course of the experiment) evolves uniformly with size ?

Page 17, lines 19-24 : "...organic volume fraction (ϵ_i) of 0.56 – 0.88 for these particle types if it is assumed that volume mixing rules apply (i.e. the Zdanovskii-Stokes-Robinson mixing rules (Stokes and Robinson, 1966)). Since the non-SS values range from 0.53 – 0.74, if it is assumed that the SS-type and non-SS particle types have similar size distributions, then the implied ensemble average ϵ_i would be about 0.33 – 0.52." I understand that the first time that ϵ_i is used it refers to the fraction of hydrophobic material in the non-SS fraction, while the second time it is used it refers to the fraction of hydrophobic material in the overall aerosol. If this is right, the same terminology should not be used for both.

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Page 18, lines 9-12: "Both DOC and heterotrophic bacteria concentrations increased as the bloom progressed until they stabilized around the point when Chl-a concentrations had returned approximately to their pre-bloom levels, with DOC concentrations ranging from 200 to 300 $\mu\text{M C}$ and heterotrophic bacteria concentrations from 1×10^6 to a peak of $1.7 \times 10^7 \text{ mL}^{-1}$ (Figure S5B)." Are those values realistic for natural seawaters ?

Technical comments

Page 5, line 8 : mesocosm or microcosm ?

Figure 3 (B) : description of Org not in the figure text. "the reported uncertainties for all properties is 1 sigma. . ." should be "the reported standard deviations for all properties is 1 sigma. . ." as those are not uncertainties on the measurements

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