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Atmospheric Chemistry and Physics Discussions

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

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This manuscript investigates the origin of aerosols in the marine boundary layer at the sub-Antarctic island of Bird Island. This was done during austral summer by deploying an aerosol mass spectrometer. The derived chemical composition of submicron aerosol is then discussed in terms of sources especially focusing on the organic fractions that account for 22%. The organic aerosol fraction is made of marine oxygenated organic aerosol (M-OOA, 40 %), methanesulfonic acid (25 %), amino acids/amine attributed to local penguin colony emissions (18%), sea salt organic (7 %) and locally produced hydrocarbon-like OA (9 %). The quality of this work is good and innovative and the manuscript is mostly well written. At some places however the discussion in

terms of sources may be improved a bit (see more detailed comments below). I recommend publication of this work that is definitely relevant for ACP after the authors consider the following comments or suggestions.

Response: We thank the reviewer for the comments and suggestions which add important information to the manuscript especially with respect to the MSA-OA and particulate sulfate issue.

1. There are too many abbreviates in the text: while AMS, AA, MSA, MOOA, SSOA, and HOA are useful, the use of other like BI for Bird island, POA for primary organic aerosol, MOA for marine organic aerosol, BAS for British Antarctic survey, IE for ionisation efficiency, CE for collection efficiency, UMR etc making the text unwieldy.

Response: While we understand the reviewer's comment, we would like to point out that all these are standard abbreviations. We have replaced all "BI" and "BAS" by the full names.

2. It is a pity that, asides from the sophisticated methods like AMS and SMPS, no common bulk filter sampling was made to fill the gap of sea-salt aerosol. Page 8278 (line 21) some unpublished data are mentioned ammonia) but again did really no bulk aerosol sampling was done?

Response: There will be a companion paper as indicated on page 8278 which however will focus on soil and atmospheric gas phase analysis. Filter samples were taken, however they have not been analyzed. We cannot wait with the publication of this manuscript until this might happen.

3. Line 13 page 8262: by definition there is no organics in sea salt: please change this wording (sea spray would be OK without changing your abbreviate).

Response: Thank you for pointing this out. We have made the changes accordingly throughout the manuscript, also in response to Reviewer 1.

4. Page 8266, line 14: say something like "the local topography and quasi-permanent

significant winds strengthen the atmospheric turbulence and hence the mixing of local emissions in the lower atmospheric layer at the site".

Response: We have modified 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.”

5. Page 8269 line 10: say that emit large amount of ammonia leading to atmospheric concentrations up to 350 micrograms m-3.

Response: We have modified the sentence to: “However, Bird Island 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 μg m-3 (unpublished data, paper in prep.)”

6. Page 8278, line 22: Since there is not so many works reporting ammonia concentrations at remote sites at which large bird colonies are sitting I would suggest to add "such high concentrations of ammonia (from 20 to 100 microgram m-3) were also measured in summer at the Dumont d'Urville site located on the Ile des Pétrels at the East Antarctic coast (66S) where 15000 breeding pairs of Adélie penguins are living (Legrand et al., 2012).

Response: Done.

7. Page 8279, line 9: you can also add that "For the coastal Antarctic site of Neumayer located at 70S facing the south Atlantic ocean and free of penguin colony Legrand et al. (1988) reported typical ammonium to non-sea-salt sulfate ratio close to 2% pointing out the very acidic nature of non-sea-salt sulfate aerosol there.

Response: Done.

8. Section 3.6: This short section needs to be reworked since (1) there are some mistakes on the DMS oxidation pathways and (2) we can discuss a bit further your figure

19 (correlation between MSA and sulfate). Both MSA and sulfate are produced via the DMS oxidation but you cannot oxidize MSA into SO2 (the direct oxidation of MSA into sulfate is possible on hydrated aerosol but though to be slow). So please modify the text accordingly. Concerning your Figure 19 you may extend a bit the discussion as follows: The lower envelop of the relationship between sulfate and MSA shows a slope close to 4.7 (i.e. a MSA to sulfate ratio close to 20%). 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)).

Saltzman, E., Savoie, D.L., Zika, R.G., and Prospero, J.M.: Methane sulfonic acid in the marine atmosphere, J. Geophys. Res., 4, 227-240, 1983. Jourdain, B., and Legrand, M.: Seasonal variations of dimethyl sulfide, dimethyl sulfoxide, sulfur dioxyde, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d'Urville (December 1998-July 1999), J. Geophys. Res., 106, 14,391-14,408, 2001.

Response: Thank you for pointing this out for proving such in depth explanation. We have entered the following correction: “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 you 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."

9. 9. Section 3.8: I agree with the assumption that amino acids and amines are related to the penguin activities. Possible to strengthen this assumption, did the authors try to relate AAOA and non sea salt potassium (see section 3.10.3) ?

Response: AAOA and non sea salt were found to be not correlated (R2 below 0.002). Thus, we cannot use it to strengthen the assumption that amino acids and amines are related to the penguin activities.

10. Section 3.10.3. First sentence: High wind speeds would also enhance emissions of ornithogenic soils as well.

Response: We have included this statement in the section.

Page 8295, line 2: This sentence needs to be reworded since bacterial decomposition of uric acid provides ammonium (ammonia) and oxalate but not potassium. In fact, the observed enrichment in potassium with respect to sea-salt (indeed observed by Legrand et al. 1998) is due to penguin nasal excreta.

Response: Thank you for the clarification. We have reworded the sentence to: "High enrichment of potassium with respect to sea salt in aerosol has been found during the summer months in Antarctica in the vicinity of a penguin colony, originating from penguin nasal excreta (Legrand et al., 1998)."

11. Conclusions: the text needs to be shortened. Also avoid references there.

Response: We have deleted the paragraph on the local island fauna to shorten the text and removed some of the references.

12. Figure 11: can you calculated (and show in Figure 6 as well) non sea-salt potassium ?

Response: Non-sea salt potassium is excluded from the PMF analysis because it is not part of the data input. So we cannot include it in figure 6. We have included non-ss K in figure 11 .

13. Did the authors have some idea of which chemical species would be a good proxy of marine oxygenated organic aerosol in the marine boundary layer? What about oxalate or longer chain dicarboxylates for instance: Indeed, first ethene emitted from the marine biosphere may act as a precursor of oxalic acid via the aqueous phase oxidation of glyoxal and hydroxyacetaldehyde into glyoxylic acid thereafter oxidized into oxalic acid. Warneck [2003] estimated that in the marine atmosphere, 8 to 16 ng m-3 of oxalic acid may be produced by the oxidation of ethene. Second, unsaturated fatty acids such as linoleic and oleic acids, that are common in phytoplankton, may act as precursors of C4 and C5 diacids via the breakdown of azelaic acid provided by reaction of fatty acids with ozone.

Response: Based on the particle phase only data that we have and the performed PMF analysis together with the high resolution mass spectra, we unfortunately cannot infer any of these chemical processes. Some of the organic ions found in the M-OOA factor are shown in Fig. 10.

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