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

## Anonymous Referee #1

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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 is was an extended 8week 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 C2097

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.

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.

## 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).

## Introduction

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

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).

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

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 8weeks, 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.

Experimental and Methods

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

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).

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).

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

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 600C".

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

C2099

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.).

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

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.

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.

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 120hours unrealistic. For instance, 120hour 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.

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).

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.

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.

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

Chapter 3.5 Consider uncertainty of the trajectories in this chapter as commented be-

C2101

fore.

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? 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 4.37um.

Chapter 3.7 There is no Na37CI+isotope – it is isotopologue. When stating Na37CI same applies to Na35CI, not NaCI+. Same in line 9. 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).

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.

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.

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

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 R2 is a variance and it is squared correlation coefficient. The correlation with wind speed was already commented above.

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.

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

C2103

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.

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

Table 5. AA mode at 1.48um 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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 8261, 2013.