

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

Anonymous Referee #3

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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

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consider the following comments or suggestions.

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.
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 Page 8278 (line 21) some unpublished data are mentioned (ammonia) but again did really no bulk aerosol sampling was done?
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).
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".
5. Page 8269 line 10: say that emit large amount of ammonia leading to atmospheric concentrations up to 350 micrograms m⁻³.
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 Pétréls at the East Antarctic coast (66°S) where 15000 breeding pairs of Adélie penguins are living (Legrand et al., 2012).
7. Page 8279, line 9: you can also add that "For the coastal Antarctic site of Neumayer located at 70°S 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.

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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 dioxide, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d'Urville (December 1998-July 1999), *J. Geophys. Res.*, 106, 14,391-14,408, 2001.

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) ? 10. Section 3.10.3. First sentence: High wind speeds would also enhance emissions of ornithogenic soils as well. 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. 11. Conclusions: the text needs to be shortened. Also avoid references there. 12. Figure 11: can you calculated (and show in Figure 6 as well) non sea-salt potassium ?

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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.

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