

## Response to Reviewer #2

### Review of Schmale et al. paper

#### General comments

This manuscript investigates the origin of marine aerosols in a sub-Antarctic region (Bird island), especially focusing on the importance of organic biogenic sources. First an overview about the aerosol chemical composition, size distribution and acidity at this location is provided. Then positive matrix factorization is applied in order to retrieve organic components from aerosol mass spectrometer data. Three organic marine sources were identified (a methane sulfonic acid OA factor, a marine oxygenated OA factor, and a sea salt OA component). In addition an amino acids/amine related factor (having a biogenic origin) and an HOA component were separated. The sources of organic and inorganic nitrate are also described. A method to identify sea salt particles contribution using aerosol mass spectrometer measurements is also presented. Interesting correlations between air mass origin and OA sources are also reported. The overall quality of this work is good and the manuscript is quite well-written. I recommend publishing this work after the authors respond to the following comments.

#### Specific comments

-Page 8263, line 3: is 13% the sum of primary and secondary OM? Otherwise report all the percentages for POA, SOA and sea salt.

**Response:** Yes, the 13 % refer to both primary and secondary OM. For clarity we have included the following note: “including primary and secondary organic matter (together 13%)”

-Page 8264, line 13. Not only DeCesari et al. 2011 investigated MOA origin, but other studies about MOA are available in literature (e.g. Chang et al., ACP, 2011)

**Response:** Thank you. We have included the reference.

-It would be interesting to see in the supplementary material some plots for the collection efficiency estimation using the SMPS data.

**Response:** We did not use the SMPS data for CE estimation because the relationship was too variable. We tried to derive a linear regression between the calculated mass based on the SMPS measured particle volume and the total mass concentration measured by the AMS. To derive a particle density we used the following specific densities: Organics: 1.6 g/cm<sup>3</sup>; ammonium nitrate: 1.73 g/cm<sup>3</sup>; ammonium sulfate: 1.77 g/cm<sup>3</sup>; sulfuric acid: 1.84 g/cm<sup>3</sup>. The average particle mass density for the whole campaign was 1.71 g/cm<sup>3</sup>. We used both the complete volume measured by the SMPS, and only up to  $d_{mob} = 500\text{nm}$  which corresponds to a  $d_{va}$  of about 855 nm where the AMS inlet starts to cut off significantly larger particles.  $R^2$  is well below 0.1 in both cases, while the slope is 0.73 when including all SMPS data, and 0.78 when only using SMPS data up to 500 nm. The colour

coding indicates that the relationship is poorer for lower particulate sulfate concentrations, and seems to be partly due to non-refractory particles such as sea salt contributions (see colour coding by the PIKA derived sea salt species). Based on the low  $R^2$  values and available literature (Middlebrook et al. 2012) we decided to use  $CE = 0.5$ .  $CE = 0.5$  can be interpreted as the lower envelop (see attached Figure S1, now also included in the supplementary material).

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.

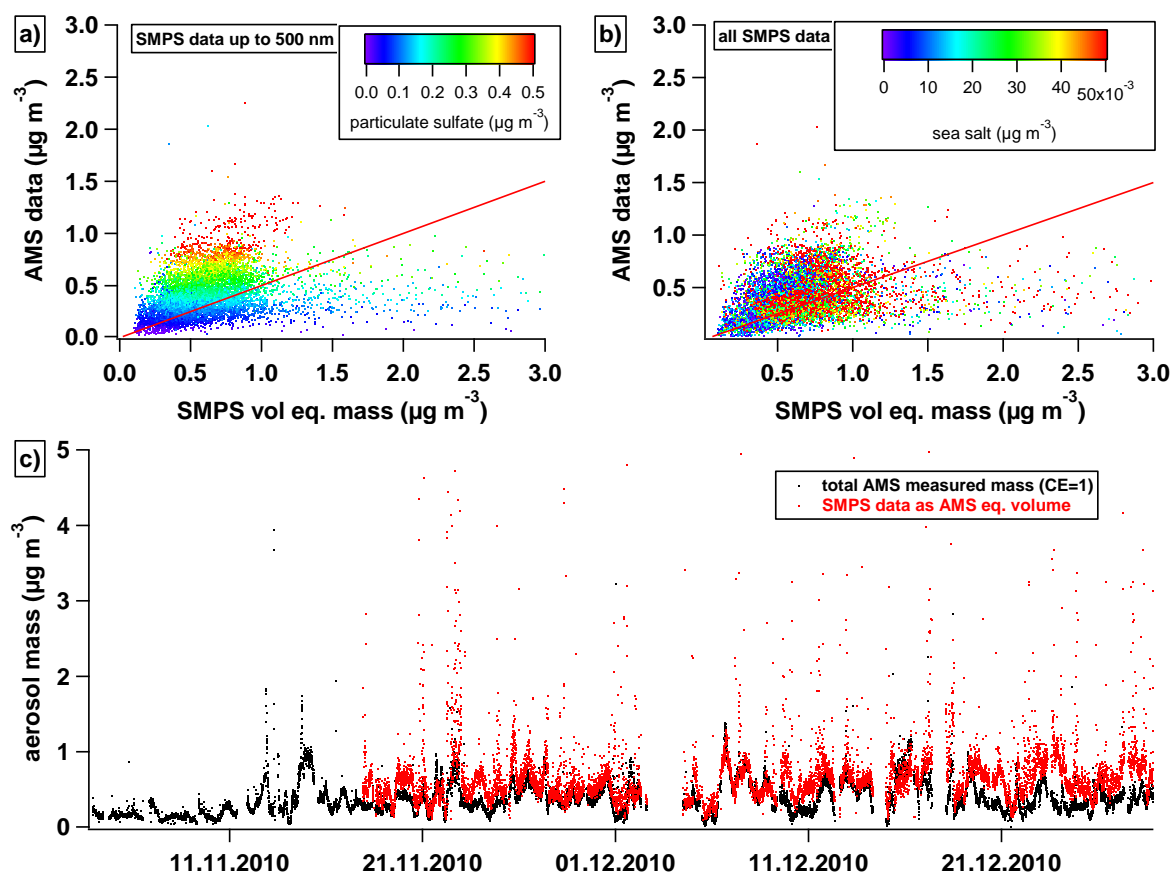


Fig. S1: AMS aerosol mass versus SMPS volume equivalent mass for a) SMPS data up to 500 nm  $d_{mob}$  and b) for all SMPS data. C) Time series of AMS aerosol mass versus SMPS volume equivalent mass data. Note that the AMS data is not corrected for sea salt after Ovadnevaite et al. (2012) by upscaling  $m/z$  57.95 ( $\text{Na}^{35}\text{Cl}^+$ ) by a factor of 51.

-Page 8269, line 10: is 350  $\mu\text{g}/\text{m}^3$  the ammonia emission? Be clearer if you want to report an emission factor, a concentration etc.

**Response:** The manuscript now says: “However, BI is characterized by many large seabird colonies and Antarctic fur seal rookeries that emit quantities of ammonia leading to ambient concentrations of up to 350  $\mu\text{g m}^{-3}$  (unpublished data, paper in prep.)”

-Page 8271, line 19: did you scale up by a factor of 51 the signal corresponding to the ion  $\text{NaCl}$  or  $m/z$  58? You should report the exact mass of  $\text{NaCl}$  or clearly write that you used the  $\text{NaCl}$  ion signal.

**Response:** We have clarified in the manuscript that we refer to  $m/z$  57.95, i.e. the  $\text{Na}_3\text{SCl}^+$  ion.

-Up to which  $m/z$  did you perform the ions fit for the HR analysis? You should mention it in the text.

**Response:** Up to  $m/z$  128. The information is now included in section 2.2.1.

-It is not clear why the UMR PMF was performed and not the HR PMF. However, the authors report several information about the elemental composition measured by the AMS (elemental ratios, some ion fits, mass spectra of the PMF factors). It would have been more interesting to perform the high resolution analysis not only focusing on specific periods (fig. 6) but on the whole dataset. This seems to be a very interesting and unique dataset, therefore the application of PMF on high mass resolution data would really help in understanding important features of OA sources. Please, clarify your choice of using UMR data. It would be great to see HR-PMF results.

**Response:** This is what we answered to reviewer 1: 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. 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.

-Why do the authors report the C:N ratio instead of the N:C value?

**Response:** Thank you for pointing this out. The reported values are the N:C ratio, while we erroneously wrote C:N ratio. We have corrected this in the manuscript now.

-How was potassium measured? From AMS measurements? No discussion is reported about that, while this is an interesting topic to be addressed.

**Response:** the first paragraph in Section 2.2.1 says: "The reported mass concentrations of  $\text{SO}_4^{2-}$ , Org,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{K}^+$  were derived from the high-resolution data PIKA analysis performed up to  $m/z$  128."

-Page 8280, line 2: report a reference for the  $\text{NH}_4\text{Cl}$  related statement.

**Response:** Done. Canagaratna et al., 2007

-Page 8281, lines 6-11: again performing PMF on the high resolution data would have avoided the inclusion of inorganic ions.

**Response:** This is correct. However, deriving a sea salt PMF factor is in itself a good result, so that the "mix" of organic and inorganic ions is not a caveat at such. Moreover, this result is even able to demonstrate that sea salt and organics from sea spray are closely linked.

-Page 8281, lines 3-5: the reference to Hildebrandt et al. 2011 is correct, however their analysis is not on high resolution data and therefore m/z 58 might contain not only nitrogen containing ions but also NaCl contributions as you found in your analysis.

**Response:** This is correct. By stating “are also indicators for amines” we do not exclude the possibility that Hildebrandt et al. have seen sea salt as well. However, the authors argue that their amine-OA does not seem to be linked to sea salt.

-Page 8283, lines 7-13: How does the MSA MS comparison look like with the Zorn et al. (2008) spectrum?

**Response:** We have added the following information to the manuscript: “Although the correlation coefficient with the AMS database MSA-OA laboratory reference spectrum (L\_STD\_Q\_027\_MSA) after Phinney et al. (2006),  $R^2 = 0.14$ , and with the 600°C spectrum reported by Zorn et al. (2009),  $R^2 = 0.32$ , are rather low...”

-No discussion is provided regarding the HOA factor. Although it is not the major topic of the paper, few words are necessary.

**Response:** We have added the following sentences: “The diesel generator is the research facility’s only power supply and was thus continuously operated. It is located at an angle between 240° and 270° with an approximate distance between the generator and the sampling inlet of 30 metres. Correlation with the average HOA mass spectrum from 15 different measurements reported by Ng et al. (2011) was high with  $R^2 = 0.98$ .”

-Specify for Figures 9, 10 and 14 if the represented fit is related to the open, closed or difference signal of the AMS.

**Response:** Done.

-Your interpretation of the AA factor having origin from chicks hatching is very interesting however it is not supported by any measurement or evidence. It seems to be only a speculation while the ‘guano’ source seems to be more plausible, although some differences between the AA and reference spectra are found. How would you further support your first interpretation?

**Response:** In the manuscript we report all available evidence and show that the hatching chicks are the most plausible explanation for the observations based on a process of elimination. (1) There is no correlation with any other time series that we recorded. So, marine origin can be ruled out. (2) The signature must be of biological origin that is dominated by amines and amino acids and almost no carbohydrates which is the case for egg constituents. Both chemistry and wind directions point towards the penguin colonies. (3) The correlation with the guano spectrum is poor, and moreover

this exhibits other characteristic signatures (carbohydrates, oxalates and uric acid) that are not present in the ambient factor. In addition, guano debris is unlikely to be found in the submicron particle size range. There is no further data available that we could discuss which we state in the manuscript as well and suggest that further investigation is needed. We clearly state that we can only infer the source but are unable to provide direct evidence.

-Chang et al. 2011 identified a M-OOA factor. It would be interesting to compare your factor with this work.

**Response:** We have now added the following sentence to the manuscript: "In addition, the M-OOA spectrum appears to be similar to the marine oxygenated organic aerosol PMF factor observed by Chang et al. (2011) in the Arctic Ocean which has a correlation coefficient of  $R^2 = 0.81$  with the spectrum from Ovadnevaite et al. (2011) and an  $R^2$  of 0.63 with the Bird Island M-OOA factor ( $R^2$  would be 0.89 when including  $m/z$  28, 29, 43 and 44 in the regression). Based on the unit mass resolution spectrum the contribution of  $m/z$  44 to the organic mass spectrum ( $f_{44}$ ) is 17 % for the Arctic M-OOA while our M-OOA factor shows an  $f_{44}$  of 22 %."

-Page 8293, line 16: it seems to be a quite high O:C ratio (2.2) for the MSA-OA factor. How can you explain it? Have you compared it with any other MSA-related OA high resolution analysis?

**Response:** We compared it to the spectrum reported by Ge et al. 2012 where the O:C ratio is about 1.8. The high contribution from oxygen is due to ion fragments such as  $\text{CH}_4\text{SO}_3$ ,  $\text{CH}_4\text{SO}_2$ ,  $\text{CH}_3\text{SO}_2$  or  $\text{CH}_2\text{SO}_2$ .

-It would be useful to have summarized in a table the  $R^2$  values for the correlations between the PMF factor time series and external data (with whom you validated your solution) and between your PMF mass spectra and reference MS.

**Response:** We have added a table with the  $R^2$  correlation coefficients.

-In the SI you investigate the  $f_{\text{peak}}$  variation in the -1, +1 range. However  $Q/Q_{\text{exp}}$  does not vary much, so you are considering only mathematically equivalent solutions. You should investigate a wider  $f_{\text{peak}}$  range in order to get a  $Q/Q_{\text{exp}}$  variation of at least 10% (see Ulbrich et al., 2009).

**Response:** We have added two panels to figure S3 showing the results of exploring  $f_{\text{peaks}}$  between -5 and 5 in steps of 1. The difference of values for  $Q/Q_{\text{exp}}$  for  $f_{\text{peak}}=0$  and  $f_{\text{peak}} = -5$  is roughly 20%. We added the following sentence to the SI text: "Since Zhang et al. (2011) recommend running PMF for a range of  $f_{\text{peaks}}$  such that the range of  $Q/Q_{\text{exp}}$  values is at least 3 % above the minimum  $Q/Q_{\text{exp}}$ , and since this was not the case for the  $f_{\text{peak}}$  range -1 to 1, we additionally explored the  $f_{\text{peak}}$  range between -5 and 5 in steps of one (Fig. S3 g) and h). However, no other more plausible was found in the larger range. ". In the manuscript in Section 2.2.3 we added ". It is recommended to run PMF for a range of  $f_{\text{peaks}}$  so that the range of values for  $Q/Q_{\text{exp}}$  is at least 3 % above the minimum  $Q/Q_{\text{exp}}$  (Zhang et al., 2011). As this was not the case for running  $f_{\text{peaks}}$  between -1 and 1, we explored

solutions of fpeaks between -5 and 5 (in steps of 1), see the supplementary material for further details. “.

-In Fig. S4 you report the residual analysis. The time series of the scaled residuals show some interesting peaks which correspond to events not described by PMF. Do you have any explanation for that? Moreover the mass spectra of the scaled residuals show that some masses have much higher residuals than the average (e.g. m/z 68, 84, etc.). can you make any comment for that?

**Response:** Regarding the time series, it is well possible that cigarette smoke and kitchen activities contributed to the residuals. We used a smoking and cooking log book for everyone on the station, and took the “contaminated” data out of the time series. However there is no guarantee that we recorded all of these events or that recirculation brought affected air masses back to the measurement site at a later stage. With respect to specific m/z such as 83, 96 and 126 they belong to signatures from sea salt ( $\text{Na}_2^{37}\text{Cl}$ ,  $\text{Mg}^{37}\text{Cl}$ ,  $\text{FeCl}_2$ , respectively). M/z 79 is related to the MSA ion component  $\text{CH}_3\text{SO}_2$  and the hydrocarbon like OA ion  $\text{C}_6\text{H}_7$ . For m/z 68 the missed ion seems to be  $\text{C}_5\text{H}_8$ .

#### Technical corrections

**Response:** We have done all technical corrections and do not give a specific response to the following comments. For comments where this is not the case, we give a response.

-Page 8262, line 6: insert a comma before 2%. The sum of the AMS relative chemical composition is not 100% but 99%. Please correct it through all the manuscript and graphs.

-Page 8262, line 12: the sum of the OA PMF relative contribution is not 100% but 99%. Please correct it through all the manuscript and graphs.

-Page 8267, line 16: define “dmob”. You define it in the following page, but it is necessary to introduce this abbreviation already here.

-Page 8267, lines 18-20: check the correctness of the sentence (the W-mode MS air beam is of the V-mode...)

-Figure 2: report the slope for the linear fits in panel b

-Page 8276, line 23: “the met station” should be replaced with “the meteorological station”

-Page 8279, line 10: it is not important to mention that SMPS measurements started on 15 Nov, since the measurement periods for all the instruments are reported in Table 3.

-Page 8279, lines 11-13: check the correctness of this sentence. “a function of d<sub>mob</sub>” seems not to be well connected with the rest of the sentence.

-Figure 3 is mentioned the first time at page 8286, but you should introduce it earlier.

-Figure 4: the numbers for the pie chart referred to the 3-12 Nov are too small to be read. Modify the first sentence of the caption as following: Average mass contribution of individual chemical species (the numbers in parenthesis indicate the average mass concentration in ug/m<sup>3</sup>).

-Figure 6: some m/z are highlighted with a number and an arrow. if they are the m/z specific of each factor, for HOA you should report additional m/z (like 41, 57 etc.).

-Page 8280, lines 20 and 23: define the acronyms for HOA and M-OOA.

-Page 8282, line 4: the sentence is not clear. The word ‘allowed’ seems to be out of place.

-Figures 9, 10, and 14 could be included in the supplementary material instead of in the main text.

**Response:** We consider the information in these graphs as essential for the manuscript. Reviewer 1 even asked for an additional figure of this kind. So we keep them in the main manuscript.

-Figure 17: you can report the reference elemental ratios also for HOA (and possibly also for other factors) since available.

**Response:** We would like to keep the information focused on the marine aerosol. Further references are given in the text of section 3.10.1.

-Figure 18 and 19: draw the slopes of the linear fit and report the fitting coefficients (slope and R<sup>2</sup>).

-Page 8297, line 7: use a proper word instead of “remainder”