

Interactive comment on “Sub-Antarctic marine aerosol: significant contributions from biogenic sources” by J. Schmale et al.

Anonymous Referee #1

Received and published: 7 May 2013

The paper is beyond doubt a valuable contribution to marine aerosol research, especially considering the little explored Southern Hemisphere. The scientific strength of the paper is related to the use of a modern instrument (HR-ToF-AMS), a modern statistical tool (PMF) and most importantly it was an extended 8 week campaign in the strategically located area of Southern Atlantic at a peak of biological productivity. I must admit to the author's credit that it is pretty rare to see papers with so many relevant details included. The authors did pretty impressive job at trying to explore and convey every possible relationship. Having said that, presenting all possible information makes the story somewhat distracting as the reader becomes confused which of the relationships are most important, reliable and believable. The authors are the best experts of their measurement dataset and should present their balanced opinion to their best understanding. The paper is certainly suitable and must be published in ACP, but I stress that authors carefully consider critical comments which somewhat compromise an otherwise excellent paper. I noted major revisions required only because of numerous comments, not major problems. Instead of categorising into major and minor comments I listed comments in sequence as they appeared while reading the paper.

Response: We thank this reviewer for the constructive critique and for taking the time to look at all the details described in this manuscript. We have carefully considered all comments. Please refer to the specific responses.

The title may be altered to “dominant contribution” instead of “significant” as far as I can judge from presented results – only sea salt is not biogenic and a little bit of (if any) sulphate from South America.

Response: We changed to “Dominant contributions...”

Abstract

“Sea salt OA fraction” sounds awkward and misleading as there is no organics in sea salt. Instead, the term sea spray - as a sum of inorganic sea salt(s) and organic matter - represents particles produced by bubble bursting. Extracted SS-OA factor can be almost pure SS due to UMR PMF with only minor traces of primary/secondary material (see more extensive comment below).

Response: The term “sea spray organic aerosol” is much more suitable. We have changed the terminology throughout the manuscript.

Introduction

Reference to Vignati et al. 2010 should include particle size parameter if percentage of OM was noted?

Response: The manuscript already mentions “submicron particulate matter” as size parameter.

Page 8264, Line 12-15. The sentence should be restructured “Few studies . . . MOA in the remote. . . (5 studies) and even fewer studies conducted MOA source apportionment (Decesari et al. 2011).

Response: Done.

Page 8265, line 7-8. “and potentially increasing the range of impacts on ecosystems”.

Response: Done.

Introduction lacks references to Sciare et al. (2009) and Claeys et al. (2010) as the relevant studies in the Southern Ocean. More importantly, Sciare et al.(2009) was a long-term measurement study demonstrating seasonality of OM due to biological activity. As the Sub-Antarctic study lasted 8 weeks, it is important to place the period into context with respect to distinct seasonality and the timing of rather short, but intensive peak of biological activity in the Southern Ocean.

Response: Reference to the two studies are now included in the introduction. Sciare et al. (2009) is also referred to in section 3.6. We included the sentence “Measurements were conducted during Austral spring, the peak time for biological activity.” in the introduction.

Experimental and Methods

Page 8266, line 14. Awkward sentence “. . . topography was expected. . .to mix aerosol. . .”

Response: We changed the sentence to: “However the local topography and the quasi-permanent winds lead to atmospheric turbulence and hence to the mixing of aerosol produced locally by seabirds and seals with air masses arriving with the predominant westerlies”

Line 26. What was the rationale of 150s averaging time if all subsequent comparisons were done on 5min basis at least? Moreover, low particle concentrations in the oceanic regions would suggest longer not shorter averaging times, especially that authors struggled with AMS size distributions (understandable with 150s averaging time).

Response: The V and W-modes were alternated with 150 seconds recording/averaging time for each. This means, when using the V mode data that they refer to 5 minutes measurement intervals (150 + 150 = 300 seconds). In general, it is desirable to have the highest possible time resolution and to average the recorded data on the AMS acquisition card for the shortest amount of time possible. Averaging over longer times can be done in post analysis. With regard to the AMS derived size distributions for sulfate and ammonium, we averaged the data over the entire measurement period (see section 3.3).

Page 8268, line 24. I don't understand the sentence why SMPS would account for a larger number of particles than the AMS due to sea salt presence when authors present quantitative case of AMS sea salt detection? The fraction of sea salt AMS can see is pretty large if all the ions are summed – refer to Fig. 8 in Allan et al. 2004(JGR) or similarly high fraction in Ovadnevaite et al.(2012). Much more significant influence would have RH of the particles sampled by SMPS (with no information available in text) and non-isokinetic split of the flows between SMPS and AMS (see also comments below).

Response: In section 2.2.2 we elaborate on the laboratory experiments to quantify sea salt concentrations with an AMS and compare the results with publications by Zorn (2008, 2009) and Ovadnevaite et al. (2012). From this discussion it becomes clear that further investigation is needed, before a less instrument specific quantitative determination of AMS sea salt measurements is possible: “Also, comparison with other available literature suggests that AMS sea salt quantification needs more thorough investigation.” For the sake of comparability, we use the factor published by Ovadnevaite et al. (2012) “To be consistent with available data from the existing literature, mass concentration related data for sea salt reported in this study, have been determined on the basis of the intensity of m/z 58 (NaCl^+) and scaled up using the factor of 51, as suggested by Ovadnevaite et al. (2012).” Additionally, we explicitly state that the sea spray OA PMF factor is only qualitative. So we do not present quantitative sea salt data for the specific HR-ToF-AMS that has been deployed. “However, due to the significant influence of sea spray in the submicron particulates, the SMPS accounts for a larger number of particles than the AMS. Even though the AMS sees a fraction of the submicron sea salt, it cannot be quantified (see Sect. 2.2.2).” Hence, we doubt that the AMS was able to account for all submicron sea spray particles while the SMPS will have measured them.

Regarding humidity, the average humidity was 26 ± 5 %. The sampled air was dried by a nafion dryer, and the counterflow had been dried by passing the air through a silica gel column. The reviewer might be right that RH plays a role in the discrepancies between AMS and SMPS data, however given the rather low RH it is unlikely to be the main reason. However, the not ideal flow split might have played a role. We have now added the following sentence: “In addition, the flow split was not strictly isokinetic.”

Authors do not consider an application of variable collection efficiency introduced by Middlebrook et al. (2012).

Response: Middlebrook et al. (2012) state “The use of the default CE of 0.5 for all campaigns resulted in 81-90% of the AMS speciated and total mass concentrations comparing well with fine particle volume or PILS measurements within experimental uncertainties, with positive biases compared with a random error curve.” The variable collection efficiency would increase the match to over 92%. We think that the chemical composition of Bird Island aerosol is significantly different from the aerosol types investigated by Middlebrook et al. especially because of the sea spray components. There is almost no nitrate in Bird Island aerosol, so correction based on particulate nitrate is not possible. With respect to ammonium, Fig. 2 in the Middlebrook et al. paper and the reference to Quinn et al. suggest that a CE of 0.5 is still ok. Hence, we doubt that we could improve CE without introducing further errors through assumptions that would have to be made and that are difficult to quantify.

Page 8269, line 22. I suggest “Formerly, sea salt was considered undetectable by AMS due to refractory nature of sea salt at AMS vaporisation temperature of around 600°C”.

Response: We have changed the sentence to “Formerly, sea salt was considered to be undetectable by the AMS due to the refractory nature of sea salt at a vapourisation temperature of around 600 °C (Bahreini et al., 2003; Jimenez et al., 2003).”

Chapter 2.2.2 is quite messy. While acknowledging the study of Ovadnevaite et al. as a pioneering with respect to quantitative sea salt detection by HR-ToF-AMS, additional independent studies are necessary to check if the scaling factor presented by Ovadnevaite et al. was instrument related or more generally applicable. That would have benefited AMS and indeed the whole aerosol community greatly. The authors of this study did not attempt or were not able to investigate quantitative features of the field instrument (HR-ToF-AMS), but instead experimented with a compact AMS with a hope that it will help to establish HR-ToF-AMS scaling factor – quite a remote hope, I guess. Neither I understood why the authors attempted calibration using sea salt and ammonium nitrate as the 1:1 mixture has nothing in common with ambient aerosol – nitrate was a minor component in the author’s study (and, indeed, any clean oceanic atmosphere). Volatile nature of ammonium nitrate may have affected vaporisation (flash or surface) of sea salt when unrealistically high concentration was used in the lab. I have more specific comments as well, but they are irrelevant considering the above. The bottom line is that if the calibration of the field HR-ToF-AMS was not possible (pity why) and authors decided to use Ovadnevaite et al. scaling factor – fair enough to state that. The authors may then consider only directly relevant information along the discussion (e.g. Zorn et al.).

Response: We have moved the description of the laboratory experiment and Fig. 2 to the Supplementary Material and kept the comparison of our results, the results by Zorn et al. and Ovadnevaite in the manuscript. We agree with the reviewer that the sea salt quantification might be highly dependent on the specific AMS used and that it naturally would have been better to do the lab study with the HR-ToF-AMS deployed on Bird Island. This however was not possible in this case due to logistical reasons. Nevertheless, we think that the presented study yields important results to be shared with the community such as the different vapourisation behaviours of NaCl and sea salt, the influence on the fragmentation table and the overall quantification of particulate organics. The reviewer comments that the approach of using a 1:1 solution of sea salt and ammonium nitrate might not be appropriate given the ambient composition of the aerosol. The objective of the laboratory study was not to reproduce Bird Island ambient conditions, but to explore an AMS only based method for sea salt quantification. The results suggest that the combination of available cations and anions may have a significant influence on the vapourisation behavior (see Figure S1, formerly Fig. 2). Here, reviewer might be correct in assuming that high nitrate concentrations may have an impact on the experimental results. Generally, there seems to be a consensus that this topic will require more thorough investigation, as stated in the manuscript.

Chapter 2.2.3 It was pity that PMF was performed at UMR spectra. I understand that HR PMF is more laborious, but what a wonderful result it would have been, making interpretation of factors much more reliable (see comments below).

Response: We agree that performing PMF on HR spectra promises exciting results. However, the presented PMF results on UMR spectra present already a high degree of new information that is reliable and worthwhile to report independent of potential HR analysis results. A PMF uncertainty analysis is provided in the supplementary material and much additional information is given in the manuscript to assess the scientific rigor of the chosen PMF solution. Given the length of this manuscript, more detailed information might be too much for this specific study. There is certainly room for future work on a variety of HR data analysis on marine aerosol.

If authors admit a problem with m/z29, it should have been removed, not down weighted as its time series may have wrongly affected factor analysis even at reduced signal value. Note that m/z29 is significantly contributing in every single factor which suggests a problem in factor analysis.

Response: We consider it our duty to report that there might have been a problem with m/z 29, however we cannot prove that there has been one. Under the premise that there was a problem, we decided to strongly downweight m/z 29 for PMF analysis. Based on the information given in the supplementary material it is evident that downweighting by a factor of 1000 significantly changes the result compared to not downweighting it. The fact that there is no significant difference in downweighting by a factor of 100 or 1000 shows that the results are robust. Especially comparing the resulting HOA spectrum with the average HOA spectrum as presented by Ng et al., 2011 shows that the result is reliable. In our case, m/z 29 contributes 5 % to the overall spectrum which is well within the standard deviation, roughly 1.8 to 6 %, given by Ng et al. 2011. The overall correlation with the average HOA mass spectrum in Ng et al. (2011) is $R^2=0.98$. We have included this information at the beginning of section 3.4. Since m/z 29 is an important marker for highly oxygenated aerosol it was decided to perform PMF with it. Also, m/z 29 needs to be carried by the PMF analysis as it contains significant mass, which should not get lost in the analysis.

The change of the fragtable is justified, but different m/z 46 to m/z 30 ratio of organo-nitrates is not considered.

Response: This is correct. However, scanning through the HR fragments of the spectrum for different characteristic periods did not indicate significant contribution by organo-nitrates.

Chapter 2.3 Check last sentence – was it 15cm long inlet or 15m? Lower APS counting efficiency should be referenced (e.g. Peters and Leith, 2003). It would be useful to report Reynolds number of the sampling lines to prove it was close to laminar conditions.

Response: The inlet was only 15 cm long. We have added the reference. The Reynolds number for the long inlet line that served the AMS and SMPS was 1737.

Chapter 2.4 What kind of Naphion dryer was used? Was it adequate in terms of getting RH well below 40% - essential for SMPS due to efflorescence of sea salt particles? AMS on the other hand would probably be fine without dryer if RH was monitored. The flow split between SMPS and AMS was not isokinetic with serious consequences to be expected towards SMPS/AMS mass balance.

Response: We used a Nafion™ single tube countercurrent dryer. The counterflow was dried with a silica gel column. The average RH was $26 \% \pm 5 \%$, now this included in the manuscript in section 2.4. For more see answer above.

Chapter 2.6 Air mass trajectories have an uncertainty of 15-30% of the distance at the start/end of it (check HYSPLIT model details on NOAA site) making their length above 120 hours unrealistic. For instance, 120 hour trajectory length is of the order of 2000-3000km which introduces 300-1000km error at a backward starting point. Thus a longer trajectory puts starting point essentially in random position.

Response: We have added the following sentence “Note that air mass back trajectory locations have an uncertainty of 15 – 30 % of the distance between the start and end point. ” and the following sentence to Section 3.5: “Note that there is no significant difference when attributing either the 240 hours or 120 hours long back trajectories to the clusters.”

Chapter 3.1. Authors make a fundamental mistake when stating nss sulphate originates from MSA. Reference to a highly reputable source (Seinfeld and Pandis, 2006) does not help if the source is misinterpreted. MSA and sulphate branch out in the DMS oxidation reaction scheme which depends on temperature/radiation (Seinfeld and Pandis, 2006) or RH/dew point (Berresheim et al. 2002).

Response: Thank you for pointing this out. We have modified the following sentences in section 3.1: “It originated from three sources: sea salt, dimethyl sulfide (DMS) and long-range transport,...” and “Large variations occurred during periods with strong methanesulfonic acid (MSA) contribution...”. In Section 3.6 we corrected the statement to “When dimethyl sulfide is emitted by phytoplankton, it is oxidized either to MSA or to sulfur dioxide and sulfuric acid, which will in turn partition into the particulate phase (Seinfeld and Pandis, 2006). Thus, a correlation between particulate MSA-OA and sulfate is expected.” We have adopted the paragraph on Fig. 19 (now moved forward, Fig. 9) that reviewer 3 suggested with some minor modifications: “The lower envelop of the relationship between sulfate and MSA-OA (Fig. 10) shows a slope close to 5.3 (i.e. a MSA-OA to particulate sulfate ratio close to 19%). This value of the MSA to sulfate ratio likely corresponds to air masses that were not long range transported and correspond to quasi pure marine DMS oxidation in these regions. This value lies between the low values observed at low latitudes (less than 10%, Saltzman et al., 1983) and the higher ones observed at coastal Antarctic sites (30% at the Dumont d’Urville site, Jourdain and Legrand, 2001). Other studies, such as by Sciare et al. (2009) have shown the importance of marine biological activity related to chlorophyll observations in organic aerosol before.”

Chapter 3.3 Another misinterpretation of a reputable paper by de Carlo et al. 2004. Sea salt shape factor is 1.08, not 1.25. A 1.25 shape factor applies to free-molecular regime while authors apply that to SMPS/APS. If RH was not controlled to below 40%, shape correction should not be applied as some of the salts (e.g. MgCl₂) retain water even at 5-10% RH. If RH was strictly controlled then the shape correction should be applied to both APS and SMPS. Size distributions of sulphate and ammonium refer to Table 5, but that Table only presents modal diameters of factors, not species.

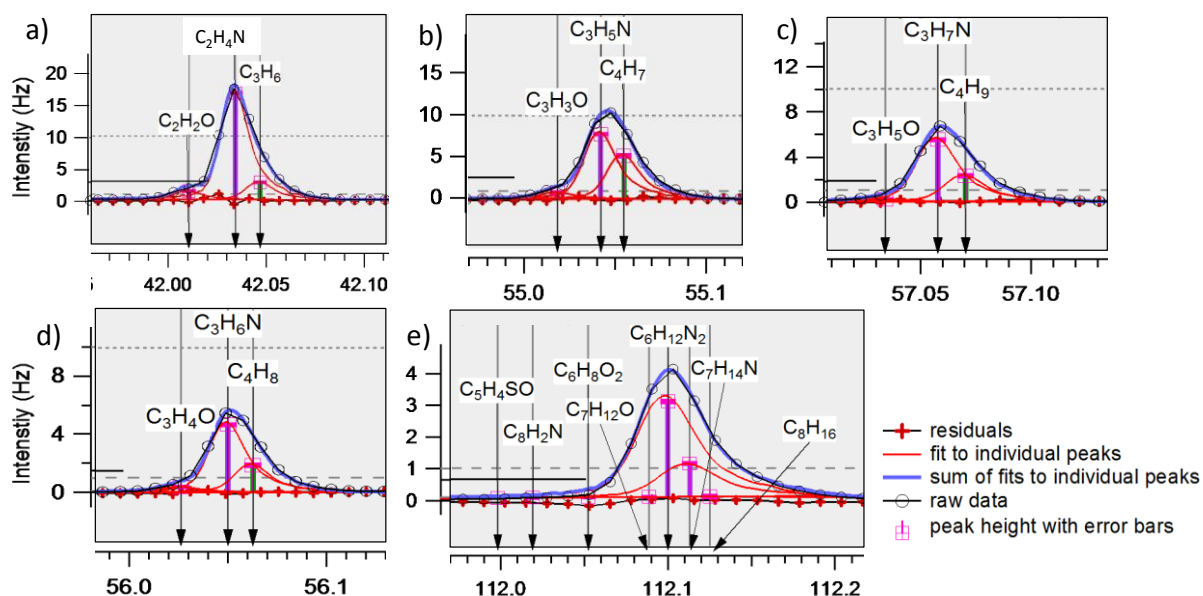
Response: Thank you for pointing this out. We would like to clarify that we have not applied this correction to the SMPS data (see Section 3.3 where this is evident). Also, please refer to the responses above regarding the RH of the sample flow to the SMPS. With respect to the APS data correction, we have now omitted the shape correction in the conversion from d_a to d_{ve} since the inlet flow for that instrument was not humidity controlled and thus particles likely did not have a cubic shape. The reference to Table 5 was deleted.

Chapter 3.4 Amines are indeed minor contributors to organic aerosol mass and their m/z signals are very close or even completely drowned in dominant neighbouring m/z signal. Authors need to demonstrate that the nitrogenated ion signals are indeed significant and can be reliably isolated (similarly as in Figures 9,10,14) alongside the absence of the correlation between major amine m/z (42,55,57 as in Table 6) and the dominant neighbouring ions.

Response: We have now added another figure (Fig. 12) similar to figures 9, 10, 14 that shows the five most important nitrogen containing ion signals of the AA factor. The correlation (R^2) between the main nitrogen containing ion signals and their neighboring ions are:

C ₂ H ₄ N (m/z 42)	C ₃ H ₆	0.17
C ₃ H ₅ N (m/z 55)	C ₄ H ₇	0.065661
C ₃ H ₇ N (m/z 57)	C ₄ H ₉	0.0690207
C ₃ H ₆ N (m/z 56)	C ₄ H ₈	0.000464959

We have added the following sentence to the manuscript: “To test whether the nitrogen containing ion signals can reliably be isolated from neighbouring ions the linear correlation between C₂H₄N and C₃H₆ (m/z 42), C₃H₅N and C₄H₇ (m/z 55), C₃H₇N and C₄H₉ (m/z 57), and C₃H₆N and C₄H₈ (m/z 56) were tested. All R^2 were smaller than 0.2.”



Line 12 “organic sea salt mass” should be changed to “sea spray organic matter mass”.

Response: Done.

Chapter 3.5 Consider uncertainty of the trajectories in this chapter as commented before.

Response: We have tested whether trajectories would be allocated to a different cluster based on 120 hours backward calculation only. However this is not the case. So the clustering is robust. We have added the following sentence to the manuscript: “Note that there is no significant difference when attributing either the 240 hours or 120 hours long back trajectories to the clusters.”.

Chapter 3.6 Zorn et al. has demonstrated that fragmentation of MSA depends on heater temperature and possibly even tuning of individual AMS – don’t over-interpret absence of the correlation. Please correct the misinterpretation of MSA/sulphate. It must be an error in referring to the bloom timing in August (that’s winter in Southern Hemisphere). Otherwise, what relevance does it have to the measurement period?

Response: We don’t think that we over interpret the missing correlation between laboratory and ambient MSA spectra. We think it is necessary to point out that the correlation is poor. However, there is no doubt that the measured spectra originate from MSA which is shown in multiples ways (the spectrum and isolated peaks, correlation with sulphate). We have changed the MSA/sulphate sentence to: “When dimethyl sulfide is emitted by phytoplankton, it is oxidized either to MSA or to sulfur dioxide and sulfuric acid, which will in turn partition into the particulate phase (Seinfeld and Pandis, 2006).” Regarding the onset of the phytoplankton bloom, we changed the sentence to: “The plankton bloom onset in the 10×10 degree square around BI (49 - 59 °S and 33 - 43 °W) happened in late September 2010, where the average chlorophyll-a concentration was 0.28 mg m^{-3} . During the AMS measurement period concentrations increased from 0.62 to 0.85 mg m^{-3} until 24 November and then decreased to 0.49 mg m^{-3} by 31 December.” In the last week of September a significant change

in the concentrations compared to the austral winter months can be seen. The onset of the bloom was however quite early in that year.

MSA modal diameters in submicron and supermicron range are consistent with Rinaldi et al. 2011 and it must be an error in supermicron diameter – Fig.7 suggests 7.28, not 4.37 μ m.

Response: Thank you for pointing this out. There was an error in the manuscript. We have corrected the information on the diameter size from 4.37 ± 0.04 to $7.28 \pm 0.08 \mu\text{m}$ as also shown in Table 5.

Chapter 3.7 There is no Na³⁷Cl⁺ isotope – it is isotopologue. When stating Na³⁷Cl same applies to Na³⁵Cl, not NaCl⁺. Same in line 9.

Response: Thank you for pointing this out. We have made the following correction in the manuscript: “The qualitative PMF sea spray factor is dominated by m/z 57.96 and 59.96, which represent the isotopologues Na³⁵Cl⁺ and Na³⁷Cl⁺, respectively, and which is characterized by a number of other inorganic ion fragments, such as m/z 90.90 FeCl, 125.87 FeCl₂, and 127.87 Fe³⁷ClCl (all marked in olive in Fig. 6c). The average ratio of the two sodium chloride isotopologues measured throughout the campaign was 3.1, as was expected for sea salt (De Laeter et al., 2003).”

SS-OA factor most significant organic matter contributors are m/z 29 and 30, suggesting that their contribution came from changed fragtable and are not unique. If m/z 29 was removed beforehand and m/z 30 downweighted due to fragtable issues this factor looked like pure sea salt which is good result. Sea salt in sea spray does not need to correlate with sea spray organics, i.e. MOOA factor, considering that both constitute sea spray. Oppo et al. 1999 demonstrated that organic matter replaces sea water in the airborne droplet due to OM enrichment at the water/air interface resulting in OM enriched sea spray particle. Therefore, enrichment depends on biological activity while the production of sea spray depends on the wind speed. Same process is claimed by O’Dowd et al. (2004).

Response: Regarding the organic fraction of the sea spray submicron aerosol, the reviewer suggests that the dominant organic ions are not unique. While this doubt might partially be true for m/z 29 due to the potential problem as elaborated in the supplementary material (also please refer to the specific response further above) this is not the case for m/z 30. As stated in the text “Note that the NO⁺ ion is not accounted for in the PMF analysis, as it is not part of the input matrix but appears in the HR analysis of the whole spectrum.” NO⁺ is not part of the input matrix and therefore the dominant ion in the mass spectrum in figure 6 is CH₂O. Other peaks shown in Fig. 10 also suggest that there are additional organic fragments such as C₂H₃O, C₃H₇ etc. There is no doubt that organic mass is present in this spectrum. The text in the manuscript discusses that the UMR PMF analysis comes up with a sea spray factor that contains 41% inorganic salts representative for sea salt and 59% organic material. In addition, we stress that this PMF factor is to be taken quantitatively. For future analysis it might indeed be useful to perform HR PMF. We agree that sea salt and organic matter from sea spray

do not necessarily have to correlate as indicated by the respective discussion on externally or internally mixed organic and inorganic aerosol in this section.

Last paragraph of the chapter implies not only AA factor, but local surf zone influence. APS particle enhancement would be observed in sea salt laden air masses (thus correlating with sea salt mass), but also during significant wave breaking in the bay depending on wind direction. The sampling was conducted at 5m above ground - inevitably affected by surf zone fluxes. Fauna related debris was the undeniable candidate as well.

Response: It is conceivable that fauna related debris is found in the supermicron particle mode. However, based on the available measurements we cannot make any general statement about this. The only information that we have is that the AA-OA mass spectrum is not similar to the guano mass spectra which is discussed in section 3.8. Filter samples of supermicron particles could be useful in this respect.

Chapter 3.8 The AA-OA factor is made central by the authors, but it seems that the implied presence of amines and amino acids is overstated substantially. The reasoning implies that OM in this factor was almost entirely dominated by amino acids and amines, however, direct evidence is lacking. The authors need to demonstrate that during dominant contribution of this factor high resolution spectra of the dominant m/z 42, 55, 57 indeed exhibit significant nitrogenated ion fragments (similarly to Fig 9, 10, 14). Figure 6 shows m/z 29 as the most dominant fragment during dominant period, but m/z 29 is absent in Table 6. Again the absence of the correlation between particular nitrogenated fragment and the dominant neighbouring ion should be demonstrated.

Response: Please refer to the specific answer above that comments on the new figure 12 showing high resolution ions for the dominant nitrogen containing mass to charge ratios. We do not agree that the presence of amines and amino acids is overstated substantially. We clearly state that statistical analysis of the factor shows that 22% of the organic mass consists of the $C_xH_yN_z$ series (see second paragraph of section 3.8). We are not quite sure what the reviewer means by “The reasoning implies that OM in this factor was almost entirely dominated by amino acids and amines, however, direct evidence is lacking.”, as we neither state that OM is “almost entirely dominated by amino acids and amines” and direct evidence for the presence of these ion fragments is given by the mass spectrum and now the new figure 12. In Table 6, we explicitly refer only to the dominant ions from the $C_xH_yN_z$ series. This is the reason why we do not include m/z 29.

Page 8287, line 27. SSML is not approximately uniform, especially considering the latest research (Gantt et al., 2011; Gantt and Meskhidze, 2013)

Response: Thank you for pointing this out. We have corrected the sentence to: “This suggests that the sea-surface micro layer (SSML) is unlikely to have been the major source of the AA factor or that SSML constituents are significantly different around Bird Island.”

Chapter 3.9 It is interesting to see very similar factor in the Southern Atlantic as it was demonstrated in the North Atlantic by Ovadnevaite et al. (2011), but even more astonishing is the similarity with the MOOA factor in the city of Paris by Crippa et al. 2013! Both correlations are statistically significant as R^2 is a variance and it is squared correlation coefficient. The correlation with wind speed was already commented above.

Response: Yes, this is indeed astonishing.

Chapter 3.10 More oxygenated MOOA factor in this study does not suggest anything more than the fact. It is not clear how exactly biogenic OM comes about into particle phase (evidence suggests primary production) nor whether oxygenation occurs in the water or the particle. Decesari et al. (2011) suggested that primary OM can be processed into OM with features of secondary produced OM making it hardly discernible from secondary. Probably only a combination of physical (mixing state, hygroscopicity, CCN activation) and chemical features (solubility, speciation) considered together can help to separate the two.

Response: We agree that more research is needed to present a clear conclusion. We have added the following sentence to the discussion: “Decesari et al. (2011) suggested that primary marine organic matter can be processed into OM resembling secondary OA making the two aerosol types hardly discernible.”.

Chapter 3.10.4 Again sulphate and MSA relationship is misinterpreted – the two species are separate branches of DMS oxidation pathway and need not be tightly related. Consequently, elevated sulphate may be related to various production pathways – temperature, radiation, cloudiness, RH dependent while MSA is differently dependent on those. If anthropogenic sulphate is suspected it must be accompanied by nitrate – it is inconceivable that anthropogenic aerosol would contain sulphate and not nitrate in internally mixed particles (as is the case with anthropogenic particles far from sources). Moreover, nitrate is a conservative tracer unlike organic matter which is continuously processed in the atmosphere. I don't quite get the purpose of trying to correlate MOOA factor with any other “standard” factor when PMF analysis have already produced all meaningful factors.

Response: We have reformulated the sentence to “Secondly, particulate sulfate was associated with DMS oxidation, as the high correlation ($R^2 = 0.69$) between the PMF derived MSA-OA factor and particulate sulfate suggests.” Regarding the comment that it might not be useful to correlate M-OOA with particulate sulphate, we think we have made our case with the following sentence in the manuscript: “Even though the correlation between M-OOA, whose trajectories have passed over the Latin American continent, and particulate sulfate ($R^2 = 0.01$) was low, there were certain periods when both particulate sulfate and M-OOA were elevated and MSA-OA and sea salt mass concentrations, the other potential sources for sulfate, were low (see Fig. 19 red ellipse).”. With respect to the comment that it is unlikely that some of the particulate sulphate originated from anthropogenic activities due to the lack of particulate nitrate, we agree that this is true for near source measurements. The inorganic nitrate detected by the AMS is usually dominated by ammonium nitrate, and forms a dynamic equilibrium with nitric acid, which depends on the presence

of ammonia. It is therefore not a conserved tracer and its transport distance is much shorter than that of sulphate, especially in remote air, low in ammonia. During transport of NH_4NO_3 to Bird Island, it is very likely to encounter regions so low in NH_3 and HNO_3 that NH_4NO_3 should thermodynamically not exist. Thus, observations of very long-range transported air masses show different results. “Aged outflow plumes exhibit a different composition with enhanced particulate sulfate and organics fractions, low particulate ammonium (below 10 %) associated to sulfate, and nitrate contributions near 1 % (Dunlea et al., 2009). The changed composition is due to several factors such as wet deposition of highly water soluble aerosol which is especially important for nitrate components, and the formation of secondary species such as particulate sulfate and secondary organic aerosol. It has been established that SOA forms roughly within one day downwind of the emission source (DeCarlo et al., 2008; Brock et al., 2008) while the exponential production time for sulfate is around 3 to 4 days in summer (Brock et al., 2008). In the absence of cloud processing this means that young (1-2 days) anthropogenic plumes are dominated by organic matter, while with increasing age sulfate will gain in importance.” (from Schmale 2011, dissertation).

Conclusions I would suggest removing details on island fauna – conclusions do not need to be a complete summary of the text.

Response: Details have been removed.

Table 5. AA mode at 1.48 μm is arbitrary as many other second mode diameters. Due to unknown APS undercounting the overlap between SMPS and APS is very poor which makes fitting unreliable or even unrealistic.

Response: Thank you for spotting this error. The second AA-OA mode is $0.71 \pm 1.61 \mu\text{m}$. This has been corrected in Table 5. All second modes occur in the SMPS spectrum, we doubt that these measurements are arbitrary. The poor overlap between APS and SMPS size distributions is a separate issue which however does neither impair SMPS nor APS size distribution fitting. The reasons for the poor overlap are discussed in the manuscript. Based on the comment regarding Fig. 7, we have now provided the original data and the fits to the size distributions for clarity.

Please note that we encountered an error in the SMPS calibration which we corrected, hence the different diameters in the submicron modes. This is relevant to Table 5 and Fig. 4 and 7.

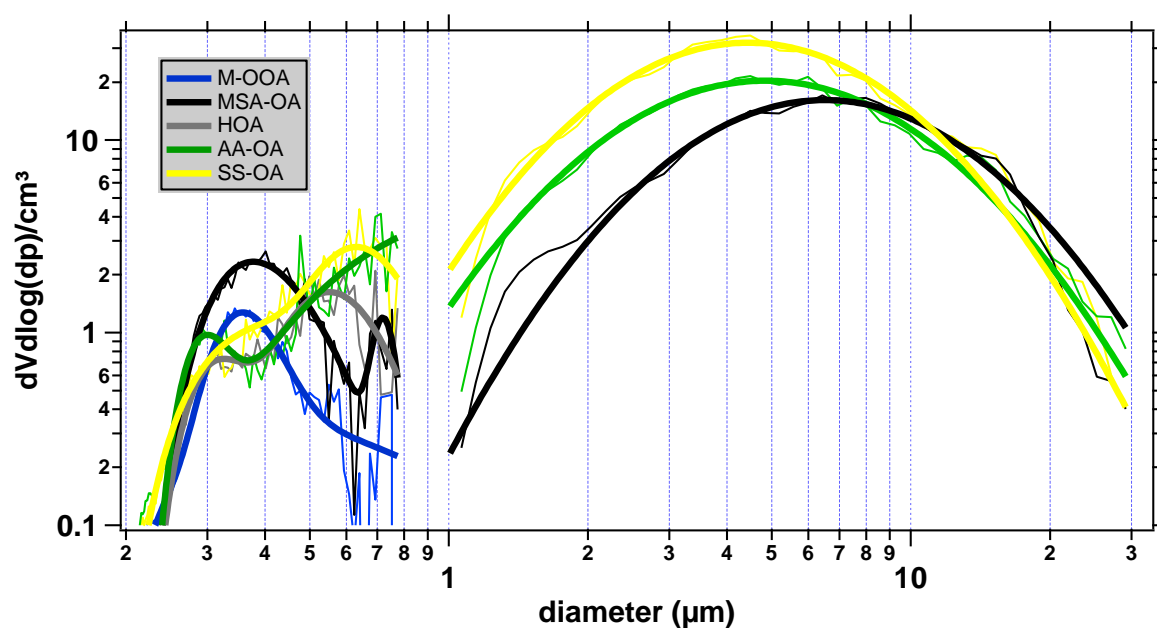


Fig.7. Why MOOA volume distribution is lacking supermicron spectrum? MSA-OA spectrum jiggle at SMPS size limit is an indication of SMPS performance issues. For transparency and clarity reasons I would suggest the authors may consider presenting actual modes in the graph.

Response: There is no M-OOA supermicron spectrum because no clear size distribution could be derived in the isolated period as shown in Fig. 6 when M-OOA was the dominant species. Please see answer above for the revised Fig. 7.

