Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-958-RC3, 2017

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #3

Received and published: 30 November 2017

In this study, the authors measured the concentrations of several alkyl amines in the both gas phase and particle phase in boreal forest intermittently over a very long period. Analysis on the temporal variation, possible sources and relationships with meteorological conditions and particle number concentrations were made. This study provides a valuable dataset for the potential source apportionment of amines, which fits the scope of ACP. Highlights are the suggestion that soil can be both sinks and sources. However, in this manuscript, many of the analyses are very vague and are not clearly explained. Some critical information is missing in the manuscript. The authors should consider addressing the following issues before publication on ACP.

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

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.

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.

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.

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).

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.

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?

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.

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

Line 131-133: More clarification.

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.

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

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?

Line 215: show quantitatively about this increase.

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

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

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.

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?

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)?

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.

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

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

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

Minor issues: Line 27: 0.63?

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

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

Line 127: reword.

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

Line 208-209: reword.

Line 215-216: reword.

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

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. Put error bars on Figure 1 and Figure 6.

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.

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

Reference: Dawson, M. L., Perraud, V., Gomez, A., Arquero, K. D., Ezell, M. J., and Finlayson-Pitts, B. J.: Measurement of gas-phase ammonia and amines in air by collection onto an ion exchange resin and analysis by ion chromatography, Atmospheric Measurement Techniques, 7, 2733-2744, 10.5194/amt-7-2733-2014, 2014. Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part I. A review, Atmospheric Environment, 45, 524-546, 10.1016/j.atmosenv.2010.10.012, 2011a. Ge, X., Wexler, A. S., and Clegg, S. L.: Atmospheric amines – Part II. Thermodynamic properties and gas/particle partitioning, Atmospheric Environment, 45, 561-577, 10.1016/j.atmosenv.2010.10.013, 2011b. Hamed, A., Korhonen, H., Sihto, S.-L., Joutsensaari, J., Järvinen, H., Petäjä, T., Arnold, F., Nieminen, T., Kulmala, M., Smith, J. N., Lehtinen, K. E. J., and Laaksonen, A.: The role of relative humidity in continental new particle formation, Journal of Geophysical Research, 116, 10.1029/2010jd014186, 2011.

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