

## ***Interactive comment on “Amines in Boreal Forest Air at SMEAR II Station in Finland” by Marja Hemmilä et al.***

**Marja Hemmilä et al.**

marja.hemmila@fmi.fi

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We thank the Referee for very detailed and helpful comments, which we address in details below.

1. There are far too many data tables and figures that are irrelevant to the structure of the results and discussion. Most can be replaced with a single sentence. These detract from the quality of the observations and should be relocated to a Supporting Information document. These are noted in detail below.

Asked figures and tables were moved to Supporting Material.

2. The Authors claim that they are reporting the longest time series of amines measurements to date, but the measurements are short-duration periods made in different

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months. A time series implies continuous data collection and the authors should revise the manuscript to be clear that they are reporting eight weeks of observations from different months over the course of a year from the same observation site. Further to this point, the sampling strategy reported and the findings discussed in the paper are all weakened because of the intermittent nature of these observations. The limitations of the dataset need to be presented clearly. Figure 7 is the only depiction of the full measurement time series and it appears that even within each observation period that there are gaps in the data which are not clearly explained. How can the Authors justify their conclusions regarding monthly/seasonal trends if they do not measure continuously throughout each?

Number of data points in each month was added to Table 4. We also added clarification in Experimental section that due to instrumental problems good quality data was captured only 8 weeks, although we measured continuously. Even though measurements cover only 8 weeks, to our best knowledge, this is still largest data set of amine concentrations.

3. The manuscript does not appear to have a clear purpose or objective. There are several discussions made throughout the manuscript that are not joined in a clear narrative, the final paragraph of the introduction for example, which confuses the meaning and scientific contribution of the findings.

a. The Authors present an advancement in atmospheric amine measurement capabilities through the use of an ion chromatography-mass spectrometry system, but do not clearly demonstrate the necessary performance metrics (e.g. a sample chromatogram demonstrating the ability to speciate the suite of analytes likely to be encountered in the atmosphere). The data then presented in the tables and figures is still largely below the instrument detection limits (e.g. Table 4), so is this improvement really meeting the observational needs of the research community?

We have added chromatogram to Supplement Material. It would be great to have better

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time resolution and lower detection limits, but this is the best which is possible at the moment. Direct mass spectrometric methods have lower detection limits and higher time resolution, but data is not species specific.

b. A timeseries of diurnal observations and linkages to known boreal biogenic processes is discussed for some amines.

We added this sentence to Introduction.

c. The relationship of gaseous DMA to a variety physical observations is made, concluding that new particle formation is higher when both DMA and RH are high. To me, this manuscript is a first long-term survey of sources and phase-distribution of amines at the sub-pptv level in a remote boreal forest environment using supporting physical measurements to initiate a better understanding of this entire class of compounds relative to what we already know about ammonia. The Authors should carefully review the findings of their work and convey the purpose of their work clearly as it will also strengthen the structure of their results and discussion. The introduction should be subject to a major revision based on the determined purpose and presented structure of the resulting manuscript as it currently does not do so.

Introduction was improved.

4. The methods section is not detailed enough to evaluate whether the DLs for the MARGA-MS are robust and reliable. There are many issues here that need to be addressed that are detailed in the Technical Comments below.

Method section was corrected according to Technical Comments

5. The manuscript has many typographical and technical errors that should have been addressed prior to submission (e.g. use of the term 'aerosol particles'). The Authors are strongly encouraged to seek external review of their work by peers and colleagues after revision prior to resubmission for further review.

The manuscript has been checked by a native speaker.

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## Technical Comments

The following comments are not an exhaustive list of the corrections required for this manuscript to be acceptable for publication. The Authors, in addressing the major comments, will likely correct much of the unmentioned issues under their own revision.

1. Page 1, Line 15: The Authors state that they can separate and detect 7 different amines, but do not show any evidence of this performance, nor does the literature cited for the methodology used. If there is prior work demonstrating the quality of this method performance for amines, specifically, it should be cited and briefly summarized. If not, then the Authors are missing an opportunity to present a significant advance in the online measurement of atmospheric amines simultaneously in the gas and particle phases.

The chromatograms have been added to Supporting Material to demonstrate the separation of amines, and we have added more information about the method to the Experimental and Results sections.

2. Page 1, Line 17: The term 'possibly' is used here, which is speculative. Such conclusions, while potentially acceptable for the discussion, should not be present in an Abstract. Major findings with solid support only should be presented here.

The sentence with 'possibly' was deleted.

3. Page 1, Lines 21-22: There is no conclusive evidence presented for DMA and TMA biogenic sources. This is only true for EA.

EA correlated with monoterpenes, which has temperature dependent sources. DMA and TMA may for example have light dependent sources, like isoprene, or they may be emitted from soil.

4. Page 1, Lines 23-24: What is the purpose of presenting the means and medians for these measurements in the Abstract? This does not seem necessary.

In our opinion the concentration levels are the most important and newest result, and therefore we want to include them in the abstract.

5. Page 1, Line 27: '0.63 EA' This is an example of missed typographical errors that should be identified prior to manuscript submission.

We corrected the miss-typings.

6. Page 2, Line 34: The amine class of compounds can be more broadly defined. R- can be used to represent both H- and alkyl- substituents.

We wanted to make a clear difference between ammonia and amines.

7. Page 2, Lines 35 and 38: 'aerosol particle' is incorrect terminology. These are interchangeable terms and typically one or the other is chosen for use throughout a manuscript.

We changed so that we use only 'aerosol', when it is possible.

8. Page 2, Lines 44-45: 'and' is used twice in a row. Another example of missed typographical error.

We corrected that.

9. Page 3, Lines 67-68: The Authors have not presented any information on the range of amines that have been measured, or are even estimated, to be present in the boreal forest prior to this sentence evaluating the potential utility of prior published methods. Depending on the chosen purpose of the manuscript, the Authors should either expand on the findings of previous boreal measurements, focus on the performance of the measurement technique relative to other reports, or link these two themes with a motivation of greater breadth.

We took off the sentence with DLs, and replaced it with "in this method ammonia/ammonium samples could impede detection of some amines". However, the method was quite impressive.

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10. Page 3, Line 89: Why are the exact dates for the measurements not given? The datasets, such as Figure 7, clearly show that these periods were not subject to continuous observation and the details should be provided here.

Measurements were continuous, except when we were calibrating, measuring blank or cleaning the instrument, or when the instrument was broken. Unfortunately, even though we visited the instrument weekly and checked it via internet almost daily, and somebody in the field visited it almost daily, still sometimes afterwards we noticed, that something went wrong; so we took that data off. Number of proper measurement data points during each month was added to Table 4.

11. Page 4, Table 1: Move this to the SI and add soil humidity and soil temperature details to this section of the methods since they don't appear anywhere, but appear regularly throughout the results and discussion.

We have moved Table 1 to the Supplement Material.

12. Page 4, Line 103: Define the MARGA acronym first and then put the acronym in brackets.

We have changed that.

13. Page 4, Lines 105-106: This is far too brief of a description for the interfacing and operation of a mass spectrometer to an ion chromatograph. Does the MARGA suppress the IC eluent prior to analyte measurement? Were conductivity measurements made prior to, but in series, with the mass spectrometer? What solvent and what ratio to the IC mobile phase was added prior to the electrospray? What were the desolvation and transmission settings of the mass spectrometer?

We have added the information to the text. MARGA does not suppress the IC eluent in cation side. Waste line from cation conductivity detector was led to ESI-needle, and no additional solvent was added. The table about MS settings was added to Supplement Material.

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14. Page 4, Lines 112-113: Was the separation an isocratic or gradient separation? What was the time required for separation? What were the dimensions of the analytical column and what was the particle size of the stationary phase?

We have added the information to the text. Separation was isocratic, and the time was 15 min.

15. Page 4, Lines 114-116: Are these the DLs for the IC system or for the MARGA? That is, were the S/N = 3 calculated from blank injections, the measurements made in 'blank- mode', or from MARGA solvents analyzed when the inlet was overflowed with zero air? Given the need for very sensitive measurement capabilities outlined in the introduction, the Authors should present a more detailed description of how the DLs were determined and the quantitative metrics evaluated to conclude that they are reliable and robust representations of the capabilities of the MARGA. Characterizations of these parameters for IC systems measuring amines have been previously described by Erupe et al. (2010), Dawson et al. (2014) and Place et al. (2017), those with atmospheric interfaces by VandenBoer et al. (2011, 2012), and IC coupled to mass spectrometry by Verrielle et al. (2012)

The DLs are for the whole MARGA-MS –system (excluding the inlet), and the measurements were made in blank-mode. The references were gratefully checked and most of them were cited in the manuscript.

16. Page 5, Table 2: This belongs in the results section of the manuscript along with the remainder of the analytical performance metrics. The Authors could consider reporting the DLs as ng/m<sup>3</sup> for the particle channel and pptv for the gas channel to improve the clarity of this table.

We have moved Table 2 to results section.

17. Page 5, Lines 122-125: How was the d10-DEA introduced to the MARGA-MS as an internal standard? Was it added to the solvent in the particle and gas channels,

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to the post-suppressor organic solvent, or only to standards that were injected offline? What is the purpose of using this internal standard and how did it perform for the set of reported field measurements? Presumably it was used to track the spray ionization efficiency on an ongoing basis in the post-suppressor organic solvent, but this is not clear. The Authors should also indicate how the internal standard was utilized in back calculating the quantities of all the measured amines and whether it reduced uncertainty in the measurements and by how much. Also, why are the calibration standard values listed as 'approximate'? Further to this, the calibration range seems to be far above the observed values, which are typically below 10 ng/m<sup>3</sup>, which is the lowest calibration standard, and is therefore extrapolating the calibration below the determined range. The Authors should provide proof that the system sensitivity response from 0.1-10 ng/m<sup>3</sup> is the same as from 10-300 with at least a 3-point calibration for all of the analytes. They should use this information to determine their measurement accuracy and precision as well, which is not evaluated.

We have added to the text "DEA10 was used, because it behaved same way in IC-separation but had different mass than studied amines. 50,0  $\mu$ l of DEA10 was added to MARGAs ISTD solution bottle. When MARGA was taking the air sample, it was at the same time taking ISTD solution to similar sample syringes. When IC-analysis started, the ISTD and air sample solution mixed, and this solution went to IC-separation, conductivity detection and finally MS-detection. DEA10 was used to correct possible losses to instrumentation and correct changes of MS response." ISTD went through the same analysis than analytes, so it corrects the possible biases of the process. We have added accuracy and precision to Table 1.

18. Page 5, Lines 128-129: Since the MARGA was not operated continuously for the analysis of amines, it is important to specify whether the instrument blank values were collected before, during, or after the periods when continuous monitoring was being performed. Again, I presume this was performed immediately before, intermittently during, and immediately after each observation period so that backgrounds could be

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corrected throughout each observation period, but the explicit information needs to be presented in the manuscript.

Because MARGA-MS was running all the time (except when it was broken, or we were calibrating or cleaning it), the blank values were supposed to collect once a month. Unfortunately the instrument had habit to stop just before or during the blank running, so we missed those blanks.

19. Page 5, Lines 131-133: If the DMA backgrounds are different due to cycling between sampling syringes, it should be possible to explicitly assign a background correction to samples collected with each set of syringes instead of averaging, which will decrease both accuracy and precision of the measurement.

We were able to get better results with averaging, since blank subtraction did not correct the difference totally.

20. Page 6, Line 135: This should be the start of a new methods section that describes the DMPS measurements.

Corrected.

21. Page 6, Line 149: Regression calculations can allow some insight into the physico-chemical nature of the amines, but the results and discussion do little to explore the reasons why the variable the authors chose were investigated. What are the chemical and physical mechanisms that may be acting to release amines in the boreal environment? Is there a precedent from laboratory work or prior observations? Given those parameters explored, the working hypothesis seems to be testing whether there is similar release and exchange of amines in the boreal as might be expected given the extensive literature on ammonia. If this is the case, this reasoning should be emphasized throughout the manuscript and supported by citing the relevant literature.

The chemical and physical mechanisms behind the emissions are beyond the scope of this manuscript.

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22. Page 7, Lines 167-168: 'amines were mainly in the aerosol phase' - the averages appear very close to 0.5 and likely are if the variability in the data is considered. The range of the gas fraction values presented in Table 3 suggests this is the case. It would be more accurate to say that the gas fraction was variable, with an average and standard deviation given for the entire dataset.

We included number of gas phase data and number of aerosol phase data above detection limit, and with this information it is correct to say, that amines were most in the aerosol phase.

23. Page 7, Figure 1: Move this to the Supporting Information. It repeats all of the data presented in Figure 2 and since the observations do not span the entire month, it may be more accurate to add the observation dates to the bar labels in the legend. It would be more informative for the authors to present some continuous data in a figure that includes many of amines, ammonia/ammonium, the uncertainty in each measurement, and the DLs so that the quality of the MARGA-MS data can be ascertained.

We have moved the Figure 1 to the Supporting Material

24. Page 8, Figure 2: How many points are off scale in each of these panels? Why are the DEA measurements suggesting that there were negative quantities detected? Where are the November and December measurements for  $\text{NH}_3+\text{NH}_4$ ?

Off scale bars showed the maxima of all measurements and this value is also shown in the figure. There are no negative values for DEA, minima are just detection limits. For some reason ammonia and ammonium data in winter was forgotten, but we have now added it.

25. Page 8, Table 3: Please check that the table formatting is done according to the guide- lines of ACP

We have changed the form of Table 3 (and other tables too).

26. Page 9, Table 4: Move this table to the Supporting Information and replace with

2- 3 simple sentences in the text. Why are both the mean and median values in this table? What does a difference between these two metrics tell us about the amine measurements and why? This table suggests that even MARGA-MS does not have adequate DLs for the boreal environment and the authors should comment on this in the discussion.

We have moved the Table 4 to the Supporting Material. With mean values we showed, that even though median (i.e. most of the data) was <DL, in some cases there still was remarkable concentrations above DL.

27. Page 10, Figure 3: Remove '(y-axis)' and '(x-axis)' from the caption. This is obvious. Consider a more descriptive caption.

We have removed '(y axis)' and '(x-axis)'.

28. Page 10, Figure 4: This date format is not consistent with previous figures, and the notation is not defined via the axis label. The data presented in this figure are clearly non-continuous between months and goes back to the points above regarding statements by the Authors suggesting that the dataset is continuous when it is not. What is the purpose of plotting rainfall on this figure? The discussion speculates on 'evaporation from melting snow and ground', but rainfall does not describe either of these processes. What is the physical or chemical rationale for this speculation? Is there precedent in the literature to support this?

We have added now the Figure 4b, which shows the effect of high night time temperature and decreasing wind speed, and this is also discussed in the text.

29. Pages 11 -18: The Authors compare their measurements for each species to those from other reports throughout. This would be more easily conveyed through the use of tables that present the data from this work in comparison to the findings of others, listing relevant parameters such as rural and urban settings.

We have made a table, that compiles the results of our and other studies.

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30. Page 11, Line 210: Why is TMA discussed before EA, but presented in Figure 6 following the description of EA in Figure 5? Please reorganize the discussion so that figures appear in the order that they are discussed.

We have re-organized the sections

31. Page 12, Figure 5: Most of the observations for EA are below the DL, so why is the line in the figure continuous? It would be more appropriate to add another trace here that denotes the cut off for the DL and to leave gaps in the EA dataset where the measurement is below the DL.

We changed the second x-axis so, that EA concentrations below DL are under it.

32. Page 13, Lines 265-266: Soils and surfaces in the boreal are acidic when measured in bulk, so it seems unlikely that deposition and re-emission is a plausible line of speculation. For example, a comparison using compensation point theory for ammonia in these environments could suggest that deposition should be the final fate of bases at the surface, and could support a similar case for the amines since they are stronger bases than ammonia. This would be strong evidence against deposition and desorption cycles and indicate other mechanisms of emission (e.g. decomposition of organic matter).

The surfaces of leaves and needles are probably not that acidic, but it is not known based on the discussion with forest scientists.

33. Page 13, Figure 6: Why did the Authors not explore the diurnal nature of TMA in July when the measured mixing ratios were highest? This compound is known to be released during the flowering of many plants to attract pollinators and should be discussed for context.

We chose to show diurnal variation in August, because it was more pronounced for DMA then. For TMA July and August looked the same.

34. Page 14, Line 279: 'concentrations of DMA vary with temperature' - Figure 7 does

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not demonstrate such a dependence, but the statistical findings in Table 5 do. There is no clear dependence to the eye in Figure 7 between DMA and air temperature.

We have made the Fig. 7 clearer, and also referenced to Table 5.

35. Page 14, Figure 7: These panels are not alphabetically labeled for reference in the caption. Previous figures suggest there were DMA measurements made in August, but they are not shown on this figure. Why is this? The findings in Table 5 suggest that the correlations between DMA and a number of parameters are worth noting and those plots would be more valuable than this figure. Consider replacing Figure 7 with a multi-panel figure showing these relationships and the regression statistics from Table 5. We have checked that all the DMA(g) data were <DL in August. We added scatter plots between DMA(g) and ambient parameters shown in Fig. 7 in to Fig. 8 according to reviewers suggestion. However we wanted to keep time series as well, because seasonal behavior is more obvious there.

36. Page 15, Table 5: There is very little here that is meaningful to the discussion. It can be replaced with the figure noted in the previous comment and a couple sentences in the text. Move to the SI or consider removing from the manuscript entirely.

Table 5 was moved to Supplement. We wanted to show that most of the compounds are not depending on ambient conditions.

37. Page 17, Table 6: Same comment as Table 5.

Table 6 was moved to Supplement.

38. Page 19-22, Figures 8 and 9, Tables 7 and 8: Only depict and present the most meaningful results. That is, present the figure panels that convey information central to the discussion which cannot be easily replaced with three or fewer sentences in the text. In this case, consider combining the most important findings from Figures 8 and 9 into one figure. Move the tables to the Supporting Information or consider removing them from the manuscript entirely.

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We have moved the Tables in to the Supplement. We removed Fig. 9, since the particles in aerosol phase observed by MARGA-MS cannot explain the cluster mode particle number concentration.

39. Page 24, Line 389: Rewrite conclusions in light of changes to the manuscript.

We have done that.

40. Page 25, Line 454: This is the incorrect format for this reference. The proper citation format is presented at the beginning of the relevant chapter in the IPCC report. Also, throughout this section, there is no need for the large indent following each new reference. A space between each reference is sufficient. There are a number of other errors throughout the reference section that the Authors should take time to address through careful inspection and consultation with the journal guidelines.

We have checked the reference lists and corrected the miss-typings.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-958>, 2017.

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