

## Author's response to reviewer's comments

We thank the two reviewers for their constructive comments and suggestions, which have helped to improve the manuscript. Before responding to the specific individual comments from the reviewers, we note that, we have made substantial changes to the manuscript based on the reviewer comments. Specifically, we changed the focus from looking at the relationship between sea spray aerosol particle hygroscopicity and ATOFMS cluster-type fractions to one between hygroscopicity and organic matter volume fractions ( $\epsilon_{\text{org}}$ ). The OM volume fractions were estimated from the AMS organic matter/PM<sub>1</sub> mass fractions that were presented in the original manuscript. In the original manuscript, we did not use the  $\epsilon_{\text{org}}$  quantitatively, as there are concerns regarding the detection efficiency of the AMS for these marine derived organics as particles containing a large fraction of sea salt have a higher susceptibility to particle bounce and organic matter contained in these particles may be inefficiently vaporized (as is suggested by the results presented by Frossard et al. (2014)). That said, in one of the references mentioned by Reviewer #2 (Ovadnevaite et al. (2012)), it was determined that sea salt aerosol had a collection efficiency ( $CE$ ) in the AMS of 0.25. We have therefore now corrected the AMS organic matter/PM<sub>1</sub> mass fractions using a  $CE$  of 0.25, and the mass fractions were converted to  $\epsilon_{\text{org}}$  assuming a density of 1 g/cm<sup>3</sup> for organic matter. The resulting  $\epsilon_{\text{org}}$  are therefore relatively uncertain in terms of absolute magnitude, but the trends with time should be reasonably robust under the assumption that the  $CE$  did not change substantially across the measurement campaign. A thorough discussion of the uncertainties in  $\epsilon_{\text{org}}$  as estimated from AMS organic matter/PM<sub>1</sub> mass fractions and the details for calculating  $\epsilon_{\text{org}}$  has been added to section 2.2.1.

“It is important to note that while the temporal trends of the AMS NR-OM/PM<sub>1</sub> fractions are likely reflective of the general behavior, the absolute values are more difficult to quantify because NR-OM associated with particles containing high sea salt fractions may not be vaporized efficiently by the AMS due to the refractory nature of sea salt (Frossard et al., 2014) and to the susceptibility of SSA particles to particle “bounce” in the AMS. Consequently, the SSA particles, including the NR-OM component, are detected with a collection efficiency ( $CE$ ) lower than unity (Frossard et al., 2014). One previous study (Ovadnevaite et al., 2012) determined the  $CE$  value for organic-free sea salt sampled when  $RH < 70\%$  is approximately 0.25. However, they also note that the  $CE$  is potentially instrument dependent, and further may not be applicable to the organic fraction in sea spray particles due to differences in ionization efficiency (which is a component of the overall  $CE$ ) (Ovadnevaite et al., 2012). It is also possible that the  $CE$  differs between particles that have differing relative amounts of OM and sea salt. Despite such uncertainties in quantification of NR-OM by the AMS for sea spray particles, the NR-OM mass concentrations for the sampled SSA particles were determined in this study assuming  $CE = 0.25$ . The measured NR-OM mass concentrations were used to calculate NR-OM volume concentrations assuming a density ( $\rho$ ) of 1.0 g/cm<sup>3</sup>. A value of 1.0 g/cm<sup>3</sup> for  $\rho_{\text{OM}}$  is consistent with that of fatty acids ( $\rho < 1$  g/cm<sup>3</sup>), which are a significant fraction of marine-derived OM (Mochida et al., 2002; Cochran et al., 2016). However, this value serves as a lower bound for  $\rho_{\text{OM}}$  because OM with higher densities, such as sugars ( $\rho \sim 1.7$  g/cm<sup>3</sup>), have also been observed in SSA (Quinn et al., 2015). The NR-OM volume

fractions of SSA ( $\epsilon_{\text{org}}$ ) were calculated as the ratio between the observed NR-OM volume concentrations and the integrated total particle volume concentrations from the size distribution measurements. Given the use of a lower-limit value for  $\rho_{\text{OM}}$  the  $\epsilon_{\text{org}}$  are likely upper limits (not accounting for uncertainty in the assumed *CE*).”

The CE-corrected  $\epsilon_{\text{org}}$  are now used as the primary compositional metric for understanding both the depression in *GF*(85%) values relative to inorganic sea salt and their temporal variability. Figures 3 and 5 have been updated to show the CE-corrected  $\epsilon_{\text{org}}$  values. Discussion regarding the temporal variability in and absolute magnitude of the CE-corrected  $\epsilon_{\text{org}}$  has been added.

“The NR-OM volume fractions of SSA varied from 0.29 to 0.50 throughout the course of the indoor MART microcosm experiment (Figure 3). The observation of such large  $\epsilon_{\text{org}}$  values is consistent with the substantial depressions in the *GF*(85%) values relative to pure, inorganic sea salt (2.1). The temporal variation in the  $\epsilon_{\text{org}}$  was generally similar to that of the *GF*(85%) values, with smaller *GF*(85%) values corresponding to larger  $\epsilon_{\text{org}}$  values, although the peak in  $\epsilon_{\text{org}}$  is somewhat sharper than the dip in the *GF*(85%). The inverse relationship between the *GF*(85%) and  $\epsilon_{\text{org}}$  is consistent with organic compounds being less hygroscopic than sea salt.”

The original Figure 4, which showed the relationship between the *GF*(85%) values and the ATOFMS non-sea salt cluster fractions, has been replaced. The new Fig. 4 now shows the relationship between *GF*(85%) and the CE-corrected  $\epsilon_{\text{org}}$ . We now use the Zdanovskii-Stokes-Robinson (ZSR) mixing rules to estimate a *GF*(85%) value for the organic matter component of the SSA particles specifically. The fitting procedure is described on Page 16 Lines 12-20 in the updated manuscript.

There has also been an evolution in our understanding of the ATOFMS clusters determined for nascent sea spray since the manuscript was originally submitted. A portion of the non-sea salt (sodium-depleted) clusters can be explained by the incomplete ionization of sea salt particles (Sultana et al., In Prep.). This change in our understanding of ATOFMS cluster types further supports our decision to use the CE-corrected  $\epsilon_{\text{org}}$  from the AMS in place of ATOFMS cluster types to understand the dependence of the *GF*(85%) on variations in particle composition. A brief discussion of this new understanding regarding the ATOFMS clusters for nascent sea spray has been added to the manuscript in the methods section.

“It is important to note, however, that dried SSA particles sampled by the ATOFMS can be spatially chemically heterogeneous, with shells depleted in Na and rich in Mg, K, and Ca (Ault et al., 2013). Thus, some fraction of the particles identified as having Mg or SSOC type spectra may be partially explained by the incomplete ionization of sea salt particles (Sultana et al., In Prep.). However, variations in the thickness of this Na-depleted shell likely reflect variations in the total particle organic content. Therefore, increases in the fraction of SSOC or Mg type mass spectra generated suggest a net increase in SSA particle organic content.”

We made other changes, where deemed appropriate and added additional figures and tables as supplemental materials. Our point-to-point response to both reviewers follows below.

**Key: Black = Reviewer, Blue = Response**

## **Response to Reviewer #2**

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 forcing impacts.

Reductions in hygroscopicity have indeed been linked to SSA particle composition changes during phytoplankton blooms in the ocean during field studies, but (to our knowledge) this is the first time this has been quantified for particles produced during a phytoplankton bloom that is completely isolated from anthropogenic influence or background particles. Thus, we believe that this work does provide a new contribution to the literature, as noted on Page 3, Lines 19-20.

The goal of this study was not to understand the size dependence of SSA particle composition, but rather to link composition to optically weighted hygroscopic growth factors for submicron particles. A figure showing the observed  $f(RH)$  relative to the  $f(RH)$  of pure sea salt for duration of both microcosm experiments has been added to supplementary material as a complement to the radiative impacts discussion in Section 4.

Finally, regarding a broader assessment of the radiative forcing impacts, although we agree with the reviewer that this would be an interesting extension, it would clearly require doing something like implementing a new scheme in a climate model and running that climate model, which is far outside the scope of this work.

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).

We have now added extensive discussion associated with Vaishya et al. in the “Implications and Conclusions” section. Specifically, we now write:

“This was previously suggested by the ambient measurements of Vaishya et al. (2013), who observed substantial differences in  $GF(90\%)$  and  $f(RH)$  values for submicron particles having very different  $\epsilon_{org}$  fractions in what were identified as clean marine air masses. (Their  $GF(90\%)$  values were measured using a hygroscopic tandem DMA (HT-DMA) for size-selected particles with  $35 \text{ nm} \leq d_{p,m} \leq 165 \text{ nm}$ . Their  $f(RH)$  values were measured for  $PM_{1.0}$ .) They observed that increases in  $\epsilon_{org}$  had no effect on the  $GF(90\%)$  until a threshold  $\epsilon_{org}$  was reached, specifically  $\epsilon_{org} > \sim 55\%$ . Below this value, they measured  $GF(90\%)$  value of  $\sim 2.3$ , which is the expected value for pure sea salt at  $RH = 90\%$ . Above this value, the observed a

rapid fall off in  $GF(90\%)$  to a plateau at 1.22. This reported behavior differs from that observed for nascent SSA particles sampled in the current study. Here, substantial depressions in  $GF(85\%)$  (and  $f(RH)$ ) relative to inorganic sea salt were observed when the  $\epsilon_{org}$  was only  $\sim 25\%$ , and a co-variation between  $GF(85\%)$  and  $\epsilon_{org}$  (and the ATOFMS SS spectral-type fraction) was observed. One plausible reason for this difference is that nascent (freshly-emitted) SSA particles are measured here whereas *Vaishya et al. (2013)* measured ambient particles that could be subject to photochemical processing. Secondary organic aerosol formed from gases, such as monoterpenes and isoprene, emitted from the ocean (*Shaw et al., 2010*) could have contributed to the NR-OM, although *Vaishya et al. (2013)* argue that this influence was negligible based on the literature. Emission rates of such species from the ocean and their relationship with oceanic processes are not well established. Although *Vaishya et al. (2013)* attempted to remove the influence of secondary organics in their analysis (as well as the influence of non-sea salt sulfate), it is possible that their analysis was complicated by the impacts of atmospheric processing. Another key difference is that relationship between the  $GF(85\%)$  values and  $\epsilon_{org}$  observed in the current study is consistent with ZSR behavior, while *Vaishya et al.* reported “bistable” behavior of the  $GF(90\%)$  values as a function  $\epsilon_{org}$  (i.e. the flat behavior at  $\epsilon_{org} < 55\%$  and the steep fall off above). The physical basis of this bistable behavior, and the functional form implied by their measurements, is not easily explained. Finally, the  $GF(90\%)$  measurements by *Vaishya et al.* were made for particles with  $d_{p,m} < 165$  nm, while the composition was characterized with an HR-AMS. It is possible that size mismatch between these measurements influenced their analysis. Mass-weighted size distributions were not shown by *Vaishya et al. (2013)*, however *Frossard et al.* show mass-weighted size distributions for ambient particles sampled in the remote marine boundary layer that suggest that much of the organic mass is contained in particles  $> 165$  nm. Our results clearly indicate that compositional changes to nascent SSA particles, driven by variation in physical and biochemical processes in seawater, can impact the influence of water uptake on scattering by submicron SSA even when  $\epsilon_{org} < 55\%$ . The comparison with the *Vaishya et al. (2013)* measurements suggests that this initial state can be further modified through atmospheric processing.”

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.

As discussed in detail at the beginning of this document, we believe that the reviewer’s suggestion of better utilizing AMS data improves understanding of the observed  $GF(85\%)$  values. Despite the uncertainties in quantifying organic matter in sea spray aerosol (SSA) particles by the AMS, we estimated organic matter volume fractions ( $\epsilon_{org}$ ) for the particles

sampled during this study. The range of  $\epsilon_{\text{org}}$  was 0.25 to 0.50, which is consistent with the observed depressions in growth factors relative to inorganic sea salt.

Frossard et al. (2014) was provided as a reference for the refractory nature of sea salt in the original manuscript (Page 15 Lines 1).

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.

It is true that the ATOFMS results are semi-quantitative. However, trends in the data are still informative and are indicative of changes in the chemistry of the particles. Therefore, increases in the number of SSOC type spectra are indicative of chemical changes in the particle population, specifically higher organic content. Though we cannot say quantitatively the degree of organic enrichment, we can say that it occurred. Also, not all organic matter would necessarily increase the ATOFMS sensitivity. If it was very lipid rich (with lots of hydrocarbon character) the sensitivity may have even decreased.

While the number-weighted distribution peaked at 100 nm, the CRD optically weighted GFs are most sensitive to particles with  $d_{p,m}$  between 400 nm to 800 nm (see Page 11 Lines 13-14 and Figure 2). The ATOFMS counts are maximum at a vacuum aerodynamic diameter of 1.5  $\mu\text{m}$  (Figure S3), corresponding to a mobility diameter ( $d_{p,m}$ ) of 830 nm, which is a little above this range. However, since the ATOFMS is no longer used quantitatively, it is no longer necessary to adjust ATOFMS cluster fractions to smaller sizes ( $d_{va} = 0.75 \mu\text{m}$ ) as was done in the original manuscript

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.

The reviewer raises an important question about the comparability of the measurements between instruments due to differences in sampling. During these experiments, flow was not split isokinetically. The particle-laden air from the MART was sampled into a manifold. The individual instruments sampled from this manifold from one of a many “ports”. The flow rate to each instrument (or group of instruments), and thus the flow from each port, varied. For example, for Group 1 the CRD + SEMS sampled a much higher flow rate (3 LPM) than the AMS and ATOFMS (~ 0.7 to 1 LPM) from the manifold. Therefore, it is possible that the instruments sampled particle populations with different sizes. It is difficult to estimate differential losses between the different ports due to flow rate differences in this configuration.

The equations describing aspiration efficiency for isoaxial sampling from an air stream typically have a form similar to:

$$\eta_{asp} = 1 + \left[ \frac{U_0}{U} - 1 \right] [other\ terms]$$

where  $\eta_{asp}$  is the aspiration efficiency,  $U_0$  is the ambient gas stream velocity and  $U$  is the sampling velocity (Kulkarni, Baron and Willeke, 2011). The last term in brackets (“other terms”) depends on particle diameter and velocity, but we will not worry about this at this time. For the manifold system here, the effective ambient gas stream velocity is very low, and will be much lower than the sampling velocity to each individual port (due in large part to the substantial difference in size between the manifold and the sampling ports. In the limit of  $U_0 \rightarrow 0$  (or more specifically,  $U_0 \ll U$ ), we can see that  $\eta_{asp} \rightarrow 1$ . Thus, it seems reasonable to think that the particle population will not be strongly influenced by the non-isokinetic sampling conditions here and the lack of explicit isokinetic sampling did not have a substantial impact on the measurements here.

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

Even though the peak was 10 $\mu$ g/l, a concentration of 12  $\mu$ g/l is consistent with MART bloom studies described in Lee et al. (2015). This line has been revised to read “Further sampling was delayed until Chlorophyll-a (Chl-a) concentrations exceeded *approximately* 12  $\mu$ g L<sup>-1</sup>”

Line 17. Was this MART reproducibility issue or else? 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?

The reason for the greater contribution of larger particles in the pre-nutrient size distribution is unknown. It may have been due to differences in water level (water was collected for offline sampling once per day) or sampling tube length.

Bacterial growth in the bulk water was indeed monitored over the course of the 2 week (not 3 week) duration of each individual MART experiment. The time-series of bacterial concentrations was shown in the original manuscript in Figure S6 and was observed to peak after the chlorophyll peak. The method for this measurement has been added to Table 1. The impact of bacteria in the source water on the chemical nature and fraction of organic matter in nascent SSA particles has been discussed in more detail in Wang et al. (2015).

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.

As stated in the original manuscript Page 6 Line 13, particles were dried (RH < 20%) prior to sizing. For all instruments mentioned, we stated that they measured “dried” particles.

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?

The PM2.5 cyclone was located prior to the drier and thus operated in “wet” conditions. The RH at the point of the cyclone was around 70%, although this was not constantly monitored. The equivalent size cut for the dried particles was therefore smaller (as suggested by the reviewer), we estimate by  $\sim 1.5\times$  (based on our derived GF values). A figure showing the cavity ring-down and SEMS sampling configuration following the manifold has been added to supplementary material (Figure S1). The RH for cyclone sampling has also been added to the manuscript (Page 8 Line 29 and Page 9 Lines 1-4).

Page 8, Line 3. Following the paragraph above referring to minimal contribution of  $>2.5\mu\text{m}$  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.

In the original manuscript, the ATOFMS size-dependent counts were shown in Figure S2. As stated in the manuscript (Page 8 Line 17-18) and indicated by this figure, the peak in the particle counts for the ATOFMS is at  $1.5\mu\text{m}$  vacuum aerodynamic diameter ( $d_{va}$ ). The particle counts fall off rapidly below  $d_{va} = 0.5\mu\text{m}$ . As discussed in the manuscript, to relate the ATOFMS measurements to the optical property and hygroscopicity measurements requires converting the vacuum aerodynamic diameters into mobility-equivalent diameters ( $d_m$ ). A value of  $d_{va} 1.5\mu\text{m}$  corresponds to a mobility-equivalent diameter of 830 nm. This value of  $d_m$  is in the upper end of the size range of the particles that most contributed to the observed scattering. However, since we no longer use ATOFMS data in a quantitative way and mainly use this data for understanding temporal changes, it is no longer necessary to adjust the ATOFMS fractions to a more relevant size.

Page 9, Line 2. Is it referred to dry or 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  $d(\text{dry})$ ,  $d(\text{wet})$  were appropriate. If AMS sampled wet particles that would explain the missing mass discussed few lines below.

As stated on Page 8 Line 18 in the original manuscript, the AMS sampled dried particles. In fact, all of the instruments used in this study ultimately sampled dried particles. Thus, instead of adopting the notation suggested above throughout the manuscript (since wet particle diameters are only discussed in the Instrumentation section), clarification has been added to specify whether particles were dried prior to sampling for each instrument in Table 1.

Also, we should correct the misconception that the RH in the MART and sampling lines was necessarily 90-100%. The RH in the MART is dictated by the balance between the evaporation rate of water and the flow rate and RH of the sampling airstream. The RH in our sampling lines was, in fact, closer to 70% RH and not 90-100%.

Line 8. AMS is typically calibrated with dry  $\text{NH}_4\text{NO}_3$  particles. Why would SS particles bounce more than the calibration particles as AMS chemical species mass is calculated on nitrate equivalent basis?

Particle bounce is not significant for ammonium nitrate because it primarily exists in the liquid phase and thus has a high collection efficiency (CE) of  $\sim 100\%$ . On the other hand, solid particles have lower CE values due to particle bounce. Issues of collection bounce for different materials and as a function of phase have been previously addressed by [Matthews et al. 2008]. Sea salt specifically has a CE of 0.25, although may vary by instrument and can depend on the extent of drying (Ovadnevaite et al., 2012).

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.

The reported GF values here are defined as “optically weighted” to indicate just what the reviewer implies, namely that they are an average over different sizes but weighted by the scattering. To further clarify, in the abstract on Page 1 Line 22, “bulk average” has been changed to “optically-weighted average.” We have also added text to Section 2.2.1 where the  $f(\text{RH})$  to GF inversion procedure was discussed to make this issue clearer. We now state:

“Unlike  $f(\text{RH})$ ,  $GF$  values are independent of the dry particle size (above about 100 nm diameter) for particles of a given composition. Thus, variations in the optically-weighted  $GF$  values are driven only by variations in particle composition, specifically variations in the average composition of particles in the size range over which the optical measurements are most sensitive. For the measurements here, the sensitive size range is between about 400 nm and 800 nm with particles below 200 nm contributing almost zero to the observed scattering (see Section 3.1 below). SSA particle composition can vary with size (e.g. O’Dowd et al., 2004), and thus the  $GF$  itself may vary with size. The optically-weighted  $GF$  averages across such size-dependent variations in composition to focus on the chemical changes that most influence water uptake by the particles that most contribute to light scattering.”

Line 28. The discrepancy can be partly due to shallow cut-off function of PM2.5 cyclone. 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.

We have now clarified the experimental configuration and the drying aspects within the manuscript. In very general terms, all instruments used in this study ultimately sampled dried particles. However, the particles that passed through the cyclone were not dried, but at an RH  $\sim$



70%; they were subsequently dried prior to sampling. Below is a figure showing the general sampling configuration, and has been added to the supplementary material (Figure S1).

Although the reviewer is correct to note that losses increase with size, it is important to realize that the effect of water uptake on particle losses is not straightforward. Water is typically less dense ( $1 \text{ g cm}^{-3}$ ) than many other common atmospheric materials. Thus, if water uptake leads to a decrease in density then this can offset, at least to some extent, the increase in size in terms of sedimentation losses. Consider an example. If a 1 micron particle has a density of  $2.0 \text{ g cm}^{-3}$  (e.g. sea salt) and doubles in size due to water uptake (e.g.  $\text{GF} = 2.0$ ) then the density of the particle will decrease to  $1.22 \text{ g cm}^{-3}$ . The percent loss of a 1 micron particle with density =  $2.0 \text{ g cm}^{-3}$  due to sedimentation in a 10 m long tube at a flow rate of 5 lpm is 9.3%. If the particle size were doubled without changing the density, the loss would increase to 32%. But, if the decrease in density is accounted for the loss only increases to 13%. Thus, the decrease in density offsets a very large fraction of the increase in size. (The above calculations were performed using the Particle Loss Calculator of Von der Weiden et al. (2009).) Now, of course, if the density of the material were closer to water (such as may be the case for organics) this offsetting effect would be smaller. But our premise is that the organic material is relatively non-hygroscopic, and thus the water uptake itself (and associated increase in size) would be smaller, negating the effect in the first place. Consequently, while it is possible that differences in the influence of sedimentation between instruments due to differences in drying, the magnitude of the difference is much smaller than one might intuit based on the size change alone. As such, while it may be possible that the optical closure may have been impacted by differential sedimentation of wet and dry particles such and impact is limited in scope. Finally, we note that the driers used to dry particles sampled into the CRD-PAS and SEMs were oriented vertically (to minimize sedimentation losses).

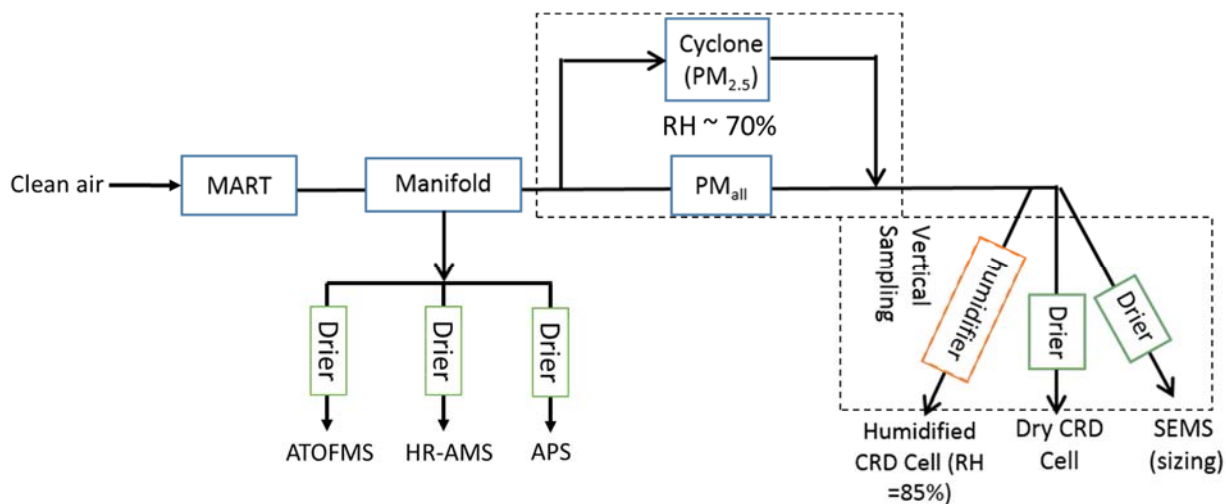


Figure S1. A detailed schematic of the general sampling scheme for the online instruments. Note that not all instruments sampled at the same time (see Table 1). Particles sampled from the MART passed through a manifold from which they were subsampled to the various instrumentation. All instruments included an upstream drier and sampled dried particles. The driers and humidifiers for the CRD and SEMs sampling group (Group 1) were oriented

vertically. The particles sampled to the CRD and SEMS alternately passed through a PM<sub>2.5</sub> cyclone. The RH at this point was ~70%.

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

The reviewer is correct that the sizing errors of different instruments can be objectively up to 10%. In our case, we characterized the sizing accuracy of the SEMS using size-selected PSLs and found that the particle sizes were characterized to within 1% of the stated PSL size (see Page 12 Lines 7-12 in the original manuscript). Thus, it seems unlikely that large instrumental sizing errors are the primary reason for differences between the observed and calculated dry particle scattering. However, we have added a reference to the Wiedensohler paper to the discussion on Page 12 as motivation for considering the possibility of sizing errors. “Wiedensohler et al. (2012) reported that sizing errors between instruments can be 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.

A GF(85%) of 2.2 was originally used as a value for sea salt and not NaCl. However, a value of 2.1 is a better estimate for sea salt (Ming and Russell, 2001) at 85% relative humidity and the manuscript has been updated using this value for sea salt.

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?

The reviewer raises a good point about differential sensitivity of the ATOFMS. However, here we are confident that the higher relative abundance of Fe-rich particles at the beginning of the experiments is due to the addition of iron rich nutrients to encourage phytoplankton growth. As the reviewer notes, the ATOFMS is very sensitive to iron compared to species such as sodium chloride making exact quantification difficult. However, we emphasize that the *trends* in the particle spectra and the particle type abundances are reflective of changes in the particle composition. During many other "microcosm" experiments using the same methodology, an initial spike in iron signal after nutrient addition was observed, which then declines as the bloom progresses and nutrients are likely taken up into the proliferating microbiology. Finally, we note that while differences in sensitivity between particle types would certainly give rise to errors in particle type quantification (relative abundance) at a given point in time, it should not give rise to time-dependent changes in the relative abundance.

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.

The reviewer again raises a good point about particle size and comparability. Here, we reemphasize that we have measured optically-weighted growth factors and, for the size distributions from the MART, particles with  $d_{p,m} \leq 100$  nm contributed very little to overall scattering measured by the CRD. As stated on Page 11 Lines 16-20 in the original manuscript, the optically-weighted GF measurements were most sensitive to  $d_{p,m}$  (mobility diameters)

between 400 to 800 nm, with median scattering occurring at  $d_{p,m} = 530$  nm. As such, we compared the optically-weighted GF values to the ATOFMS composition for particle having  $d_{va} \sim 0.75$   $\mu\text{m}$ , which corresponds to a  $d_{p,m} = 420$  nm.

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.

While it is true that many types of marine organic matter have  $\text{GF} > 1$ , we assume a  $\text{GF} = 1$  as a lower bound. Although a lower bound, this assumption is consistent with GFs for fatty acids often found in marine aerosols (e.g. Cochrane et al., 2016). That said, we have revised the sentence to read (added text in italics): “The line connecting  $\text{GF}_{\text{SS}}(85\%) = 2.2$  and  $\text{GF}_{\text{non-SS}}(85\%) = 1.0$  provides the minimum value (*lower bound*) expected for any combination of SS and non-SS particles.”

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?

As noted above, we are now using  $\epsilon_{\text{org}}$  instead of the fraction of ATOFMS non-SS particles to examine the relationship between particle hygroscopicity,  $\text{GF}(85\%)$ , and composition. Therefore, we now estimate GF values for the organic fraction of the sampled PM specifically, i.e. the  $\text{GF}(85\%)$  values after extrapolation of our fits to  $\epsilon_{\text{org}} = 1$ . We find values of  $\text{GF}_{\text{org}}(85\%) = 1.16$  and 1.23 for the two MART experiments, which are optically weighted averages. One can assume that the GF is constant with size or that it varies with size, perhaps with an inverse relationship between GF and size, since OM fraction typically increases with decreasing size, within the optically-weighted size range. As discussed in detail in response to Reviewer #1, it is fully possible to assume some relationship between particle size and GF to come up with an optically-weighted average value. To clarify, we have added the following sentence: “This value for  $\text{GF}_{\text{org}}$  can be interpreted as an optically-weighted average for the OM component of the SSA particles sampled here.”

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.

We do not dispute that the GF may be size dependent (O'Dowd et al., 2004; Prather et al., 2013). However, we emphasize again that we have measured the *optically-weighted average GF*. Thus, the measured optically-weighted GF is directly relevant to the actual impact of composition variations on SSA particle light scattering. Put another way, composition changes of e.g. 50 nm particles are almost completely irrelevant to the magnitude of light scattering by SSA particles and the direct effect (although critical to understanding the impact of SSA particles on clouds via their ability to act as CCN). It is instead variations in the average composition within the

optically-relevant range, which is around 400-800 nm in this study given the size distribution, that is most important to consider when considering the total scattering. Had we instead measured size-dependent GF values explicitly, this would have provided, perhaps, greater process-level information. However, without considering which particles in the size distribution do most of the scattering, such process-level information is limited in nature. Since the MART system generates particle size distributions that are very similar to those generated from real wave breaking (Prather et al., 2012; Stokes et al., 2014), our optically-weighted measurements are of direct relevance to understanding the impact that compositional variations have on overall light scattering. As noted above, we have revised Section 2.2.1 to more clearly address this issue of size-dependent 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.

The reviewer raises an important question about comparability between the derived organic volume fractions and the AMS measurements. As stated at the beginning of our responses, we estimated  $\epsilon_{\text{org}}$  values from the AMS measurements instead of deriving organic volume fractions from our *GF* values. The estimated GFs for the organic component are above 1 indicating that our estimates for  $\epsilon_{\text{org}}$  are reasonable.

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.

In the manuscript, we attribute the larger Chl-a concentrations to larger photosynthetically active radiation. However, temperature and nutrients could have also played a role. The temperature of the water in the MART was  $\sim 26^{\circ}\text{C}$ , which is larger than the 20 to  $23^{\circ}\text{C}$  measured for seawater at the Scripps pier (Table 2).

Page 19, Line 3. Consider different size ranges sampled if AMS was not dried. Table 1. AMS size range is missing.

As stated above, particles sampled by the AMS were dried. The size range is now included in Table 1.

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