

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

### **Anonymous Referee #2**

Received and published: 17 May 2013

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

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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.
- 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)
- It would be interesting to see in the supplementary material some plots for the collection efficiency estimation using the SMPS data.
- 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.
- Page 8271, line 19: did you scale up by a factor of 51 the signal corresponding to the ion NaCl or m/z 58? You should report the exact mass of NaCl or clearly write that you used the NaCl ion signal.
- Up to which m/z did you perform the ions fit for the HR analysis? You should mention it in the text.
- 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

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your choice of using UMR data. It would be great to see HR-PMF results.

- Why do the authors report the C:N ratio instead of the N:C value?
- How was potassium measured? From AMS measurements? No discussion is reported about that, while this is an interesting topic to be addressed.
- Page 8280, line 2: report a reference for the NH<sub>4</sub>Cl related statement.
- Page 8281, lines 6-11: again performing PMF on the high resolution data would have avoided the inclusion of inorganic ions.
- 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.
- Page 8283, lines 7-13: How does the MSA MS comparison look like with the Zorn et al. (2008) spectrum?
- No discussion is provided regarding the HOA factor. Although it is not the major topic of the paper, few words are necessary.
- Specify for Figures 9, 10 and 14 if the represented fit is related to the open, closed or difference signal of the AMS.
- 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?
- Chang et al. 2011 identified a M-OOA factor. It would be interesting to compare your factor with this work.
- Page 8293, line 16: it seems to be a quite high O:C ratio (2.2) for the MSA-OA factor.

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How can you explain it? Have you compared it with any other MSA-related OA high resolution analysis?

- It would be useful to have summarized in a table the R<sup>2</sup> 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.
- In the SI you investigate the f<sub>peak</sub> variation in the -1, +1 range. However Q/Q<sub>exp</sub> does not vary much, so you are considering only mathematically equivalent solutions. You should investigate a wider f<sub>peak</sub> range in order to get a Q/Q<sub>exp</sub> variation of at least 10% (see Ulbrich et al., 2009).
- 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?

Technical corrections

- 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

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- 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 dmob" 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 mz are highlighted with a number and an arrow. if they are the mz specific of each factor, for HOA you should report additional mz (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.
- Figure 17: you can report the reference elemental ratios also for HOA (and possibly also for other factors) since available.
- 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"

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#### References

Chang, R. Y. W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhardt, J. F., Stohl, A., Orr, L. H., Hayden, K., Li, S. M., Hansel, A., Tjernström, M., Leaitch, W. R., and Abbatt, J. P. D.: Aerosol composition and sources in the central Arctic Ocean during ASCOS, *Atmos. Chem. Phys.*, 11, 10619-10636, 2011. Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, 9, 2891-2918, 2009. Zorn, S. R., Drewnick, F., Schott, M., Hoffmann, T., and Borrmann, S.: Characterization of the South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer, *Atmos. Chem. Phys.*, 8, 4711-4728, 2008.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C2476/2013/acpd-13-C2476-2013-supplement.pdf>

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

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