

Interactive comment on “High Summertime Aerosol Organic Functional Group Concentrations from Marine and Seabird Sources at Ross Island, Antarctica, during AWARE” by Jun Liu et al.

Anonymous Referee #3

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Comments on Liu 2018 Antarctica aerosol

General Comments

This paper covers a year’s worth of organic aerosol measurements in a region that is rarely sampled and sheds valuable insight into the chemical composition of Antarctic aerosol. The paper is well-written and the figures and tables are clear and legible. Aside from minor corrections and qualifications, I have just one concern with the current form of the manuscript. The authors claim a connection between carboxylic acid variability and downwelling radiation that, for reasons I describe below, is misleading. Unless the authors can clarify and justify this correlation, I would recommend that the discussion of that connection be omitted. Otherwise the paper needs only minor revision before it is suitable for publication. Given that this aspect may take more work to revise, I am selecting major revision in the online evaluation. However, the changes should not be overly burdensome.

The authors thank the referee for the review. We have addressed the concern about the carboxylic acid discussion and have clarified that point below. We also addressed other minor comments and concerns, and these have improved the manuscript as itemized below. **(Page and line numbers in this response reference the location in the discussion paper where the text is inserted. The revised manuscript will note these revisions separately with tracked changes when it is posted.)**

Specific Comments

Pg 2 line 22: please give a value range for the “high fraction” of OH observed previously
We added the range requested as follows: "...high fraction of hydroxyl group (61% of OM for the North Atlantic and 47% of OM for the Arctic)..." (P2 line22)

Pg 2 line 25: similarly, what range of ON mass fractions have been observed? Is it a minor component, or major? Or highly variable?

We added the range as follows: "Organic nitrogen has also been identified as a tracer component (0.02 to 10 ng m⁻³)..." (P2, Line 25)

Pg 5 line 5: I don’t see SLCE defined before it is use as an abbreviation

We thank the referee for noticing this and have corrected this as follows: "...which we attributed to short-term local contamination events (SLCE) (Figure S1)." (P4 Line 29)

Pg 7 line 4: I’m unclear as to what the “factors identified as urban combustion emissions” is that correlates to the FFC factor. Do the authors mean “factor spectra”? Like, other FTIR PMF spectra? Please clarify.

We have clarified this as follows: "... with factor spectra identified previously..." (P7 Line 4)

Figure 6 and discussion on page 8 (and in conclusion/abstract): Drawing any relationship about photochemistry from the correlation between M&S carboxylic acid and DWR is misleading. The observed correlation, as I understand it, is simply the correlation between the M&S factor strength and downwelling radiation time series, since the carboxylic acid attributed to the M&S factor is always the same fraction of the factor (given in Fig 4), and so varies only as the strength of that factor. The same correlation coefficient (r) would be obtained for any of the functional groups present in the M&S factor and for the factor as a whole, as correlation coefficients do not change with addition/subtraction or multiplication by constants to the vectors being compared. Further, the downwelling radiation is varying only because of the season change (Fig 1) and the strength of the M&S factor, associated with the Adelie penguins, is also due to seasonal migration, so the observed correlation to downwelling is really just a product of the M&S factor and downwelling both having season characteristics. The authors would have to do more analysis and include other metrics to state that there was any connection to photochemistry evident in this data set. I would need to see this suggestion/discussion removed before recommending publication.

We thank the referee for this comment. We agree that the correlation to radiation itself does not indicate secondary aerosol formation given the overlap of the seasonality of the emissions and radiation. We have revised this discussion to note that carboxylic acids have been shown to be from secondary aerosol formation and that in this study they are associated with the natural seabird emission source. We have revised this section in the Discussion, in part in response to Referee #1:

[FROM RESPONSE TO REFEREE #1]"The measured acid group concentration is likely to be a secondary aerosol contribution since photochemical oxidation has been shown to form highly oxidized molecules including carboxylic acids by photochemical reactions (Alves and Pio, 2005; Charbouillot et al., 2012) . Acids are also present in trace amounts in seawater (Gagosian and Stuermer, 1977; Kawamura and Gagosian, 1987) , but the higher concentrations measured here are likely to only be explained by secondary processes. The carboxylic acid group mass concentration that was associated with the M&S factor was correlated moderately to downwelling shortwave irradiance ($r=0.75$, Figure 6), supporting the idea that the carboxylic acid group mass was from photochemical reactions." (P8 Line 7)

[FROM RESPONSE TO REFEREE #1]"Carboxylic acid group mass fractions have also been identified as secondary photochemical products based on their correlation to solar radiation in clean, open-ocean conditions (Frossard et al., 2014) . However, since the seabird emissions were only high in summer when radiation was also generally high, the correlation to radiation does not provide evidence of photochemical contributions in this case. Interestingly, the carboxylic acid group associated with the FFC factor had no correlation ($r= 0.09$) to downwelling shortwave irradiance. This difference may be because the local emissions from McMurdo Station facilities reached the Cosray site in less than 5 min (since McMurdo Station was 2 km away and wind speeds were 6 m s⁻¹ on average) making them essentially "fresh" primary particles, whereas those from the large upwind penguin colony took 6 hr (since Cape Crozier was 100 km away and wind speeds were 6 m s⁻¹ on average) to reach the site giving them approximately 50 times

more time for photochemical reactions leading to SOA production. It is also possible that the anthropogenic gas-phase precursor emissions had lower SOA acid yields but there is little evidence to support this (Rickard et al., 2010; Wyche et al., 2009; McNeill, 2015). The source of the vapor-phase organic precursors of the summer seabird acid groups is not known, but given their substantial contribution to mass is worthy of further investigation." (P8 Line 13)

In addition, we have revised the following sentences in these two paragraphs to better support this point:

"The carboxylic acid group mass concentration that was associated with the M&S factor was correlated moderately to downwelling shortwave irradiance ($r=0.75$, Figure 6). "(P8 Line 7)

"The measured acid group concentration is likely to be a secondary aerosol contribution since photochemical oxidation has been shown to form highly oxidized molecules, including carboxylic acids (Xu et al., 2013; Barbaro et al., 2017; Kawamura and Gagosian, 1987; Sax et al., 2005; Charbouillot et al., 2012; Alves and Pio, 2005; Claeys et al., 2007; Alfarra et al., 2006; Stephanou and Stratigakis, 1993)."(P8 Line 13)

We also revised the Abstract and Conclusion as follows:

Rephrased from "...sources were correlated to incoming solar radiation, indicating that some OM formed by secondary pathways." to "Carboxylic acid group contributions were high in summer and associated with natural sources, likely forming by secondary reactions. "(P1 Line 25)

Rephrased from "was well correlated to downwelling shortwave irradiance ($r=0.69$) and was likely from secondary products of photochemical reactions" to "...was high in summer and was likely from secondary products of photochemical reactions..." (P9 Line 4)

Technical Corrections

There are extra spaces after most of the references when they end a sentence. Please edit the Latex code that is causing that.

The format is corrected as suggested.

In a number of cases there are spaces between value and % symbols, beginning in the abstract.

We thank the referee for noticing them. The format is corrected as suggested.

Pg 2 Line 1: insert a space between In and 1966; Pg 2 line 18: omit comma after "found that"

We have corrected these two typos as suggested.

References

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