Please find our responses to the reviewers' comments below. The complete original text of the reviews is below in regular text, and our responses are in italics.

We thank the reviewers for their thorough and clear comments and suggestions. They have helped improve the manuscript and we hope our revisions will satisfy their concerns.

Reviewer #1

Interactive comment on "Composition of 15–80nm particles in marine air" by M. J. Lawler et al.

Anonymous Referee #1
Received and published: 24 March 2014

General comments

This paper presents aerosol chemical composition at Mace Head, Ireland inferred by hygroscopic tandem differential mobility analysis (HTDMA) and measured by a thermal desorption chemical ion mass spectrometer (TDCIMS) during the second half of May, 2011. The primary observation is the sudden occurrence of particles 10-60 nm in diameter. These events are dominated by sulphate, as measured by the TDCIMS and inferred by the HTDMA. The authors attribute these events to particle nucleation over open oceans from biogenic sources. They also measured detectable chloride ion levels throughout the study for particles < 80 nm, demonstrating that sea-salt can be present in even the smallest particles.

These are perhaps the first in-situ measurements of the composition of marine aerosol < 80 nm in diameter and represent an exciting new addition to our under-C683 standing of aerosol in these environments. While these measurements alone would merit publication in this journal, the discussion section should be expanded and the results interpreted at greater depth. Much of this manuscript is devoted to describing the observations without much accompanying analysis. The language could use more polish and was imprecise in the authors' discussion of events. Five types of events are presented, however, the text often refers to "an event" without specifying the type. This made it difficult to follow some of the arguments.

After the first discussion of event types, all the events referred to are the nanoparticle enhancement events, either <50 nm or 50 types. We now clearly state that these are the two types of nanoparticle enhancement events, and we no longer write simply "event."

Overall, I recommend that this manuscript be published if the comments below are adequately addressed.

Specific comments

Page 2089, line 8
It is important to note that particle growth can only occur if these compounds do not fragment and revolatilise.

Added: "net" before "condensation of low volatility vapors and/or multiphase reactive uptake" to indicate the possibility of revolatilization.

Page 2091, line 15-17
The text states that the SMPS is comprised of a long DMA with a model 3010 CPC. According to the manual from the manufacturer, this combination of instruments only measures particles with diameters larger than 10 nm. However, the size distributions shown in Figure 1 panel b show measurements for particles as small as 4 nm. Was there a second instrument used? If so, the details should be included here.

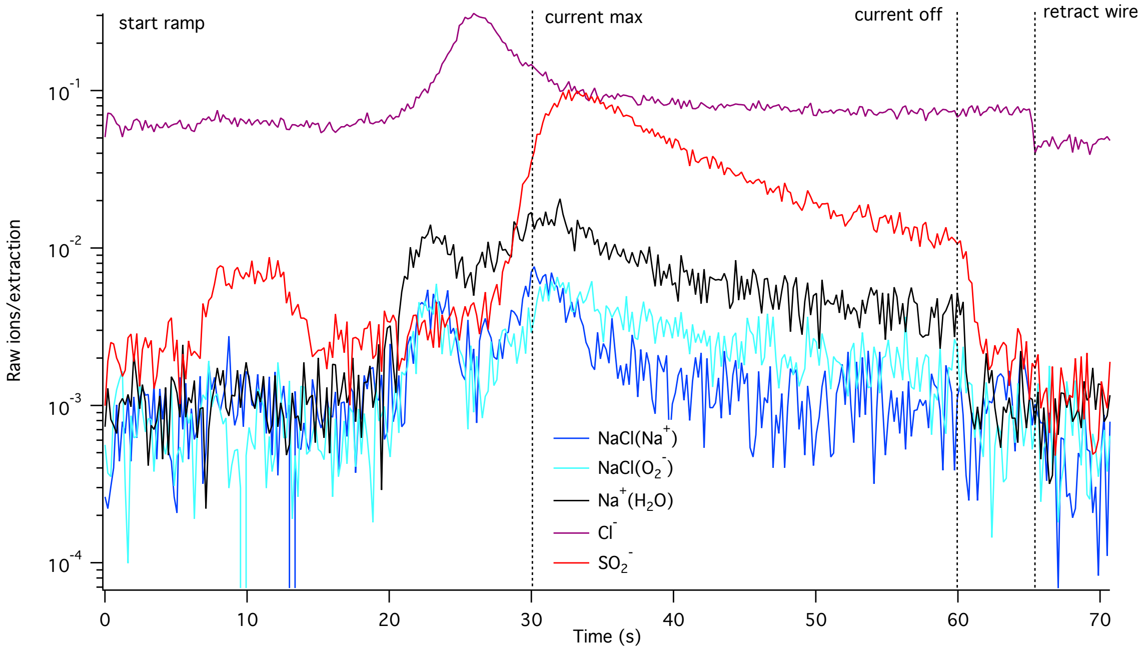
This was an oversight. We used a pair of SMPS systems to characterize this size range. The smaller particles were measured using a TSI nanoDMA and ultrafine CPC, and we include this information now.

Page 2092, line 7
Can the authors elaborate on how they are able to measure sodium chloride from sea salt when its melting point is 800_C but the wire is only heated to 600_C?

The very small NaCl particles collected are volatilized by the TDCIMS approach. It is not necessary to reach the melting point to achieve significant volatilization, even for bulk NaCl, but for very small particles it is even easier. NaCl aerosol can be generated by heating of solid NaCl in a furnace at temperatures below 600 C (Hämeri et al. 2001, Biskos et al. 2007, Scheibel and Porstendörfer 1983), and the melting point for NaCl is reduced substantially as the number of bonded salt molecules becomes very small (~30 units, or ion pairs) and as impurities are introduced (Breaux et al. 2004). An ambient 30 nm particle made up mostly of NaCl could have on the order of 100 ion pairs and likely contains ionic impurities.

We have performed calibrations with a variety of salts recently using a more recent version of the instrument with improved ion transmission. The relative sensitivities are probably different compared with the Mace Head measurements, but the desorption behavior of the wire is the same. The TDCIMS is able to detect NaCl with a sensitivity comparable to or even greater than that of ammonium sulfate, and we have added this statement in the instrument description. We tested a 1 microliter droplet of 1 mg/L each (1 ng each) NaCl, KI, ammonium sulfate, and ammonium nitrate on the desorption wire. We found that ammonium nitrate, then ammonium sulfate, then potassium iodide, then sodium chloride peaks are observed, as the wire becomes hotter. A subsequent blank (millipure 1 microliter droplet) showed less than 10% of the standard signal, indicating that the majority of the salt was removed after the desorption cycle.

As evidence that the TDCIMS efficiently volatilizes NaCl, we will include a sample thermogram (as below) from the field measurements in the Supplemental Material. The desorption thermogram shows an increase in the observed salt ions (Na+(H2O), Cl-, NaCl(Na+), and others) as the temperature increases, followed by a decrease to near-baseline levels. If NaCl were removed only slowly and inefficiently from the wire, there would not be such a clear desorption peak. It I also possible that Cl- and Na+ ions *can be generated from the volatilization of other species such as HCl and NaOH, which are much more volatile and may be present as the collected mass is removed during the desorption. However, the timing of the NaCl(Na+) peak matches the other positive Na+ peaks, and this peak clearly derives from volatilized NaCl based on its composition. If sea salt continually accumulated on the wire without being fully desorbed, the background signal for NaCl-derived ions would gradually increase during the study, and this was not observed.*



A single sample desorption from May 25, 2011 for unit mass resolution peaks. The main species associated with each nominal mass are indicated. Times when current was applied to the wire are indicated.

We added this statement in the instrumental section:

"The ions observed result from different heating and volatilization processes for different compounds. Ammonium sulfate thermally decomposes before it desorbs appreciably, while many organic compounds can desorb as whole molecules. Solid sodium chloride has a higher melting point than the maximum wire temperature, but Na+ and Cl- were nonetheless detectable in this study. This was probably due primarily to the very small amount of mass collected. Significant amounts of bulk NaCl can be volatilized at temperatures below the melting point (Hämeri et al. 2001), and there is a decrease in melting point for very small (non-bulk) crystals (Breaux et al. 2004). Some of the signals also may derive from the desorption of less volatile species like NaOH and HCl."

Page 2091, line 11 and Page 2097 lines 9-13

The terminology throughout the paper is unclear. On page 2091, "nanoparticle enhancement events" are described, but on page 2097, four other types of events are described. Do the "nanoparticle enhancement events" include the sub-50 nm and 50 nm events in the latter cateogrisation? Subsequent paragraphs refer simply to "the events" which is ambiguous. Please clarify this throughout the manuscript.

Yes, the 50 nm and < 50 nm events are now clearly described as nanoparticle enhancement events. As noted above, we will refer to the events by their full description throughout.

Page 2096, lines 14-15
Please be more quantitative. How many of these events occurred during the two weeks of sampling? Of these, how many were associated with polar marine air? Including a sample trajecotry for these periods would also be helpful.

It's difficult to number them because some boundaries appear to just be temporary breaks in the same event during a day. We added an example trajectory figure and this statement:

"The strongest, most consistent period of enhancement events occurred from May 22 - 25, when air masses reaching the site traveled in the marine boundary layer on a trajectory that passed between Greenland and Iceland. The other major nanoparticle enhancement period was during May 18-19 and was characterized by air masses originating from a more westerly direction, closer to Greenland About 25% of the sample period from May 14-31 was characterized by these events."

Page 2097, line 1
From Figure 1, it would appear that no HTDMA data were collected during the background aerosol event. However, data are shown in Figure 3. It would be helpful if data from the entire two weeks of sampling were shown in Figure 1 and then averages for specific periods shown in separate figures (see below).

The graphs in the multiplot become difficult to compare when the whole time series is present. We expanded it by a couple days to include the background period with HTDMA data.

Page 2097, lines 8-10
It would be helpful to include average SMPS distributions for the four periods, similar to Figure 3.

We added an average SMPS figure with the four periods as suggested.

Page 2098, line 23
Can the authors be more quantitative? What does the scatterplot look like? What is the r2?

We added scatterplot figures for Cl/Na and sulfate/Na and r2 values for all discussed correlations.

Page 2099, lines 10-15

Figures showing the average ion signal fraction (both negative and positive), as well as chloride to sulphate ratio for each of the periods would be helpful. That way they can be objectively compared instead of trying to estimate their differences based on the time series.

We now state the average sulfate to chloride ratios for the different periods, and we have added sulfate to sodium ratios. We find that the new, slightly lengthened time series plot conveys the ion ratios in the different periods well and that an average figure would be redundant.

Page 2099, lines 12-14
Based on the discussion on page 2097, it would make sense that these sulphate-rich particles were smaller than 51 nm and therefore not detected by the HTDMA.

That's right. We added a statement to this effect.

Page 2099, line 14
Providing a study-long chloride to sulphate ratio and comparing it to the two periods that are specified would be more quantitative.

We have added mean and standard error chloride to sulfate ratios for the nanoparticle enhancement events and the sea spray period.

Page 2099, lines 19-23
Are the relative sensitivity of the instrument to chloride and sulphate expected to vary throughout the study? A calibration in the laboratory using an artificial sea water solution should be able to determine the actual sensitivity, so that the authors can be more specific than "slightly higher", as stated on line 21. This way the non-sea salt sulphate contribution can be better understood.

Under consistent operating conditions, the relative sensitivities are not expected to vary much over time. The mass spectrum and reagent ion signals do not change much, and the sampled signals are also ratioed to the reagent signals to reduce effects of nay changes. However, there was a power outage and subsequent change in ion source temperature on May 21 which probably resulted in sensitivity changes. Therefore in the revised manuscript we do not quantify the chloride/sulfate or sulfate/sodium signal ratios prior to that time.

Unfortunately we do not have further calibration data for this version of the instrument, though we have performed additional salt calibrations with an updated version of the instrument as described above. To demonstrate the non-sea-salt sulfate contribution, we now include a figure and text comparing the relationship of sodium to chloride (r2 ~= 0.6) and the relationship of sodium to sulfate (r2~=0.2). Most of the variability in sulfate is not related to sea spray. We also include a plot of sulfate to sodium ratios for the various periods. This ratio reaches some of its lowest levels during the sea salt period (~10) while it is higher and variable during the nanoparticle enhancement events, up to about 35 during these periods. The low values are an upper bound for the sulfate/sodium signal ratio that would be found in fresh sea spray, and values above this demonstrate the presence of non-sea-salt sulfate.

Page 2100, line 23
The plots in Figure 4 and the associated r2 show the explanatory power of collected mass on the selected ions, not the other way around, as implied by this sentence.

The r2 is the same whichever variable is treated as explanatory. We have replaced these figures with correlations with particle number instead of mass. Our reasoning is found below in the response to reviewer 2.

Page 2100, line 24
Which events are referenced here? The sea salt events? The sub-50 nm events? Or the 50 nm events?

The rest of the paper besides the introduction refers to the nanoparticle enhancement events, which applies to the <50 nm and the 50 nm events. We now write this out in all cases.

Page 2101, line 5
The discussion section should be its own section and should be expanded. For example, the results in the last paragraph of section 3.2 could be moved here and the C686 measurements from the TDCIMS incorporated in the discussion. Putting these results in context to past measurements would also be helpful.

We reorganized this as suggested by the reviewer with respect to an independent Discussion section and moving some of the 3.2 discussion there. The HTDMA-TDCIMS comparison is now discussed in more detail here, and the implications of the findings are discussed in more detail.

Page 2101, line 7
Can the authors rule out the possibility that the aerosol were primary organic particles that are coated by sulphate, as suggested by Leck and Bigg (2005)? It would appear that the TDCIMS is not necessarily sensitive to these primary organics. They could also contribute to the reduced growth factor observed in the HTDMA.

Such a source for the nanoparticle enhancement event particles is not likely for the same arguments given that primary sea salt aerosol is not likely. Namely, there is little reason to expect a bubble bursting aerosol source with such a narrow range of (small) diameters for the emitted particles. This suggestion implies that there is a population of many 100s per cc of sub-4 nm primary particles which are then activated when there is sufficient sulfuric acid to condense and grow them. Given our current understanding, we find the homogeneous nucleation of gas phase precursors to be a more likely explanation. We now refer to Leck and Bigg on this point.

Page 2102, line 3
Please quantify “essentially always”. Was it 50% of all measurement times? 90%? And please be specific about the particle size fraction. According to the HTDMA data for 51 nm particles, the 50 nm event did not contain any sea salt.

Added “>95% of the time”. The 50 nm averaged HTDMA data show a greatly reduced but nonzero sea salt component (Fig. 3).

Page 2102, line 9
It seems like a big leap to extrapolate the observations from these two weeks in May.
Some qualifications should be included and the language relaxed.

We wrote instead that the frequency of events suggests that "these events were a significant source of nanoparticles over the measurement period. If these events are indeed similar to the events described in O'Dowd et al. 2010, they may be important for much of the spring and summer in the Atlantic."

Technical corrections

We accept all these corrections directly, or modified as described below:

Page 2091, line 15
Change to "a Scanning Mobility".
Page 2095, line 14
Change to "measurements are given".
Page 2097, line 1
Why is Figure 3 mentioned before Figure 2? The figure order should be updated.
Page 2098, line 17
C687
The sentece could be improved by rewording it to "the volume and mass increase as the particle diameter cubed".

Removed this sentence.

Page 2100, line 18
Change the wording to "Sulphate signal . . . was best explained by collected mass".
Removed this sentence and the plot due to an updated analysis.
Page 2100, line 18
The r2 in the figure is 0.37 but is 0.36 in the text.
The figure and text have been replaced.
Page 2100, lines 19-21
Reword this sentence so that it is clearer. Something along the lines of "This can be explained by the fact that the mass collected was highest during the nanoparticle enhancement events, which generally contained significant fractions of sulphate."

As above, this sentence has been removed.

Page 2100, line 23
Add "(not shown)" after 0.08.
Removed.
Page 2101, line 9 and 17
Change idea to "hypothesis".
Reworded.
Page 2101, line 16
Change operate to "occur".

Figure 1
This figure is referenced throughout the text. However, the numerous panels can be difficult to locate and it would help if the panel letter could be included every time it is discussed. That way the reader can easily determine the relevant part of the referenced figure.

References

Leck, C. and Bigg, E.K.: Source and evolution of the marine aerosol–A new perspective, J. Geophys. Res., 19(32), 28–31, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 2087, 2014.

References for Response to Reviewer 1:

Biskos, G., Malinowski, a., Russell, L. M., Buseck, P. R., & Martin, S. T. (2006). Nanosize Effect on the Deliquescence and the Efflorescence of Sodium Chloride Particles. Aerosol Science and Technology, 40(2), 97–106. doi:10.1080/02786820500484396

Breaux, G. A, Benirschke, R. C., & Jarrold, M. F. (2004). Melting, freezing, sublimation, and phase coexistence in sodium chloride nanocrystals. The Journal of Chemical Physics, 121(13), 6502–7. doi:10.1063/1.1786921

Hämeri, K., Laaksonen, A., Vgkevg, M., & Suni, T. (2001). Hygroscopic growth of ultrafine sodium chloride particles, Journal of Geophysical Research, 106(D18), 20749–20757.

Scheibel, H., & Porstendörfer, J. (1983). Generation of monodisperse Ag- and NaCl-aerosols with particle diameters between 2 and 300 nm. Journal of Aerosol Science, 14(2), 113–126.

Reviewer 2

Review of "Composition of 15-80 nm particles in marine air"

This paper discusses a combined TDCIMS and HTDMA approach to understanding aerosol composition and hygroscopicity for marine aerosol in the relatively pristine environment of Mace Head, Ireland. The TDCIMS data in the ~50 nm size range has the potential to be a very useful addition to the understanding of sea spray aerosol < 100 nm. While TDCIMS is a promising technique for marine aerosol analysis, the paper needs further lab test to quantify instrumental issues, does not sufficiently justify its conclusions, makes very broad claims without sufficient support from the data (in particularly in light of instrumental limitations), and does not consider related work. Specifically, the paper is missing discussion of much of the most recent sea spray aerosol literature, a great dealt of which directly relates to particles in this size range. With some new lab calibrations/quantification and further analysis/justification the manuscript could be publishable in the future. However, as is there are significant shortcomings to this manuscript and it is not publishable in the current form.

Major Points

- At a number of points in the manuscript the authors discuss a differential in sensitivity where sensitivity to nitrate > sulfate > chloride. A rough value of 100x greater sensitivity is given for ammonium nitrate > ammonium sulfate, but no quantitative value is given for the sensitivity of sulfate versus chloride (other than stating "TDCIMS sensitivity to sulfate was likely slightly higher than to chloride"). The authors do not discuss the sensitivity to sodium nitrate, which is likely the form of the nitrate in sea salt particles (through the traditional chloride displacement mechanism). Given the emphasis that the authors place on Cl-/SO2- ratios and other rationalizations as to how the sulfate is from 1 source (nucleation) and chloride from another (sea salt) this needs to be addressed more rigorously and is a major deficiency in the paper. An example of why this is needed is that chloride/sulfate ratios of 1-3 compared to a seawater ratio of 17:1 (chloride/sulfate) are used as justification for the sulfate coming from nucleation. However, if the instrument is more sensitive to sulfate a value is needed to clearly show that this difference is not due to differing sensitivities. The sulfate might not be as enhanced as the paper indicates in part due to the temperature of the heating element (in this case 600 C). NaCl has a boiling point of ~1400 C and very likely won't be volatilized to a great extent at 600C this at least it might partially explain the relative sulfate enhancement. If calibration data exist showing that Cl is being efficiently volatilized at 600C (or at least is of similar magnitude to sulfate as suggested) it would greatly strengthen the authors' case. Without a more quantitative justification that the sulfate is truly substantially enhanced a key finding of the paper is not sufficiently supported. Overall, more quantitative discussion of sensitivities to different species is needed.

The reviewer suspects that particle NaCl is not efficiently volatilized during the desorption stage of the analysis. There are many considerations that demonstrate that it is essentially all volatilized. These are detailed in our response to Reviewer 1 above.

The reviewer's main concern here seems to be that we demonstrate that the observed small particle sulfate was mostly non-sea-salt sulfate, as we claim, and s(he) suggests that we perform relative calibrations for the various components observed in the particles. We have performed calibrations (described in the response to Reviewer 1) that show the sensitivity is comparable for ammonium sulfate and sodium chloride. Unfortunately, calibrations for sodium nitrate are not available.

In the revised manuscript, the relative signals of chloride and sulfate are not the only argument that the observed sulfate is mostly non-sea-salt sulfate. We now include correlation analyses of the total ion signals as well as sulfate/sodium signal ratios to demonstrate this, as described above in the response to Reviewer 1.

The event-period sulfate enhancement we described in the original manuscript was at least in part an artifact of the correlation analysis we used. We have removed this analysis, as described in the response to the next question.

- In the abstract, discussion, and conclusions sections that authors discuss nucleation events involving sulfuric acid and organics, which are attributed to biological sulfur sources. Considering the instrumental limitations regarding chloride vs. sulfate (discussed above) further information is needed to substantiate these claims. Perhaps the authors could use satellite chlorophyll to show that there was sufficient biological activity to generate enough DMS to lead to the nucleation and growth. Also there is a bit of a discrepancy between the abstract where the authors claim the growth is due to sulfuric acid and in the paper where it is attributed to organics (which is in line with the literature). This should be made consistent. Since a mode of primary OC-sulfate particles from wave breaking have been observed with a lower kappa than salts (1-4) further evidence is needed that these events are from nucleation than is presented.

We have revised our views on the relative roles of organics and sulfate in the updated manuscript, on the basis of an updated analysis. In our submitted manuscript we linked the sulfate signal to the estimated collected mass and used this correlation to argue for a large sulfate component in the collected particles. There is a connection, but it is strongly dependent on the amount of mass collected. This depends in part on instrument parameters, and the period around May 29th, when very small particle sizes were selected and mass yields were very low, had an inordinately large impact on the correlation. Therefore we have removed this analysis. However, the large non-sea-salt sulfur influence, particularly on the 24th, is now shown by a sulfate/sodium ratio time series plot.

In the revised manuscript, we correlate ions with the sum of ambient particle number in the 15-60 nm range. This is a more direct measure of the nanoparticle enhancement phenomenon we seek to understand, and it is less dependent on instrument parameters and estimation than is collected mass. We now exclude the period of low mass collection as well. We found that sulfate, sodium, chloride, and nitrate all had essentially no relationship with this parameter. However, in the time since this manuscript was submitted, we have improved the detectability of peaks in our high resolution mass spectra by averaging the desorption and baseline mass spectra prior to high resolution fitting and subtraction. We have also identified more high resolution ions. These actions have enabled more frequent detectability for some organic species, and the ion C7H7O2+ correlates well (r2 = 0.4, p <0.001) with the sum of 15-60 nm particle number. This ion is most likely benzoic acid[H+]. Nonanoic acid is also occasionally detectable and appears to be connected to the enhancement events. The stronger association of these organic species than the inorganic species with the particle number enhancements leads us to conclude that organics are important in the processes responsible for the events.

We addressed the instrumental sensitivity issue in the response to Reviewer 1, with the conclusion that most of the observed sulfate is nss-sulfate. We do not intend to demonstrate that the sulfate must derive from biological sources, and even with the inclusion of a map of satellite chlorophyll, we would not be able to conclude this. We suspect that this is the case, however, given the air mass origins, one of which we now include. We think that organics are largely responsible for the growth, and the revised manuscript is more consistent on this point.

It is certainly possible that some small primary OC-sulfate particles were included in our observations. However, the number enhancements observed were substantial, and were dominated by a small mode which is likely to be short-lived and can therefore not be very old. We are not aware of literature which suggests that wave breaking can generate large numbers of 10-40 nm particles without also generating large numbers of ~100 nm particles, whether many surface organics are present or not (Fuentes et al. 2010, Clarke et al. 2006, Sellegri et al. 2006). Also, the "<50 nm" events clearly show enhancement at nucleation mode sizes. These arguments are detailed in the revised manuscript. We now cite Ehn et al. 2010, which describes an open ocean nucleation event that was observed at sea in the North Atlantic, and the resulting plume which reached the Mace Head site.

- The authors in this work do not discuss a great deal of the recent literature regarding sea spray aerosol generation, including publications from the groups of Keene, Bigg, Prather, Fuentes, Bates, Quinn, Facchini, Leck, etc. Many of these groups are leaders in the fields of marine aerosol research and not a single paper is referenced from any of them. This lack of discussion does not place the work in the appropriate context and is a significant shortcoming. Examples of issues that should be addressed including the following.

- Bigg and Leck have argued that no NaCl is present in particles less than 200-300 nm, a direct contradiction to this work. While the authors' observations agree with Clarke, it is important to at least discuss how these findings fit into the hotly debated topic of < 200 nm particle composition. Numerous other papers from this group discuss particles in this size range with electron microscopy.

- Facchini has shown that water soluble organic material grows in substantially at smaller sizes . Since the instrument has limited abilities to see organic material (WIOM), the potential for this WIOM to play a role in the lower GF more should be discussed. Further discussion of the organic components as studied through NMR and other techniques is important to discuss with the lack of organic information from this work (8,9).

- Prather and the CAICE center have shown that there are different populations of particles within sea spray aerosol that could also explain many of the findings in this paper. In Prather et al. 2013, 3 different populations of particles are shown for sea spray aerosol (OC (with sulfate), SS-OC, and SS) (3). At ~60 nm particles ranged from mostly SS-OC to mostly OC under different seawater conditions (2) and these two types had vastly different Kappa values which could explain the GF's observed (1). Since these particles were produced and sampled in a matter of seconds and no evidence for nucleation in the sealed ocean-atmosphere wave apparatus was observed the possibility that primary OC-sulfate could be contributing to this lower GF mode should be considered.

- Fuentes has shown a range of kappa values under different seawater conditions, which would likely lead to different growth factors as well. This could explain the range of GFs without aging or nucleation as the paper suggests (4,10).

We have added significantly to the discussion of recent work on this topic, both in the Introduction and the Discussion sections. We now point out the Bigg and Leck argument for no NaCl in sub-200 nm particles and also more recent (and strong) contradictions to this view. We now cite the Facchini et al. observations of 125-8000 nm primary particles. Our observations of nonanoic acid are consistent with their finding that aliphatic and long chain species are common, but the presence of benzoic acid suggests a different formation mechanism than primary particle generation, particularly for the nanoparticle enhancement events.

We accept that there are alternate hypotheses to explain the different GFs observed during the different experimental periods. We no longer explicitly describe them as a succession of aerosol states. However, for reasons outlined in the previous question, we still find that homogeneous nucleation of new particles is required to explain the observed enhancements in nanoparticles, as opposed to the hypothesis that these were solely primary sea spray.

- In the discussion the authors assert that they are observing a progression of fresh sea salt to aged that has a lower hygroscopicity. This possible explanation is not well supported beyond stating there is a lower GF mode. First, as sea salt particles age they likely take up nitric acid and displace chloride, which will only serve to increase their hygroscopicity. One possible explanation is that with decreasing pH a phase separation occurs with a concentrated organic layer forming on the outside of the particle that lowers the GF as suggested in Ault et al last year.11 The more likely explanation though is that the relative proportions of different primary particles formed through bubble bursting has changed.6 Sea spray aerosol particles from regions with different seawater composition can easily have greater primary organic or salt/organic mixtures that would lead to a second mode. Both an active mode and a less active mode have been observed simultaneously under many seawater conditions as f(size) (3). Further justification of why the "aged" salt-containing particles have a lower GF and are aged versus coming from different seawater should be added.

As noted above, we have relaxed our stance on the "progression" issue, and included language that allows for different source seawater conditions to explain some of the differences. However, we do not understand the reviewer's claim that uptake of HNO_3 and loss of HCl will increase particle hygroscopicity. $NaNO_3$ is less hygroscopic than NaCl (e.g. UMan SysProp, http://umansysprop.seaes.manchester.ac.uk).

Minor Points

- Why is no positive TD-CIMS spectrum shown? It would be helpful to support the negative spectrum given in figure 2.

Added.

- In section 3.3.3 "time series presented in Fig. 3" are referenced, however Fig 3 is of GF data. This should be corrected/clarified.

Fixed.

- A little bit more information regarding the 50% uncertainties for mass should be given in the methods section.

Added ", based on the error in the fitting approach described below and in the Supplement."

References:

1. Collins, D. B.; Ault, A. P.; Moffet, R. C.; Ruppel, M. J.; Cuadra-Rodriguez, L. A.; Guasco, T. L.; Corrigan, C. E.; Pedler, B. E.; Azam, F.; Aluwihare, L. I.; Bertram, T. H.; Roberts, G. C.; Grassian, V. H.; Prather, K. A., Impact of marine biogeochemistry on the chemical mixing state and cloud forming ability of nascent sea spray aerosol. Journal Of Geophysical Research-Atmospheres 2013, 118, (15), 8553-8565.

2. Ault, A. P.; Moffet, R. C.; Baltrusaitis, J.; Collins, D. B.; Ruppel, M. J.; Cuadra-Rodriguez, L. A.; Zhao, D.; Guasco, T. L.; Ebben, C. J.; Geiger, F. M.; Bertram, T. H.; Prather, K. A.; Grassian, V. H., Size-Dependent Changes in Sea Spray Aerosol Composition and Properties with Different Seawater Conditions. Environmental Science & Technology 2013, 47, (11), 5603-5612.
3. Prather, K. A.; Bertram, T. H.; Grassian, V. H.; Deane, G. B.; Stokes, M. D.; DeMott, P. J.; Aluwihare, L. I.; Palenik, B. P.; Azam, F.; Seinfeld, J. H.; Moffet, R. C.; Molina, M. J.; Cappa, C. D.; Geiger, F. M.; Roberts, G. C.; Russell, L. M.; Ault, A. P.; Baltrusaitis, J.; Collins, D. B.; Corrigan, C. E.; Cuadra-Rodriguez, L. A.; Ebben, C. J.; Forestieri, S. D.; Guasco, T. L.; Hersey, S. P.; Kim, M. J.; Lambert, W. F.; Modini, R. L.; Mui, W.; Pedler, B. E.; Ruppel, M. J.; Ryder, O. S.; Schoepp, N. G.; Sullivan, R. C.; Zhao, D., Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol. Proceedings of the National Academy of Sciences 2013, 110, (19), 7550-7555.
4. Fuentes, E.; Coe, H.; Green, D.; McFiggans, G., On the impacts of phytoplankton-derived organic matter on the properties of the primary marine aerosol - Part 2: Composition, hygroscopicity and cloud condensation activity. Atmospheric Chemistry And Physics 2011, 11, (6), 2585-2602.
5. Bigg, E. K.; Leck, C., The composition of fragments of bubbles bursting at the ocean surface. Journal Of Geophysical Research-Atmospheres 2008, 113, (D11), D009078.
6. Leck, C.; Bigg, E. K., Source and evolution of the marine aerosol - A new perspective. Geophysical Research Letters 2005, 32, (19).
7. Facchini, M. C.; Rinaldi, M.; Decesari, S.; Carbone, C.; Finessi, E.; Mircea, M.; Fuzzi, S.; Ceburnis, D.; Flanagan, R.; Nilsson, E. D.; de Leeuw, G.; Martino, M.; Woeltjen, J.; O'Dowd, C. D., Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. Geophysical Research Letters 2008, 35, (17), L034210.
8. Decesari, S.; Finessi, E.; Rinaldi, M.; Paglione, M.; Fuzzi, S.; Stephanou, E. G.; Tziaras, T.; Spyros, A.; Ceburnis, D.; O'Dowd, C.; Dall'Osto, M.; Harrison, R. M.; Allan, J.; Coe, H.; Facchini, M. C., Primary and secondary marine organic aerosols over the North Atlantic Ocean during the MAP experiment. Journal Of Geophysical Research-Atmospheres 2011, 116, D016204.
9. Rinaldi, M.; Decesari, S.; Finessi, E.; Carbone, C.; Mircea, M.; Fuzzi, S.; Ceburnis, D.; O'Dowd, C. D.; Facchini, M. C., Marine organic aerosol: Characterization by proton nuclear magnetic resonance spectroscopy (H-1 NMR). Geochimica Et Cosmochimica Acta 2009, 73, (13), A1102-A1102.
10. Fuentes, E.; Coe, H.; Green, D.; de Leeuw, G.; McFiggans, G., Laboratory-generated primary marine aerosol via bubble-bursting and atomization. Atmospheric Measurement Techniques 2010, 3, (1), 141- 162.

11. Ault, A. P.; Guasco, T. L.; Ryder, O. S.; Baltrusaitis, J.; Cuadra-Rodriguez, L. A.; Collins, D. B.; Ruppel, M. J.; Bertram, T. H.; Prather, K. A.; Grassian, V. H., Inside versus Outside: Ion Redistribution in Nitric Acid Reacted Sea Spray Aerosol Particles as Determined by Single Particle Analysis. Journal of the American Chemical Society 2013, 135, (39), 14528-14531.

References for Response to Reviewer 2:

Clarke, A. D., Owens, S. R., & Zhou, J. (2006). An ultrafine sea-salt flux from breaking waves: Implications for cloud condensation nuclei in the remote marine atmosphere. Journal of Geophysical Research, 111(D6), 1–14. doi:10.1029/2005JD006565

Ehn, M., Vuollekoski, H., Petäjä, T., Kerminen, V.-M., Vana, M., Aalto, P., de Leeuw, G., et al. (2010). Growth rates during coastal and marine new particle formation in western Ireland. Journal of Geophysical Research, 115(D18), D18218. doi:10.1029/2010JD014292

Fuentes, E., Coe, H., Green, D., de Leeuw, G., & McFiggans, G. (2010). Laboratory-generated primary marine aerosol via bubble-bursting and atomization. Atmospheric Measurement Techniques, 3(1), 141–162. doi:10.5194/amt-3-141-2010

Sellegri, K., O'Dowd, C. D., Yoon, Y. J., Jennings, S. G., & de Leeuw, G. (2006). Surfactants and submicron sea spray generation. Journal of Geophysical Research, 111(D22), D22215. doi:10.1029/2005JD006658