

## ***Interactive comment on “Particulate trimethylamine in the summertime Canadian high Arctic lower troposphere” by Franziska Köllner et al.***

### **Anonymous Referee #3**

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Köllner et al present aircraft-based single-particle mass spectrometry (SPMS) results from flights in July 2014 in the Canadian High Arctic during NETCARE. The main individual particle types observed included trimethylamine and levoglucosan-containing particles. This is an important dataset that provides the first insights into amines in the changing Arctic and greatly improves our knowledge of Arctic aerosol mixing state. Concerns and suggestions (including major concerns about particle type assignments and associated conclusions) are described below.

During revision, the authors should work to improve the writing, as there are some grammar mistakes throughout the manuscript, some of which are noted below. Also,

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there are over 10 “paragraphs” that consist of 1-3 sentences each and do not represent full paragraphs with fully developed thoughts; these sentences should be incorporated into longer paragraphs in the revision. There are two in preparation manuscripts that are referenced in the manuscript – Bozem et al 2017 and Molleker et al 2017 – yet neither the full reference or manuscript are provided for review purposes.

Major Comments:

- In particular, I have concerns about the low fraction of particles that appear to have been classified/identified. While over 7000 particles were chemically analyzed in the study, the percentages discussed in Section 3.2 and shown in Figure 5 indicate that only 46% of the particles were classified/identified in the data analysis. This is very low and seems concerning in that other particle types may be missing in the analysis. To help better inform the reader, it would be useful in the methods section to state the number of particles chemically analyzed (mass spectra produced) by ALABAMA during the study, as well as the fraction with dual-polarity mass spectra and fraction classified by the CRISP software. In addition, the phrasing “Chemical classes” in Table 1 is confusing, as it appears in the text that these refer to marker species, rather than particle types; the authors might consider using the phrasing “ion markers” or similar to differentiate Tables 1 and 2, or the authors might consider combining Tables 1 and 2 for improved clarity.

- Page 1 Line 6, Figure 2, Section 2.5, and Page 19 Lines 4-5: These sentences, figure, and section detail the laboratory measurement of TMA. However, the mass spectrum of TMA has already been published, using 266 nm LDI single-particle mass spectrometry, by Angelino et al. (2001), and the other literature cited in Section 2.5 (Healy et al 2015, Rehbein et al 2011) simply cite Angelino et al. (2001) for this assignment, which isn't clear as written. Therefore, unfortunately, this does not represent a new result. The authors are encouraged to move Figure 2 and Section 2.5 to the supplemental and to remove the sentences highlighting this result in the abstract and conclusions.

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- Table 1: It would be most useful to cite SPMS lab characterization studies when possible and include the citation (e.g. Angelino et al (2001)) in the table itself, as it appears there is room. Non-SPMS literature (e.g. #6, 10-12) is not appropriate to cite here for the assignment of ion markers. No SPMS literature is cited for EC, for example. When lab study literature is available, field study literature is less appropriate, as it often simply cites other lab studies (e.g., Healy et al 2015 and Rehbein et al 2011 simply cite Angelino et al 2001 for TMA ion markers, so all three references are not necessary; Corbin et al 2012 also cites Silva et al 1999 for the levoglucosan assignment), and including field + lab literature in a comprehensive manner has not been done here (nor would it be necessary). Silva et al (1999) is the only study cited that shows a SPMS mass spectrum of levoglucosan. In that work,  $m/z$  -73 does not appear to be discussed as a tracer, so it is not clear where this ion attribution is coming from (could  $m/z$  -73 correspond to glyoxylic acid?).

- For greater clarity for the non-SPMS reader, the authors are encouraged to label the “Na/Cl” particles as “sea spray aerosol”, after defining and explaining the corresponding mass spectrum and citing SPMS laboratory studies of sea spray aerosol (e.g. Gard et al 1998 (Science), Prather et al 2013 (PNAS), Guasco et al 2014 (ES&T)). In the abstract and Section 3.2.2, the authors attribute peaks at  $m/z$  -45, -59, and -71/-73 to carbohydrates (stated as levoglucosan and cellulose), but no single-particle mass spectrometry sea spray aerosol literature is cited to support these assignments and attribution to organic carbon coating sea spray aerosol. Further Prather et al and Guasco et al (noted above here), show SPMS spectra of individual sea spray particles produced in the laboratory and internally mixed with organic carbon but do not mention these peaks. The authors are encouraged to view these papers to see if greater knowledge of the Arctic sea spray aerosol can be gained through comparison to these previously published laboratory studies of sea spray aerosol produced from biologically active waters. Also, the authors might look at Cahill et al 2015 (Analytical Chem.) and Pratt et al 2009 (Nat. Geosc.), which shows ATOFMS of primary biological particles and has some of these markers.

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- I would argue that the lack of negative ion mass spectra in high RH environments, particularly marine environments (e.g. Spencer et al 2008 (JGR)), is common. Therefore, I think that the authors can more strongly state that the lack of negatives is likely due to particle water suppression of negative ion formation. Recently, Guasco et al 2014 (ES&T) observed  $m/z$  19 ( $H_3O^+$ ) in sea spray aerosol particles that did not produce negative ions, further supporting the previous work of Neubauer et al.

- Simoneit et al 1999 (Atmos. Environ.) showed that levoglucosan can be used as a tracer of biomass burning (BB), so it is confusing that the authors attribute the levoglucosan to pollution plumes (e.g., Page 11 Line 6) rather than BB. Hu et al 2013 (Sci. Rep.) published a manuscript, using levoglucosan as a tracer of BB, and showing a significant impact of BB in the Arctic. The authors should be aware, however, that levoglucosan is not a conservative tracer as it can degrade during transport (e.g. Hennigan et al 2010, GRL). Further, the authors should consider comparing the K-dominant spectra to SPMS BB mass spectra (e.g. Silva et al 1999 (ES&T), Hudson et al 2004 (JGR), Pratt et al 2011 (ACP)), as the K-dominant particles are likely BB in origin (although they can have significant organic aerosol coating still – see Pratt and Prather 2009, ES&T). Given the significant number of SPMS papers attributing  $K^+$  to BB, it is unclear why the authors state that “potassium in a single particle spectrum must be interpreted with caution” (Page 16, Line 11). It would be useful to conduct air mass trajectory analysis and look at satellite smoke/fire maps to investigate if transported BB plumes could be detected to support the observations discussed herein of the levoglucosan-containing and  $K^+$ -containing particles. I would encourage the authors to consider a broader particle class of BB particles.

- Ge et al 2011 (Atmos Environ) shows that TMA is also emitted from BB. Given that the non- $K^+$ -containing TMA particles are primarily found within the BL (so a marine source makes sense) and the  $K^+$ - and levoglucosan-containing TMA particles are found at higher altitudes, consideration of TMA from BB may be warranted. Currently this potential source of TMA is not mentioned.

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-  $m/z$  -26 (CN-) and -42 (CNO-) are typically attributed to organic nitrogen fragments (e.g. Fergenson et al 2004 (Analytical Chem.) and Pratt et al 2009 (Nat. Geosc.)), rather than cyanide (Table 2 and text), in SPMS. These are also common peaks in BB SPMS spectra (e.g. Silva et al 1999). On Page 11 Line 3, the authors cite Li et al 2000 for the assignment of cyanide, but that is not a SMPS paper.

- Page 11 Line 5: It is stated that there is no vertical dependence in the EC-containing particles, but do the authors have sufficient statistics to test this with only 138 EC particles detected over the entire study at all altitudes? How many at each altitude were detected?

- Figure 9 and associated text: Given the issue of mostly positive-only mass spectra, the authors are encouraged to consider analysis of only the dual-polarity mass spectra here, as MSA as a negative ion would be similarly affected compared to sulfate. Without knowledge of the fraction of total mass spectra not having negative ions, this analysis is difficult to interpret.

- For further support of the presence of SOA, the authors might consider looking at  $m/z$  -43 (Qin et al 2012, Atmos. Environ.). It would also be useful to show the non-K-containing TMA average mass spectrum, as the marine source of these particles is a big highlight of this work – and yet Figure 4 shows particles with a large K peak, which may be from BB, as discussed above.

#### Minor Comments:

- Page 1 Lines 6-9: This sentence can be clarified, as the comparisons are incomplete as written.

- Page 2 Lines 5-6: Fix sentence structure – particles are not a process.

- Page 2 Lines 9-10: Need references.

- Page 2 Line 9: Suggest changing “pollution sources within” to “pollution transport to”, as the polar dome changes transport patterns, not the emissions themselves.

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- Page 2 Line 10: Change “leading” to “leads”.
- Page 2 Lines 12-15: Not all of this literature corresponds to nucleation papers as implied, and many recent Arctic aerosol growth papers are also missing here. Also citations are not properly included in the sentence (formatting issue).
- Page 2 Lines 29-31: Sentence is missing reference.
- Page 3 Line 23: Fix grammar – change “parameters, several trace gases as well” to “parameters, and several trace gases, as well”.
- Figure 1 caption: Change “Image are” to “Image is”.
- Figure 1: Flight paths are difficult to view on small inset.
- Page 4 Line 2: Delete sentence as it is unnecessary and not incorporated in a paragraph.
- Page 5 Line 5: Give size range of PSLs used.
- Page 5 Line 8: Suggest adding the phrase “of individual particles” after “bipolar mass spectra” for clarity for the non-SPMS reader.
- Page 7, Lines 6-8: This statement seems to contradict the statement on page 5 line 25.
- Page 8 Lines 6-7: Rather than “biogenic emissions”, the authors might consider the phrase “Arctic oceanic and terrestrial emissions” here, as the data is not presented to support the current statement (and the results show near equal contributions from TMA- and levoglucosan-containing particles).
- Page 8 Line 21: Word “respectively” is misplaced.
- Figure 4 caption: Fix grammar – “spectrum” vs “spectra” – and repetition of this word.
- Table 2: For greater clarity, align the text in the right-most column with the ion assignments in the third column.

- Page 12 Lines 1-2: This sentence is redundant – essentially the repeat of the previous sentence.
- Page 12 Line 9: Sorensen et al 2005 is not appropriate here. The authors might also consider Gard et al 1998 (Science), which showed SPMS of sea spray aerosol aging.
- Page 12 Lines 11 & 13: “NaCl<sub>2</sub>” should be “NaCl<sub>2</sub>-“ as these are ions.
- Figure 7 seems redundant and unnecessary considering the spectrum in Figure 4.
- Figure 8: This could be moved to the supplemental as it essentially repeats the information already in Figures 5 and 6, is more difficult to interpret, and has fewer particles included per bin to allow robust trends to be easily observed.
- Figure 10: To make the figure easier to read and interpret, the authors should consider showing as a fraction of TMA particles, rather than all particles, and also show the TMA particle numbers, rather than total particle numbers, as that information is already in Figure 5.
- Page 16, Line 2: Do the authors have sufficient statistics in all size bins to state that these particles are only from 280-380 nm?
- Page 17, Lines 4-5: If 8 July is a focus here, why did the authors choose not to show the wind data, even in the supplemental?
- Figure 14: Please define “potential emission sensitivity” in the caption or text. The units of seconds are not clear.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-505>, 2017.

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