

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

Anonymous Referee #1

Received and published: 14 November 2017

The manuscript “Amines in Boreal Forest Air at SMEAR II Station in Finland” provides an in-situ observation of 7 amine species in both particle and gas phases along with ammonia and ammonium ion over a continental rural area at the Finnish boreal forest site, Hyytiälä, in year 2015 from March to December. The study lasted for a total of 8 weeks, spread out over 8 months. It applies a newly developed measurement technique for amines that combines online ion chromatography and an electrospray ionization quadrupole mass spectrometer. The data analysis relies on simple linear regression to explore the relationships between amines and several environmental factors including rainfall, soil temperature, soil moisture, ambient air temperature and ambient air relative humidity. In addition, the work is used to explore amine species, especially dimethylamine in new particle formation through nucleation process. The authors pro-

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vide considerate insights of diurnal and seasonal variations of amines over the study region, and highlight the different production mechanisms and sources among the detected amines.

The topic of this paper is relevant to the journal and has important scientific contributions to the knowledge of amines in remote continental area, especially with relative longer period observations compared with previous studies. The experimental design is good. However, improvements are needed in the Results section, especially for the quality of figures and tables, in order to deliver to readers more concise and better visualized results. Also, authors should provide more thoughtful interpretations before drawing conclusions.

Prior to publication, the authors should address the specific comments below.

1. Please provide detailed information of the sampling period. What was the rationale to pick the 8 weeks during the 8 months? Since the study emphasizes seasonal variations, how confident can one be with measurements from relative short sampling periods in each month to make conclusions about seasonal changes?

2. Section 2.2: Authors simply use one sentence to cite previous work as Junninen et al. 2009 without a brief description of what this portal is. A bit more information is warranted. In addition, Junninen et al. 2009 is missing in the reference list. Please check and add in.

In table 1, do environmental conditions have small or big variations during each month? please add standard deviations to each mean value. Also, it would be helpful to make statements of diurnal changes (i.e. day vs. night). Also, please provide information about rain, soil moisture, and soil temperature, as they are important environmental factors in the discussion.

3. Misleading description at the very beginning of section 3.1: "Figure 1 shows the monthly means and medians of total amine concentrations (sum of gas and aerosol

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phases) “. Figure 1 only shows means. Correction is needed.

It is confusing to claim monthly mean changes as seasonal variations (shown in figure 1) unless the authors define the seasons at first. In the figure, half of the species (EA, DEA, PA and BA) have different scales than the rest. Please consider using two different y-axis scale in one plot or having two separate plots in order to provide more clear trends for each species.

Please clarify the meaning(s)/significance of showing the sum concentrations of gas and particle phases measurements (Figure 1 and 2). Tables 3 and 4 seem to deliver similar cumulative results as Figures 1 and 2 but in separate phases, which are arguably better to understand.

4. Line 185-190: “The concentration increase in March is characterized with rain (Fig. 4) and the later increase in April took place during night with decreasing wind speed and higher temperature. This increase could be due to evaporation from melting snow and ground.”

In Figure 4, the time scale on x-axis is too rough to provide clear vision of diurnal variation. Improvement is needed.

It indicates rainfall is featured with high MMA concentration in March (Figure 4), which is mostly in the particle phase, as shown in Table 4. Does such high MMA relate to previous cloud processing? Except rainfall, do the other environmental conditions have potential influences? Authors should expand discussion here.

No detailed information of wind speed and ambient temperature is provided to support the discussion. More explanations and possible references could assist the discussion about evaporation from melting snow and ground.

5. For Section 3.1.4, the authors should include discussion to more extensive literature examining this species. There are a number of references in fact for all of the amines, but for DMA, at the minimum a couple of references with discussion of sources and

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behavior of DMA are the following:

Youn, J. -S., et al. (2015). Dimethylamine as a major alkyl amine species in particles and cloud water: observations in semi-arid and coastal regions, *Atmos. Environ.*, 122, 250-258, doi:10.1016/j.atmosenv.2015.09.061.

Murphy, S. M., et al. (2007). Secondary aerosol formation from atmospheric reactions of aliphatic amines, *Atmos. Chem. Phys.*, 7, 2313–2337.

6. Figure 5: Time scale on x-axis is too rough to tell diurnal circle. Improvement is needed.

7. Section 3.1.4: Authors emphasize DMA (and TMA) concentration higher in summer (i.e. August) due to biogenic sources. However, interpretations/discussion leading to that conclusion are not convincing in my opinion. It mentioned that DMA does not show correlation with biogenic tracer such as monoterpenes, while isoprene is noted as having light dependent emissions. Please provide supportive BVOC tracer information if the data is applicable. Are there BVOC tracers other than isoprene found related to variations of DMA and (or) TMA?

In Figure 6, DMA shows strong diurnal cycle while TMA doesn't. Is the DMA diurnal cycle found only during summer, especially August? Why is it that TMA does not have such a strong diurnal cycle as it also mentioned in section 3.1.2? Authors should expand discussions here.

8. Figure 7: The current plot is hard to show the clear relationship between DMA and selected environmental factors, especially for data around July and December.

Please consider zooming in time scale on x-axis, for an example, using a discontinued time series.

9. Line 295- 300: Does TMA negatively correlate with ambient temperature consistently or is this sensitive to season?

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Minor comments

1. Authors should consider adding a site map in section 2.1 in order to provide readers visualized information of study area.
2. Line 115: Why are the DL calculation methods for DMA and TMA different from the rest? In table 2, DMA shows different DLs in two time periods, while TMA doesn't. Please clarify the reason(s).
3. Table 1: What is the difference between “mean” and “average”? If they are same, please be consistent.
Grey shade is not necessary if the color does not have meaning. Same comment applied to Table2.
4. Table 2: Some species have a comma after their names while the others do not. Why NH₃ and NH₄⁺ are not mentioned in gas (particle) phase as the rest? Keep consistent style please.
5. Table 4: Typo for DMA median value (particle phase) in July. “4,9” should be “4.9”.
6. Figure 4: Add label for x axis. Same comment for Figure 5. The x-axis represents dates, but it is unclear. In contrast, Figure 7 has better x axis format. Please be consistent in plot style.
7. Figure 7: Units on y axis should be in parentheses.

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