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

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

Major issues:

1. The introduction to the manuscript consists of one paragraph talking about the importance of amines on new particle formation (NPF), and four paragraphs introducing existing measurement techniques. However in the results and discussion part, NPF events were not identified, and the detection method was also not the main focus of this paper. The authors should rethink the contents in the introduction so that it can motivate the highlights of this study. Because the authors use a novel measure- ment

technique, it would be valuable if they spent more time explaining its advantages and drawbacks.

We have improved the Introduction. We also have added more details and evaluation of the method to Experimental and Results sections

2. As amines are known for their very low ambient concentration (Ge et al., 2011a), it should be mentioned the length of measurement days, the total valid measurement numbers, and number of measurements above detection limits for each amines in each month. When the authors calculate mean or median concentrations, how do they account for the measurements that were below the limit of detection (e.g. in Figures 1 and 2)? Given how frequent these are, it will be very important for the interpretation of their subsequent analyses.

More detailed descriptions about the measurements have been added. In Table S2, number of data points in each month is presented. When we are calculating means or medians, the values bolew DL were taking account as 0,5*DL.

3. Also, it is hard to understand N numbers in Table 3. For example, DEA has only 6 data above detection limits. However, according to Table 5 and 6, there were at least 81(=79+2) valid gas phase concentration measurement and 26 valid aerosol phase concentration. If there were only 6 measurement with simultaneous detectable level of DEA in both gas phase and particle phase, it means that gas phase was more likely to have detectable concentration considering both channels had the same detection limit (Table 2). In that case, the authors should rethink about the statement made in Line 167 that amines were mainly in aerosol phase. The same problem happens to other amines as well.

We have improved former Table 3 (now Table 2). Beforehand it only presented the data above DL at the same time in gas and aerosol phase.

4. In the contents, the authors sometimes miss the indication of the phase in which

amines were talking about, such as line 185, line 212, line 230. I suggest the authors use NR3(g), NR3(p), NR3(tot) to indicate gas phase, particle phase and total concentration, respectively.

We have changed to NR3(g), NR3(a) and NR3(tot).

5. MARGA measures cations and anions simultaneously. How about anions such as nitrate and sulfate? They were not mentioned in this study. However, for the study of phase partitioning of amines, it is quite beneficial to learn whether amines are in the form of sulfate salts, nitrate salts or free amines (Ge et al., 2011b).

Unfortunately we don′t have the data from anion side.

6. Line 94 and table 1: The average humidity was very high in March, November and December, was it because of multiple rainy days? How rainfall would affect on-line sampling? Also, indicate the main wind direction.

There was rain and also in March melting snow and ground. Inlet line was sheltered for rain. We have added the main wind direction to Table S1.

7. Line 111: Were particles dried before measurement? If yes, was it before or after the inlet? Also, why chose to collect PM10 instead of PM2.5 or PM1.0?

No, the particles were not dried, because in Steam Jet Aerosol Collector they get wet, and also the eluent is water. We chose PM10 because it was available and commonly used with MARGA.

8. Line 114: Metrosep C4-100/4.0 is a short column designed for quick measurement of major inorganic ions. Can it separate seven aminiums with no interference from inorganic ions? Does DEA also co-eluent with TMA? It's better for authors to show sample/standard spectrum in the supplement.

We have added the chromatogram of standard to Supplement Material. DEA and TMA were co-eluating a bit, but MS detection separate them totally due to different masses.

9. Line 115: Where did blank signals of DMA and TMA come from? Was it contamination?

It was instrument background.

10. Line 131-133: More clarification.

We added to the text that we were not able to found more accurate reason for that.

11. Line 166 to 168: The data presented in Figure 1 and Table 4 have some discrepancies. The sum of gas phase and particle phase concentration (Table 4) did not equal to the total concentration in Figure 1.

Former Fig. 1 (now Fig. S4) contains also the values below the detection limit as 0.5*DL. In the former Table 4 (now Table S2) they are marked as <DL.

12. Figure 2: Why no ammonia/ammonium signals in November or December?

The signals were added, for some reason they were forgotten.

13. Line 188-189: more evidence or discussion is required to draw to that conclusion. Why melting snow could be a source when no linear regression was not identified between air temperature and MMA(g), and even negatively correlated with MMA(p) as stated in Table 5 and 6?

Also mixing and reactivity affect the concentrations of amines, and therefore hourly values do not correlate directly with temperature. In Table 5 and 6 there are the data from whole year, and snow melting period is not studied independently.

14. Line 215: show quantitatively about this increase.

Since this statement was too weak, we took of the sentence.

15. Line 222-224: In the study of Dawson et al. (2014), their TMA measured concentration ranged from 1.3-6.8 ppb, not ppm.

Corrected

16. Line 230-231: It's hard to tell on the graph when the maximum appeared.

Figure was clarified.

17. Line 231-232: EA and monoterpene having similar diurnal variation is the main evidence for the authors to address that EA has biogenic source. However, as shown in Figure 5, on July 11th, very high concentration of monoterpenes was observed, while EA concentration remained low. Compared to July 11th, on 12th, the monoterpenes concentration was only half of that on previous day, but EA concentration was more than tripled. On 14th, monoterpene had only one peak while EA exhibited two diurnal peaks. Their behavior was not consistent.

Concentrations in ambient air are determined by the balance between emissions, reactivity and mixing in the atmosphere. We are not claiming that sources are exactly the same, but similar. The source areas may not be the same either, and therefore wind direction affects too.

18. Line 255: The highest mean concentration of amines were usually observed in July, while the maximum concentrations prefer to appear in spring. Were there any intensive sources only in spring?

We are thinking melting snow, as we say in the text. We are going to study the spring snow more in future.

19. Line 264-270: Were the diurnal behavior the same for each sampling day? It is hard to tell solely from average data whether they were uniform pattern or influenced by some extreme data. Could DMA come from the re-suspension of soil since the authors measured PM10 (include coarse mode particles)?

Diurnal variation for every measurement day (tot. 5) were similar. We expect that amines are in small particles.

20. According to Figure 6, DMA also had nighttime peak at around 1:00 am. The double peak characteristic of DMA suggested it could be more than light-dependent

sources.

This is true and we have added a sentence to the text.

21. Line 296 to 297 and Line 304: R2 is too small to address the linear relationship.

We agree the reviewer, however, looking at the summer data only, there is a positive correlation between temperature and TMA(g). We added a figure to Supplement (Fig. S6).

22. Line 299: Previous text only discussed that MMA could originate from melting snow and ground, not TMA.

We added discussion also to chapter 3.2.2.

23. Line 344-349: The link between DMA and numbers of 1-2 nm particles is very weak. The authors should consider removing this section. The 'improved' relationship under high RH condition does not support amines contribution to NPF as high RH would suppress NPF (Hamed et al., 2011).

We considered it is important to show it is weak, since there has been lots of discussion about the contribution of DMA to NPF. We saw contradictory result than Hamed et al., and that is important to show.

24. Line 378-279: The correlation between PM10 NH4+ with cluster mode particle numbers is not very meaningful.

We agree, but that is an important information too. The Table 8 was moved to Supplement.

Minor issues: 1. Line 27: 0.63?

We took that off.

2.Line 47: HPLC is the abbreviation for high performance liquid chromatography.

We have changed that

3. Line 112: It is very unlikely to use 3.2 mol/L oxalic acid as eluent, as oxalic acid solu- bility under 25 degrees is only 1.6 mol/L.

There was a typing mistake; we have changed the unit to mmol/l.

4. Line 127: reword.

We did.

5. Line 202: Change ammonia to NHx=(NH3+NH4+)

We did.

6. Line 208-209: reword.

We did.

7. Line 215-216: reword.

We did.

8. Figure 3: there are four points largely deviated from the linear regression. Are they included in the calculation of linear regression as well?

Yes they are.

9. Figure 1 and Figure 3: change units to nmol/m3 or neq/m3 when comparing the relative importance of amines with NHx because amines have much higher molecular weight.

10. Put error bars on Figure 1 and Figure 6.

11. Figure 7: use breaks on x-axis to show clearer time series. Currently, it is hard to tell whether or not DMA shows similar temporal trend as T, ST or SH based on the graph.

We did

12. Table 6 is not discussed in the main contents, the authors can move it to supplement.

We did.

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