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 provide 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?

Our plan was to measure from spring to autumn, and not only 8 weeks. Unfortunately, the instrument had failiers and leaks, and 8 weeks was only we could achieve. Our data includes 117 data points in March, 112 in April, 163 in May, 91 in July, 133 in August, 128 in November and 54 in December and we have included this information to the Table 4. This is much more data than has been published earlier.

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.

“SmartSmear is the data portal for vizualisation and download of continuous atmospheric, flux, soil, tree, physiological and water quality measurements at SMEAR research stations of the University of Helsinki” sentence was added to section 2.2. We also added the missing reference to the list. Table 1 was moved to Supporting Material (Table S1), because Referee 2 asked. We added standard deviations to the Table S1. We also added information about rain, soil humidity and soil temperature to the Table S1, but the day and night means we did not find meaningful to add to the Table.

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 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.

The word “median” has been deleted.
We have added which months refer to which season in chapter 2.1.
Sentence “Total amine concentrations were used because we wanted to study amine sources and partitioning between aerosol and gas phase are dependent on environmental parameters.” was added to chapter 3.1.
Figure 1 was moved to Supporting material because the Referee 2 asked.

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 ar 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.

We have split the Figure 4 in three pieces to make it clearer. We also add wind speed and ambient temperature data in April to the figure.

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 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.

We have added more discussion to Section 3.2.2 (former 3.1.4) with Youn et al. We could not find much discussion about dimethylamine in Murphy et al, but the reference was valuable to Introduction.

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

More detailed time scale for x-axis was added.

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 circle found only during summer, especially August? Why is it that TMA does not have such a strong diurnal circle as it also mentioned in section 3.1.2? Authors should expand discussions here.

The DMA diurnal cycle is found only in summer. It is determined by the balance between emissions, reactivity and mixing in the atmosphere. Therefore the compounds emitting from the same sources can have different atmospheric concentrations. Usually the diurnal variation is mainly determined by mixing, causing daytime minima, but if emissions are light dependent or strongly temperature dependent, then the maxima is at daytime. This is mentioned in section 3.2.4. However, we have not mentioned in the text that higher summer time concentrations also indicate biogenic sources. This has been added to the text. Sources and source areas of DMA and TMA are not known, and different diurnal cycles can be caused by different balance between emissions, reactivity and mixing.

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.

We have made the Figure clearer according to the reviewers wish.

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

Yes, it is sensitive to season, we added a picture to Supplement (Figure S5).

Minor comments

1. Authors should consider adding a site map in section 2.1 in order to provide readers visualized information of study area.

We have added a site map to Supporting material.

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).

The DMA and TMA DLs were calculated from blank-values, because they had some blank, when the other compounds did not. We have added explanation to the text.

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.

We have changed "averages" to "means" and took the color off.

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.

We have added commas after every amine. We have added "gas" and "particle" after ammonia and ammonium.

5. Table 4: Typo for DMA median value (particle phase) in July. "4,9" should be "4.9".

We have changed it from "4,9" to "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. ase be consistent in plot style.

We have added the labels.

7. Figure 7: Units on y axis should be in parentheses.

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

Anonymous Referee #2

Received and published: 16 November 2017

General Comments

The Authors present several weeks of ambient observations of seven atmospheric alkyl amines in the gas and particle phases using the MARGA system interfaced with a quadrupole mass spectrometer. The quantities of these amines from each of the observation periods is reported and trends discussed from a variety of perspectives (e.g. diurnal, inter-monthly, etc.) They investigate a variety of correlations of the measured amines with accompanying physical observations made at the same location. Overall, this manuscript is not suited for publication in Atmospheric Chemistry and Physics without many major issues being addressed.

Major Comments

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 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 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.

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.

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.

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.

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.

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.

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.

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.

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.

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

We corrected that.

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 impressing.

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 than 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.

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.

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

We have changed that.

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 leaded to ESI-needle, and no additional solvent was added. The table about MS settings was added to Supplement Material.

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.

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 Verriele 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.

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/mˆ3 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.

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, 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 effi-

ciency 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 is are the calibration standard values listed as '~' which means approximate? Further to this, the calibration range seems to be far above the observed values, which are typically below 10 ng/mˆ3, 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/mˆ3 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 "DEA_{10} was used, because it behaved same way in IC-separation but had different mass than studied amines. 50,0 µl of DEA_{10} 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. DEA_{10} was used to correct possible loses 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.

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 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.

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.

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

Corrected.

Page 6, Line 149: Regression calculations can allow some insight into the physicochemical 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.

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.

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

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 NH3+NH4?

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.

Page 8, Table 3: Please check that the table formatting is done according to the guidelines of ACP

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

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.

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)'.

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.

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.

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

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.

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.

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.

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

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.

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.

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

Table 6 was moved to Supplement.

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.

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.

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

We have done that.

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.

References

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Interactive comment on

“Amines in Boreal Forest Air at SMEAR II Station in Finland”

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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.

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

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.

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.

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).

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.

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.

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.

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.

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

It was instrument background.

Line 131-133: More clarification.

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

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.

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

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

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.

Line 215: show quantitatively about this increase.

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

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

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

Figure was clarified.

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.

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.

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.

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.

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).

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.

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.

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:
Line 27: 0.63?

We took that off.

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

We have changed that

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.

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

Line 127: reword.

We did.

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

We did.

Line 208-209: reword.

We did.

Line 215-216: reword.

We did.

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.

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.

We did

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

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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Amines in Boreal Forest Air at SMEAR II Station in Finland

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Abstract. We measured amines in boreal forest air in Finland both in gas and particle phase with 1-hour time resolution using an online ion chromatograph (instrument for Measuring AeRosols and Gases in Ambient Air, MARGA) connected to an electrospray ionization quadrupole mass spectrometer (MS). The developed MARGA-MS method was able to separate and detect 7 different amines: monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA). The detection limits of the method for amines were low (0.2–3.1 ng m^{-3}), the accuracy of IC-MS analysis was 11–37% and the precision 10–15%. The proper measurements in the boreal forest covered about 8 weeks between March 2015 and December 2015. ~~With MARGA-MS we were able to separate and detect 7 different amines: monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA).~~ The amines were found to be an inhomogeneous group of compounds, showing different seasonal and diurnal variability. Total MMA (MMA(tot)) peaked together with the sum of ammonia and ammonium ion already in March~~, possibly due to evaporation from melting snow and ground~~. In March monthly means for MMA were <2.4 ng m^{-3} and 6.8±9.1 ng m^{-3} in gas and aerosol phase, respectively, and for NH$_3$ and NH$_4^+$, 52±16 ng m^{-3} and 425±371 ng m^{-3}, respectively. Monthly medians in March for MMA(tot), NH$_3$ and NH$_4^+$, were <2.4 ng m^{-3}, 19 ng m^{-3} and 90 ng m^{-3} respectively. DMA(tot) and TMA(tot) had summer maxima indicating biogenic sources. We observed diurnal variation for DMA(tot) but not for TMA(tot). The highest concentrations of these compounds were measured in July. Then~~In July~~ monthly means for DMA were <3.1 ng m^{-3} and 8.4±3.1 ng m^{-3} in gas and aerosol phase, respectively, and for TMA 0.4±0.1 ng m^{-3} and 1.8±0.5 ng m^{-3}. Monthly medians in July for DMA were <DL and 4.9 ng m^{-3} in gas and aerosol phase, respectively, and for TMA 0.4 ng m^{-3} and 1.4 ng m^{-3}. When relative humidity of air was >90%, gas phase DMA correlated well with 1.1–~~-~~2 nm particle number concentration (R^2=0.63) suggesting that it participates in atmospheric clustering~~new particle formation~~. ~~0.63~~ EA concentrations were low all the time. Its~~,~~ July means were <0.36 ng m^{-3} and 0.4±0.4 ng m^{-3} in gas and aerosol phase respectively, but ~~they~~ individual concentration data correlated well with monoterpene concentrations in July. Monthly means of PA and BA were all the time below detection limits.

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1. Introduction

In atmospheric chemistry and secondary-aerosol production bases are crucial since they can neutralize acids and therefore accelerate several processes, like e.g. subsequent growth of newly born aerosol particles. Furthermore bases are significant since they diminish acidification. Amines are gaseous bases, whose general formula is RNH_2, R_2NH or R_3N. Due to their effective participation in neutralization it is hard to detect their real atmospheric concentrations. Globally, the main known anthropogenic amine emissions are from animal husbandry, industry and compost processes, and the natural sources of amines are assumed to be ocean, biomass burning, vegetation and soil (Ge et al., 2011). It has been shown that ~~Amines~~ amines ~~also~~ affect hydroxyl radical (OH) reactivity and therefore all atmospheric chemistry (Hellén et al. 2014, Kieloaho et al. 2013).

Models based on quantum chemistry data have shown that ~~they~~ amines could participate in ~~aerosol~~ new particle formation (NPF) with sulfuric acid even at very low mixing ratios (Kurtén et al. 2008, Paasonen et al. 2012), and also experiments in laboratory have proved formation of aminium salts when amines react with nitric or sulphuric acid (Murphy et al. 2007). ~~Also~~ In addition the recent ~~laboratory~~ experiments at the CLOUD chamber shows that ~~already~~ even at minute concentrations of dimethylamine (DMA) ~~are able to produce~~ new particles with sulphuric acid are produced (Almeida et al. 2013, Kürten et al. 2016). Atmospheric aerosol~~ particle~~s ~~affect~~affect the climate, because they can act as cloud condensation nuclei (IPCC 2014). They also scatter and absorb ~~sun~~ solar radiation. ~~Amines also affect hydroxyl radical (OH) reactivity and therefore atmospheric chemistry (Hellén et al. 2014, Kieloaho et al. 2013).~~

Ambient concentrations of ~~gas~~ gas-phase amines have been measured earlier using different methods~~.~~: ~~Samples~~ samples have been collected in ~~phosphoric~~ phosphoric-acid-impregnated fiberglass filters (Kieloaho et al.~~,~~ 2013), to solid phase micro extraction fiber (SPME, Parshintsev et al. 2015), ~~-~~and to ~~ion~~ ion-exchange resin (Dawson et al. 2014) and they have also been percolated through an acidic solution (Akyüz ~~M.,~~ 2007). Samples have been analyzed later in the laboratory with various chromatographic techniques, such as gas chromatography coupled to mass spectrometry (GC-MS) (Akyüz 2007, Parshintsev et al., 2015), ion chromatography (IC) (Dawson et al. 2014) and high ~~pressure~~ performance liquid chromatography coupled to mass spectrometry (HPLC-MS) (Kieloaho et al. 2013). The above mentioned techniques have various shortcomings: quantitation based on collection onto fibers is problematic, collecting in filters requires long sampling times (usually several days), and percolating in acidic solutions requires intensive sample pre-treatment. Dawson et al. (2014) used weak cation exchange resin as a substrate for collection of gas-phase ammonia and amines. The method minimizes sample losses on walls during sampling and has quite short sampling times (less than an hour), but the detection limits remain too high for the boreal forest environment.

~~Also~~ In addition novel in-situ methods for measuring ambient air gas-phase amines have been developed, usually based on mass-spectrometric detection: chemical ionization mass spectrometry (CIMS), (Sellegri et al. 2005, You et al. 2014), ambient pressure proton transfer mass spectrometry (AmPMS) (Hanson et al. 2011, Freshour et al. 2014), chemical ionization atmospheric pressure interface time-of-flight mass spectrometry (CI-APi-TOF) (Kulmala et al. 2013, Sipilä et al. 2015, Kürten et al. 2016) and TOF-CIMS (Zheng et al 2015). These in-situ techniques have short time resolution and the limits of detections are small. However, these methods cannot separate amines with same masses (e.g. DMA and EA) and identification of the measured compounds remains uncertain. Chang et al. (2003) used high-efficiency planar diffusion scrubber IC (HEDS-IC) to successfully separate amines with identical masses.

~~Particle~~Aerosol phase amines have been sampled onto filters and analyzed later in the laboratory with similar techniques: LC-MS (Ruiz-Jiménez et al. 2012), GC-MS (Huang et al. 2014) and IC (Huang et al. 2014, van Pinxteren et al. 2015). With these methods sampling time was long (24~~–~~–133 h) and biases may be introduced due to transport and pretreatment of samples. VandenBoer et al. (2011) measured amine concentrations both in gas and particle phase with an ambient ion monitor –IC (AIM-IC). This method had 60-~~-~~min sampling time and relatively low detection limits (5~~–~~–9 ng m^{-3}). However, it could not separate TMA and DEA from each other. ~~and~~ Also because in atmospheric samples~~detection limits remain too high for measurements in the boreal forest.~~ ammonia/ammonium can be present in concentrations several orders of magnitude higher than amines in this method they can impede detection of some amines (e.g. MMA and EA).

These methods have been utilized in short campaigns from a couple of days to a couple of weeks. Only Kieloaho et al. (2013) measured for a longer period, but their sampling time was long (24~~—~~72 h). Most of the ~~measurements~~ studies discussed previously were made in urban or sub-urban areas, and only ~~some~~ a few measurements (Sellegri et al. 2005, Kieloaho et al. 2013, Kulmala et al. 2013 and Sipilä et al. 2015) were made in a boreal forest~~ site~~. In these studies the observed alkylamine concentrations ranged from below detection limit to ~150ppt$_v$, depending on the sampling time and the analysis method used.

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~~The~~ Here we present the in-situ ~~-~~method developed for atmospheric amine measurements in this study, using an online ion chromatography, instrument for Measuring AeRosols and Gases in Ambient air, coupled with mass spectrometer (MARGA-MS). ~~for atmospheric amine measurements~~ The method was used in the boreal forest, where amines are expected to affect secondary aerosol ~~particle~~ formation even at extremely low concentrations (Kurtén et al. 2008, Paasonen et al. 2012, Almeida et al. 2013). We report seasonal and diurnal variations of amines in boreal forest air and their partitioning between gas and ~~particle~~aerosol phase. A time series of diurnal observations and linkages to known boreal biogenic processes is discussed for several amines. Our investigation is the first long-term survey of sources and phase-distribution of amines at the sub-pptv level in a remote boreal forest environment. In this study we use supporting physical measurements to initiate a better understanding of this entire class of compounds relative to what we already know about ammonia.~~To our best knowledge our measurements constitute the longest time series of amine concentration measurements that have been made.~~

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2. Experimental

We measured amine and ammonia concentrations in 2015 from March to May (spring), July to August (summer) and November to December (early winter) with one-hour time resolution. However, due to instrumental problems, good-quality data were captured for a total only about 8 weeks.

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2.1 Measurement site

Measurements were performed in a Scots pine forest at the SMEAR II station (Station for Measuring Forest Ecosystem-Atmosphere Relations) in Hyytiälä, ~~Southern~~ southern Finland (61°51~~0~~´N, 24°17~~0~~´E, 180 m a.s.l., Hari and Kulmala, 2005, Fig. S1). The largest nearby city is Tampere, situated 60 km southwest from the station with approximately ~~364~~ 222 000 inhabitants in the city itself (although 364 000 in the wider metropolitan area). The instrument was located in a container about 4 met~~ers~~ers outside the forest in a small opening. In addition to pines, also small spruces (Picea abies) ~~were~~ grow~~ing~~ nearby. The forest was planted about 50 years ago and its current tree height is about 19 m. ~~We measured amine and ammonia concentrations from March to May, July to August and November to December 2015.~~

2.2 Meteorological conditions

~~Data for the m~~Meteorological ~~parameters~~ quantities were obtained from the SmartSmear AVAA portal (Junninen et al. 2009). SmartSmear is the data portal for visualization and download of continuous atmospheric, flux, soil, tree, physiological and water quality measurements at SMEAR research stations of the University of Helsinki. Table S1 shows the meteorological conditions during measurements periods.

~~Table 1. Mean temperature and average wind speed and humidity during measurements. We have used only the data that was measured at the same time as our amine data for the calculations.~~

~~**Month**~~	~~**Mean Temperature (°C)**~~	~~**Average Wind speed (m/s)**~~	~~**Average Humidity (%)**~~

~~**March**~~	~~0.4~~	~~2.6~~	~~87~~
~~**April**~~	~~3.7~~	~~2.4~~	~~75~~
~~**May**~~	~~9.7~~	~~1.8~~	~~69~~
~~**July**~~	~~13.8~~	~~1.5~~	~~75~~
~~**August**~~	~~17.8~~	~~1.4~~	~~74~~
~~**November**~~	~~2.7~~	~~2.9~~	~~95~~
~~**December**~~	~~-0.1~~	~~1.9~~	~~94~~

2.3 Measurement methods

2.3.1. MARGA-MS

~~In the present study w~~We used the ~~MARGA (~~instrument for Measuring AeRosols and Gases in Ambient air (MARGA, Metrohm-Applikon, Schiedam, Netherlands) (ten Brink et al. 2007) for sampling and ~~measuring~~separating amines. MARGA is an online ion chromatograph (IC) connected to a sampling system. In addition, this system was connected to an electrospray ionization (ESI) quadrupole MS (Shimadzu LCMS-2020, Shimadzu Corporation, Kyoto, Japan) to improve sensitivity of amine measurements (see Table S2 for MS settings). The MARGA instrument earlier used for measuring anions and cations in Helsinki and Hyytiälä is described in more detailed in earlier papers (Makkonen et al. 2012 and 2014).

Ambient air was taken through a PM10 cyclone (URG 1032, Teflon coated) and polyethylene tubing (ID 0.5", length ~1 m) with a flow rate of 16.7 l min^{-1}. After passing the inlet, sample air entered to a wet rotating denuder (WRD), where the gases diffused into the absorption solution (10 ppm hydrogen peroxide). Particles passed through the WRD and entered the steam jet aerosol collector (SJAC), where they were collected in a supersaturated environment (in 10 ppm hydrogen peroxide). During each hour liquid samples from the WRD and SJAC were collected in the syringes (25 ml), mixed with the internal standard (LiBr and deuterated diethyl-d10-amine) and injected to the cation ion chromatograph. The two sets of syringes worked in tandem, so that when a set of samples was collected, the previous ones were injected. In the cation chromatograph 3.2 mmol l^{-1} oxalic acid (Merck, Darmstadt, Germany) solution was used as an eluent (constant flow 0.7 ml min^{-1}). To get the detection limits lower we used a concentration column (Metrosep C PCC 1 VHC/4.0) before the analytical column (Metrosep C4-100/4.0, 100 mm x 4.0 mm i.d., stationary phase silica gel with carboxyl groups, particle size 5 µm). After

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passing the cation column and the conductivity detector, samples were guided to the ESI-needle of the mass spectrometer without any additional solvent. All solutions used were made with ultrapure water (Milli-Q, resistivity ≥18 MΩ·cm)~~This new set-up enabled amine concentration measurements in ambient air both in aerosol and gas phases. With MARGA-MS we sampled, separated and detected 7 different amines: monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA).~~

~~The sampling air flow was 16.7 l min^{-1} for a sampling time of 1 hour. We used PM10 inlet (URG-1032, 16.7 l min^{-1}) with polyethylene tubing (ID 0.5" and length ~1 m). The eluent used was oxalic acid (3.2 mol l^{-1}, Merck, Darmstadt, Germany) with a flow of 0.7ml min^{-1}. We used a concentration column (Metrosep C PCC 1 VHC/4.0) before the analytical column (Metrosep C4 100/4.0).~~ Detection limits (DL) for MARGA-MS were calculated from signal-to-noise ratios (3:1) for most of the compounds and they were similar in gas and ~~particle~~aerosol phase, because their blank-values were so small ~~-~~(Table ~~2~~1 in section 3.1). However, DLs for DMA and TMA were calculated from blank-values (3 times standard deviations of blank-values) and the DLs were different for gas and ~~particle~~aerosol~~-~~phase measurements.

~~Table 2. Detection limits (DL) of different amines, ammonia and ammonium. Conversions from (ng m^{-3}) to ppt$_v$ has been made using conversion factor ppt$_v$ = c(ng m^{-3}) : (0.0409*(MW)) by Finlayson-Pitts (2000).~~

~~**Amine**~~		~~**DL (ng/m^3)**~~	~~**DL (ppt$_v$)**~~
~~**MMA**~~		~~2.4~~	~~1.9~~
~~**DMA(March to August)**~~	~~**gas**~~	~~3.1~~	~~1.7~~
	~~**particles**~~	~~1.1~~	
~~**(November to December)**~~	~~**gas**~~	~~0.37~~	~~0.20~~
	~~**particles**~~	~~0.76~~	
~~**TMA**~~	~~**gas**~~	~~0.2~~	~~0.1~~
	~~**particles**~~	~~0.5~~	
~~**EA,**~~	~~**both gas and particle**~~	~~0.36~~	~~0.19~~
~~**DEA,**~~	~~**both gas and particle**~~	~~0.24~~	~~0.08~~
~~**PA,**~~	~~**both gas and particle**~~	~~0.31~~	~~0.13~~
~~**BA,**~~	~~**both gas and particle**~~	~~0.26~~	~~0.09~~
~~**NH$_3$**~~		~~11.4~~	~~16.4~~
~~**NH$_4^+$**~~		~~2.9~~	

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Deuterated diethyl-d$_{10}$-amine (DEA$_{10}$, Sigma-Aldrich: Isotec™; Sigma-Aldrich, St. Louis, MO, USA) was used as an internal standard (ISTD) for all amines. DEA$_{10}$ was used, because it behaved same way in IC-separation but had different mass than studied amines. 50.0µl of DEA$_{10}$ was added to the MARGAs ISTD solution bottle (LiBr). After the ion chromatograph the ISTD mixed with the sample entered the MS-detection. DEA$_{10}$ was used to correct for possible losses to instrumentation and correct changes of MS response. A 3-point external calibration was used for all measured alkyl amines (concentration levels 10, 50 and 300 ng m^{-3}). The system was calibrated every two weeks, by stopping the air flow of the MARGA and directing standard solutions to the sample syringe pumps, before analysis by IC-separation and MS-detection. Ammonia (NH$_3$) and ammonium (NH$_4^+$) (the sum of them referred to as NH$_x$) were also measured with MARGA at the same time with the method described in Makkonen et al. (2012 and 2014), except we used oxalic acid solution for eluent. For NH$_x$-measurements only conductivity detector was used and the internal standard was lithium bromide (Acros Organics, New Jersey, USA). Instrumental blank values for MARGA-MS were measured every month or every other month with MARGAs blank-mode: the sample airflow was stopped, and the analysis cycle was running for 6 hours without sampling.

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~~Deuterated diethyl-d$_{10}$-amine (Sigma-Aldrich: Isotec™; Sigma-Aldrich, St. Louis, MO, USA) was used as an internal standard for all amines and a 3-point external calibration was used for all measured alkyl amines (concentration levels ca. ~10, 50 and 300 ng m^{-3}). The system was calibrated every two weeks, by stopping the air flow of MARGA and directing standard solutions to the sample syringe pumps, before analysis by IC-separation and MS-detection. Ammonia (NH$_3$) and ammonium (NH$_4^+$) were also measured with MARGA at the same time with the method described in Makkonen et al. (2012 and 2014). For these a conductivity detector was used and the internal standard was lithium bromide (Acros Organics, New Jersey, USA). Instrumental blank values were measured every month or every other month with MARGA's blank-mode: the sample airflow was stopped, and the analysis cycle was running for 6 hours without sampling.~~

In calculations the values under DLs were taken account as 0.5×DL. In the figures we used a moving average for DMA, because every other measured DMA concentration was a little higher than the ~~other~~ in-between one. The system used different syringes for sample collection every other hour and the reason for differences are expected to be losses or contamination in the syringes. Further causes for these minor differences were not found.

2.3.2 Aerosol measurements

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To study the role of amines in atmospheric particle formation, particle number concentration measurements were utilized. The particle number size distribution between 3 and 1000 nm was measured with a twin- Differential Mobility Particle Sizer (DMPS) system (Aalto et al.~~,~~ 2001). From these measurements, the particle concentration between 3 and 25 nm (N$_{3\text{-}25\ \mathrm{nm}}$), referred to as the nucleation mode, and the total particle concentration between 3 and 1000 nm (N$_{tot}$) were obtained. In addition, the concentrations of sub-3 nm particles were measured with an Airmodus Particle Size Magnifier (PSM A11; Vanhanen et al.~~,~~ 2011). The PSM is a mixing-type condensation particle counter, in which particles are first grown to 90 nm size by condensation of diethylene glycol, after which butanol is used to grow them to detectable sizes. The cut-off size of the PSM can be changed by altering the mixing ratios of saturated and sample flows, which allows the measurement of particle size distribution in the sub-3 nm size range. In this study, the particle concentration obtained for the size range between 1.1 and 2.0 nm ($N_{1.1\text{-}2nm}$) was used. In addition, the particle concentration between 2 and 3 nm ($N_{2\text{-}3nm}$), was obtained by subtracting the total particle concentration measured with the highest cut-off size of the PSM from the total particle concentration measured with the DMPS. For ~~the~~ more discussion about the particle concentration measurements and their uncertainties, see Kontkanen et al. (2017) who have published the data set used in this study.

2.4 Regression calculations

Simple linear regressions were calculated to find ~~out~~ whether ~~the basic~~ meteorological conditions affect ~~the~~ amine concentrations. The statistical significance of the slope of the linear regression of the amine concentration y vs. the ambient condition x, i.e. $y = \beta_1 x + \beta_0$ was estimated. The null hypothesis, which means that the slope β_1 is not dependent on the ambient condition x (i.e., $\beta_1 = 0$), was examined using test statistics given by the estimate of the slope divided by its standard error ($t = \beta_1$/s.e.). The test statistics were compared with the Student's t distribution on n - 2 (sample size ~~–~~minus the number of regression coefficients) degrees of freedom. The analysis yields also the p value of the slope. The lower the p-value is, the stronger the evidence against the null hypothesis is. The statistical significance of the slope can be interpreted so that if $p > 0.1$ there is no evidence against the null hypothesis, and p-values in the ranges 0.05-0.1, 0.01-0.05, and < 0.01 suggest respectively a weak, moderate and strong evidence against the null hypothesis in favor of the alternative. The regressions were calculated for amine concentrations vs. air temperature, relative humidity, wind speed, soil temperature and soil humidity.

3. Results

3.1 Characterization of MARGA-MS

An on-line method for sampling, separating and detecting amines from the ambient air both in the gas and aerosol phase has been developed. With MARGA-MS we studied 7 different amines: monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), ethylamine (EA), diethylamine (DEA), propylamine (PA) and butylamine (BA), see Figure S2 for the chromatogram. The time resolution of measurements was one hour, and as can be seen in Table 1, the detection limits were low, and precision (10–15%) and accuracy (11–37%) for the analytical method of MARGA-MS were moderately good. In addition to improved DLs, MS detection after MARGA also solved the problem with co-elution of amines with different

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molecular masses and inorganic cations (e.g. K+, Mg2+). Verriele et al. (2012) developed also an IC-MS method for amines with offline sampling with midget impingers. They also noticed that adding MS detection after a conductivity detector overcomes the co-eluting problem of IC separation. They had a 4-step gradient elution in their method, and suppression before the conductivity detector. We wanted to keep our method as simple as possible to make it easy to use in the field, and isocratic elution without suppression was good in that purpose.

The whole analysis was conducted in the field, so the method had no biases from sample transportation. However, the drawback in the analysis was that DEA and BA, which have the same molecular masses, did not separate completely. From a technical point of view one of the drawbacks of the MARGA-MS was that the system was quite vulnerable. We lost many measuring days because some part of the system was broken. The MARGA side also needed ~40 l solutions (e.g. eluents, absorbation solution for sampling, and internal standard solution) that needed to be changed weekly. The ESI-chamber of the MS needed to be cleaned weekly, because oxalic acid was crystallizing into it. Despite the drawbacks, to our knowledge with the MARGA-MS method we achieved the largest data set of amine concentrations available at the moment.

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Table 1. Detection limits (DL) of different amines, ammonia and ammonium. Conversions from (ng m^{-3}) to ppt_v has been made using conversion factor $ppt_v = c(ng\ m^{-3}) : (0.0409\times(MW))$ by Finlayson-Pitts (2000), with MW the molar mass of the amine, ammonia or ammonium.. The precision for IC-MS analysis was defined by calculating standard deviations of liquid 200 ng m^{-3} standard measured 6 times in a row. In the data series there were both gas and particle side measurements. The accuracy for IC-MS analysis was calculated by subtracting the averages of the data series described earlier from the expected values, dividing those with the expected values and multiplying them by 100%.

Amine	**DL (ng m^{-3})**	**DL (ppt_v)**	**Precision (%)**	**Accuracy (%)**
MMA, both gas and aerosol	2.4	1.9	10	24
DMA, (March to August) gas aerosols	3.1	1.7	11	31

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(November to December)	gas	1.1			
	aerosols	0.37	0.20		
		0.76			
TMA,	gas	0.2	0.1	14	11
	aerosols	0.5			
EA,	both gas and aerosol	0.36	0.19	11	16
DEA,	both gas and aerosol	0.24	0.08	15	37
PA,	both gas and aerosol	0.31	0.13	11	21
BA,	both gas and aerosol	0.26	0.09	12	14
NH_3,	gas	11.4	16.4		
NH_4^+,	aerosol	2.9			

3.1.1 Particle collection in the denuder of the MARGA

Theoretical calculations of diffusional losses through an annular tube have been derived, e.g., by Winiwarter (1989). The numerical solution of the diffusional losses in an annular denuder presented by Fan et al. (1996) and Baron and Willeke (2001) were applied to calculate the size-dependent penetration in the denuder of the MARGA. The calculation needs as input the diameter of the inner and outer tubes (36.4 mm and 39.9 mm, respectively), the tube length 26.5 cm and the flow rate 16.7 LPM.

The result of the calculation (Fig. 1) shows that 50% of particles smaller than about 6 nm are collected in the denuder and get interpreted as gas-phase compounds. It also shows that essentially all particles larger than about 20 nm get transported through the denuder and finally get interpreted correctly as particles. The cluster-mode particles are smaller than 2 nm and behave primarily like gases and more than ~80% of them do not penetrate the denuder, whereas more than ~85% of particles larger than 10 nm go through it. The size of nucleation-mode particles is approximately between 2–10 nm, or up to ~25 nm, depending on the definition of the size ranges, and they appear in the atmosphere mainly during NPF events. During these events they could be found both in the denuder and in the steam-jet aerosol collector, but that does not play an essential role because of their small mass even when the number concentration is high. An estimate of the masses involved can be given by assuming that the number concentration in a nucleation mode is 10 000 cm^{-3}, its geometric mean diameter D_g = 4 nm, and the geometric standard deviation σ_g = 1.5. Assuming that the density of particles is 1.5 g cm^{-3} the mass of that mode is ~1.05

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ng m^{-3}. The diffusion losses in the denuder result in a growth of the geometric mean of the size distribution and decrease of mass concentration to ~0.69 ng m^{-3} which means that 65 % of the mass gets into the SJAC. The fraction of mass penetrating to the SJAC grows with a growing modal diameter so that for a single-mode distribution of D_g = 10 nm and σ_g = 1.5 the penetrated mass fraction is 95%.

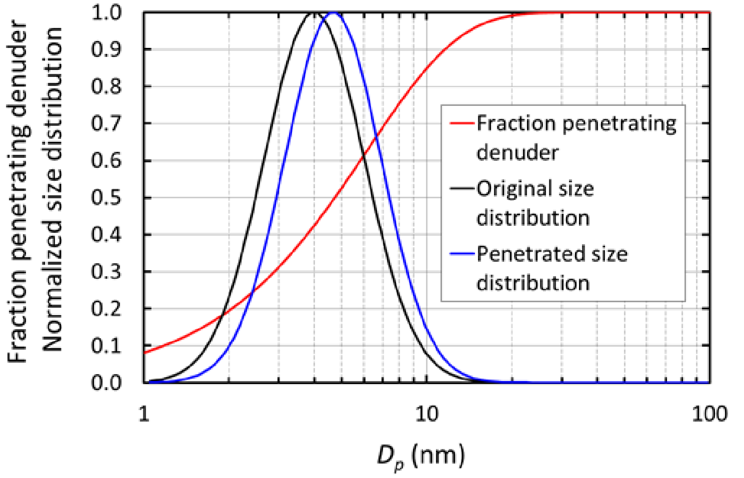

Figure 1. Size-dependent particle penetration probability in the annular denuder of the MARGA and a normalized number size distribution (dN/dlogD_p, D_g = 4 nm, σ_g = 1.5) of a nucleation mode before and after penetrating the denuder.

3.~~1~~ 2 Variability of the concentrations

Figure ~~1~~ S4 shows the monthly means and medians of total amine concentrations (tot, sum of gas and aerosol phases) and Figure ~~2~~ 2 shows the box and whisker plots to describe the ~~statistics~~ distribution of the measured concentrations. Total amine concentrations were used because we wanted to study how amine sources and partitioning between aerosol~~-~~ (a) and gas phase (g) depend on environmental quantities. Even though the average ratios (gas/(gas+aerosol)) for values above DL in ~~t~~Table ~~1~~2 are close to 0.5, a~~A~~mines were still mainly in the aerosol phase (Table ~~3~~ 2 and ~~4~~S2), which is shown by the more data points >DL in the aerosol phase. Table S3 shows the number of data points in each month, as well as the mean and median values of concentrations of different amines, ammonia and ammonium. It can be seen, that most concentrations were below DL especially in the gas phase, so we can conclude that concentrations of amines in the boreal forest are low compared to for example ammonia or monoterpene concentrations (Hakola et al. 2012). In Table 3, concentrations in other

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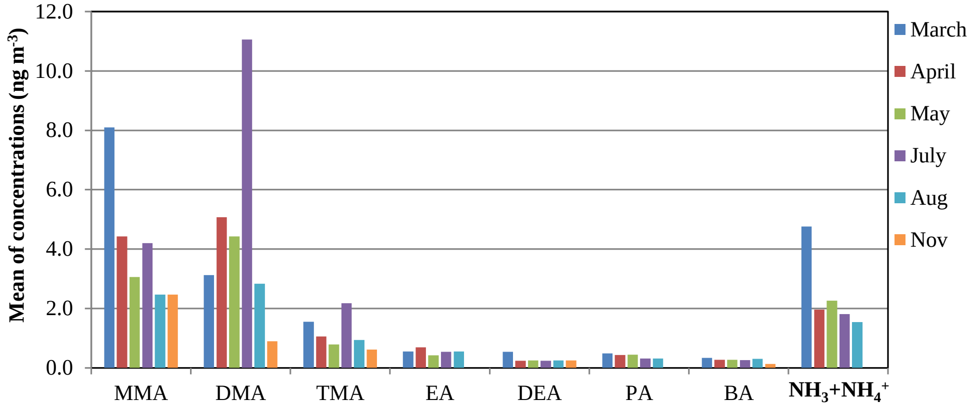
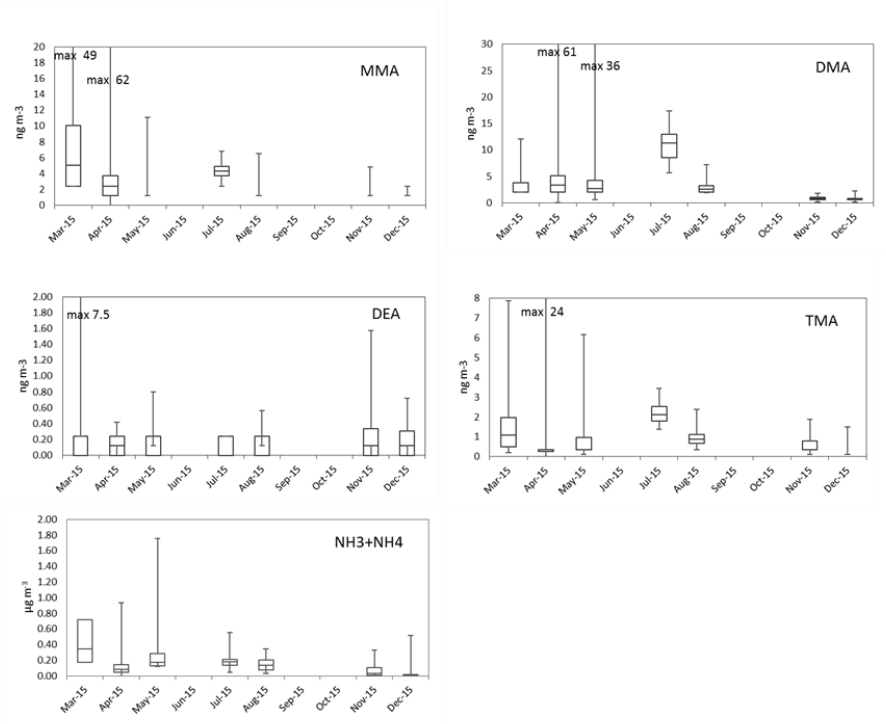
studies are compared to our findings. Different seasonal patterns were found for different amines and they are described below.



~~Figure 1. Monthly means of total amine and summed up ammonia and ammonium ($NH_3+NH_4^+$) concentrations (ng/m^3). $NH_3+NH_4^+$ concentrations have been divided by 100, to fit the scale.~~


MMA
ng m-3
max 49
max 62
0
2
4
6
8
10
12
14
16
18
20
DMA
max 61
max 36
0
5
10
15
20
25
30
DEA
max 7.5
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
TMA
max 24
0
1
2
3
4
5
6
7
8
NH3+NH4
µg m-3
Mar-15
Apr-15
May-15
Jun-15
Jul-15
Aug-15
Sep-15
Oct-15
Nov-15
Dec-15

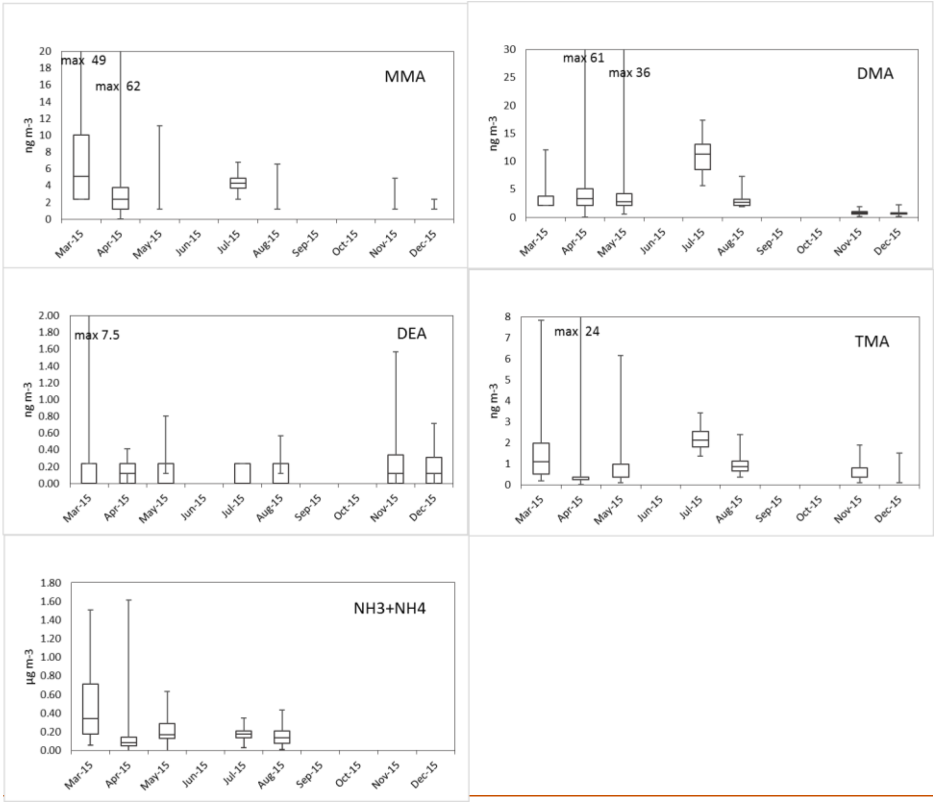


Figure ~~2~~2: Monthly box and whisker plots of the most abundant amines (tot~~sum of gas and particle~~aerosol ~~phases~~) and summed up ammonia and ammonium. ~~Boxes~~ The boxes represent the second and third quartiles and ~~vertical~~ the lines in the boxes the median values. The ~~W~~whiskers show the highest and the lowest observations.

Table ~~3~~2. Ratio of gas and aerosol phases. N(g)=number of gas phase data above detection limit (DL), N(a)=number of aerosol phase data above DL and N=number of data above ~~detection limit~~DL at the same time both in the gas and aerosol phases, ratio=gas/(gas+aerosol) (when both values were above the DL).

	MMA	DMA	TMA	EA	DEA	PA	BA	~~NH_3~~NH_x
N(g)	29	116	308	62	86	20	38	285
N(a)	183	550	391	82	29	35	26	844
N	9	53	208	21	6	5	3	~~596~~282
Average ratio	0.41	0.44	0.29	0.48	-	-	-	0.35

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Min ratio	0.18	0.09	0.10	0.05	-	-	-	0.05
Max ratio	0.52	0.83	0.90	0.95	-	-	-	0.84

Table 3. Comparison of concentrations of MMA, DMA, TMA and EA in different sites and seasons, gas and aerosol phase.

~~Table 4. Monthly mean and median (med.) of gas and particle phase amines and ammonia.~~

~~ng m^{-3}~~	~~March~~		~~April~~		~~May~~		~~July~~		~~August~~		~~November~~	
	~~mean~~	~~med.~~	~~mean~~	~~med.~~	~~mean~~	~~med.~~	~~mean~~	~~med.~~	~~mean~~	~~med.~~	~~mean~~	~~med.~~
~~Gas~~												
~~DEA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~BA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~DMA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~0.4~~	~~<DL~~
~~TMA~~	~~0.4~~	~~<DL~~	~~0.4~~	~~<DL~~	~~0.3~~	~~<DL~~	~~0.4~~	~~0.4~~	~~0.3~~	~~<DL~~	~~0.2~~	~~<DL~~
~~PA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~EA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~MMA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~1.2~~	~~<DL~~
~~NH_3~~	~~52~~	~~19~~	~~52~~	~~<DL~~	~~81~~	~~22~~	~~45~~	~~<DL~~	~~66~~	~~<DL~~		
~~Aerosol~~												
~~DEA~~	~~0.3~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~BA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~DMA~~	~~1.5~~	~~<DL~~	~~3.1~~	~~3.0~~	~~2.7~~	~~<DL~~	~~8.4~~	~~4,9~~	~~1.3~~	~~<DL~~	~~<DL~~	~~<DL~~
~~TMA~~	~~1.1~~	~~<DL~~	~~0.7~~	~~<DL~~	~~0.5~~	~~<DL~~	~~1.8~~	~~1.4~~	~~0.6~~	~~0.6~~	~~0.5~~	~~<DL~~
~~PA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~EA~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~0.4~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~MMA~~	~~6.8~~	~~<DL~~	~~2.9~~	~~<DL~~	~~<DL~~	~~<DL~~	~~3.0~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~	~~<DL~~
~~NH_4^+~~	~~425~~	~~90~~	~~144~~	~~64~~	~~145~~	~~97~~	~~136~~	~~92~~	~~88~~	~~28~~		

Amine	**Gas (ppt)**	**Aerosol (ng m^{-3})**	**Site description**	**Location**	**Season**	**Year**	**Reference**
MMA	<DL–8.8	<DL–61.2	Rural forest	Finland	Spring-early winter	2015	This study
	~~3.8~~max. ~2		Rural forest	AL, USA	Summer	2013	You et al. (2014)

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	5		Semi-rural	DE, USA	Summer	2012	Freshour et al. (2014)
	4		Rural	OK, USA	Spring	2013	Freshour et al. (2014)
	4		Urban	MN, USA	Autumn	2012	Freshour et al. (2014)
	0.26*		Urban	Turkey	Summer	2004-2005	Akyüz (2007)
	1.3*		Urban	Turkey	Winter	2005-2006	Akyüz (2007)
DMA	<DL–4.1	<DL–55.5	Rural forest	Finland	Spring-early winter	2015	This study
	max ~7^{a}		Rural forest	AL, USA	Summer	2013	You et al. (2014)
	28^{a}		Semi-rural	DE, USA	Summer	2012	Freshour et al. (2014)
	20^{a}		Rural	OK, USA	Spring	2013	Freshour et al. (2014)
	42^{a}		Urban	MN, USA	Autumn	2012	Freshour et al. (2014)
	2.18*		Urban	Turkey	Summer	2004-2005	Akyüz (2007)
	2.96*		Urban	Turkey	Winter	2005-2006	Akyüz (2007)
	<2.7	<2.7	Urban	Canada	Summer	2009	VandenBoer et al. (2011)
	6.5±2.1	0.1±0.2	Rural	Canada	Autumn	2010	VandenBoer et al. (2012)
	42±30^{a}		Rural forest	Finland	May-October	2011	Kieloaho et al. (2013)
	max 10		Urban	GA, USA	Summer	2009	Hanson et al. (2011)
		9.3-20.5	Semi-arid	AZ, USA	Whole year	2012-2013	Youn et al. (2015)
TMA	<DL-6.1		Rural forest	Finland	Spring-early winter	2015	This study
	34–80		Rural forest	Finland	Spring	2002	Sellegri et al. (2005)
	max. ~20^{b}		Rural forest	USA	Summer	2013	You et al. (2014)
	6^{b}		Semi-rural	DE, USA	Summer	2012	Freshour et al. (2014)
	35^{b}		Rural	OK, USA	Spring	2013	Freshour et al. (2014)
	19^{b}		Urban	MN, USA	Autumn	2012	Freshour et al. (2014)
	15^{b}		Rural forest	AL, USA	Summer	2013	You et al. (2014)
	<2.7^{c}	<2.7^{c}	Urban	Canada	Summer	2009	VandenBoer et al. (2011)
	~1^{c}	1±0.6^{c}	Rural	Canada	Autumn	2010	VandenBoer et al. (2012)
	21±23		Rural forest	Finland	May-October	2011	Kieloaho et al. (2013)
	<6.8×10^{3}		Agricultural	CA, USA	Autumn	2013	Dawson et al. (2014)
		max 9±7	Wildfire$^{\#}$	Canada	Summer	2015	Place et al. (2017)
EA	<DL-8.2		Rural forest	Finland	Spring-early winter	2015	This study
	0.35*		Urban	Turkey	Winter	2005-2006	Akyüz (2007)

a: Mass 46 i.e. DMA+EA, b: Mass 60 i.e. TMA+PA, c: TMA+DEA, *: Units in ng m^{-3}, #: Samples are collected in British Columbia during wildfires

3.~~1~~2.1 ~~MMA~~Monomethylamine

A spring maximum was observed for MMA(tot) (max. 50 ng m^{-3}) and the concentrations correlated with the sum of NH_3 and NH_4^+ (R^2=0.52, Fig. ~~3~~3). During spring we observed two occasions when MMA(tot) and the sum of NH_3 and NH_4^+

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concentrations increased considerably at the same time. The concentration increase in March is characterized with rain (Fig. ~~4~~4a) and the later increase in April took place during night with decreasing wind speed and higher temperature (Fig ~~3~~4b). This increase could be ~~due~~ connected to evaporation from melting snow and ground~~, and we are going to study spring snow more.~~. Bigg et al.~~,~~ (2001)~~,~~ suggest that water from melting snow penetrate the soil and leaf litter beneath the snow, displacing gases produced by decomposition of organic material. These gases are then released to the air, where they participate in the nucleation process. ~~On~~At humid conditions this bubbling of gases would be efficient, whereas the evaporation to air would be more efficient on warm, sunny days.

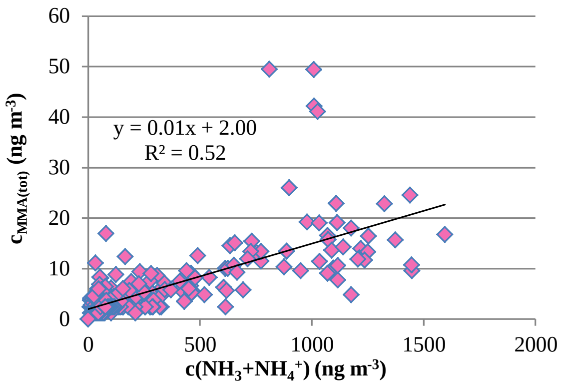

Figure ~~3~~3. Concentrations (ng/m^3) of total MMA ~~(y-axis)~~ vs concentrations of NH_3+NH_4^+ ~~(x-axis)~~ in March and April 2015.

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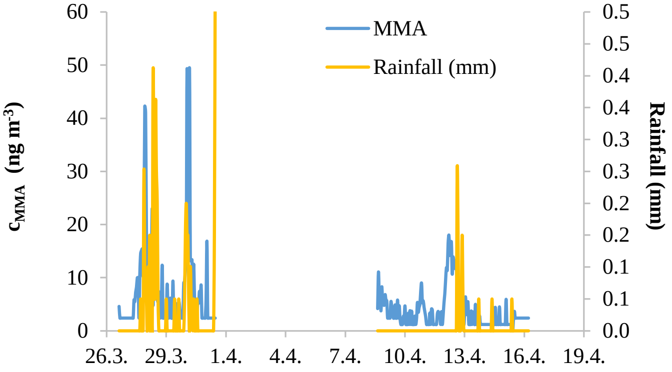
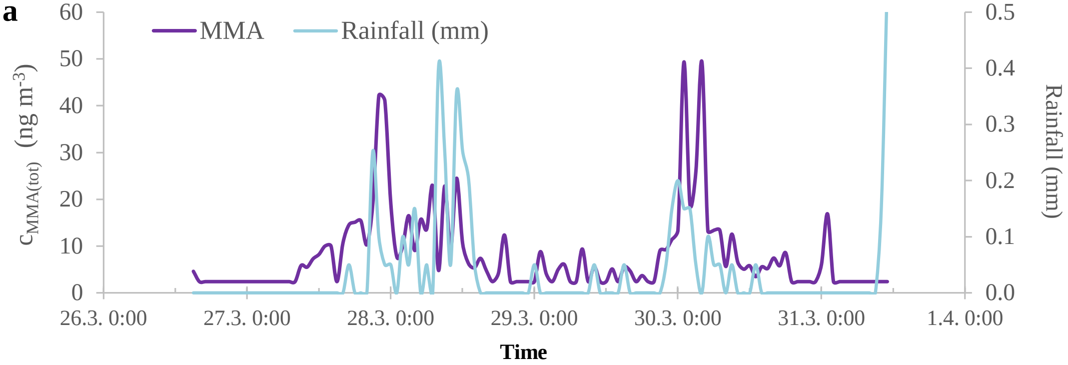
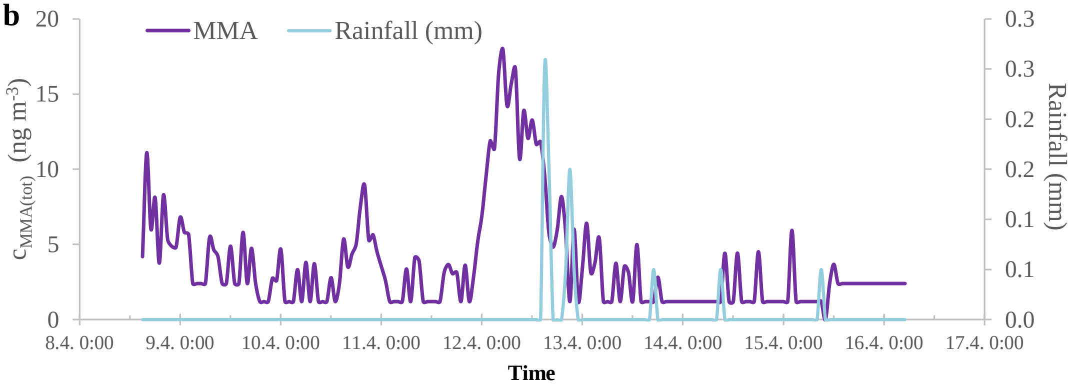

MMA
Rainfall (mm)
c$_{MMA}$ (ng m^{-3})
Rainfall (mm)
60
50
40
30
20
10
0
0.5
0.5
0.4
0.4
0.3
0.3
0.2
0.2
0.1
0.1
0.0
26.3.
29.3.
1.4.
4.4.
7.4.
10.4.
13.4.
16.4.
19.4.

a


MMA
Rainfall (mm)
c$_{MMA(tot)}$ (ng m^{-3})
Rainfall (mm)
60
50
40
30
20
10
0
0.5
0.4
0.3
0.2
0.1
0.0
26.3. 0:00
27.3. 0:00
28.3. 0:00
29.3. 0:00
30.3. 0:00
31.3. 0:00
1.4. 0:00
Time

b


MMA
Rainfall (mm)
c$_{MMA(tot)}$ (ng m^{-3})
Rainfall (mm)
20
15
10
5
0
0.3
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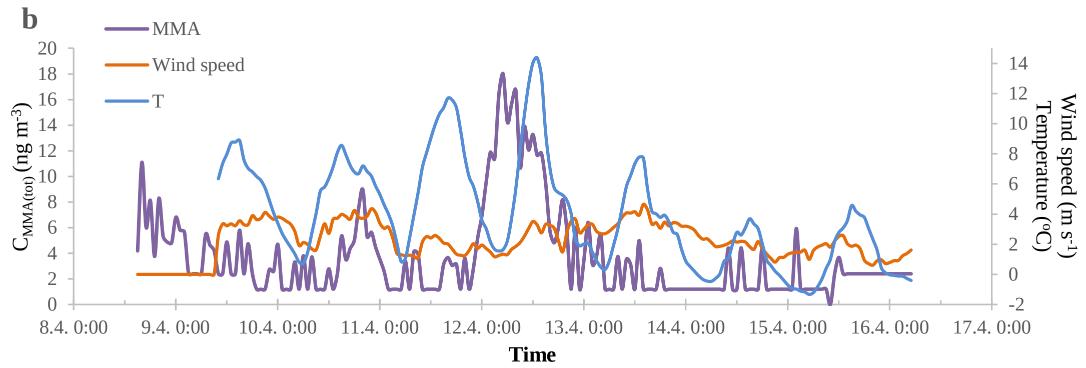

Figure ~~4~~4: MMA(tot) concentrations ~~(gas and aerosol phase)~~ and rainfall measured in Hyytiälä during spring 2015 in March (a) ~~and in April (b),~~ and MMA(tot) concentrations, wind speed and ambient temperature in April (~~c~~b).

Most of the MMA was in ~~particle~~ aerosol phase (Table 3 and ~~4~~S2): monthly mean of aerosol phase MMA(a) varied between <2.4 and 6.8 ng m^{-3} (Table ~~4~~S3), while monthly means of gas phase MMA(g) were below DL throughout the measurements. In early winter (late November to early December) MMA was not detected. ~~Ammonia~~ NH$_x$ showed similar seasonal variation as MMA with the maximum in March and lower concentrations towards the end of summer. During spring ~~ammonia~~ NH$_x$ was also mainly in aerosol phase.

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In earlier studies (Table 3) You et al. (2014) detected gaseous MMA(g) with CIMS in Alabama forest in summer, at about the same ~~level~~ concentrations as our measurements (maximum ~2 ppt$_v$, ca. 3.8 ng m^{-3}). Also Freshour et al. (2014) measured MMA(g) with AmPMS in 3 different sites in USA, and their mean concentrations were at the same level ~~than~~ as ours (4–~~-~~5 ppt$_v$, ca. 5.1–~~-~~6.4 ng m^{-3}). Akyüz (2007) took urban outdoor air samples in Turkey during summer times 2004-2005 and winter times 2005-2006, and analysed them later with GC-MS. MMA(g) mean results were 0.26 and 1.30 ng m^{-3}, respectively. Values are ~~in same~~at similar levels to ~~with~~ our measurements. That is surprising, because in urban area ~~there are lots of~~ we expect many MMA-sources (e.g. industry and ~~automobiles~~cars, Ge et al. 2011), so higher mean concentrations would have been expected.

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3.~~1~~2.2 ~~TMA~~Trimethylamine

TMA(tot) had higher concentrations in March after which they declined, before increasing again in July to their maximum concentrations suggesting biogenic sources (Fig. ~~1~~2, Fig. S4). TMA(tot) concentrations also peaked at the end of March during rain simultaneously with MMA(tot) and the sum of NH_3 and NH_4^+ increasing from about 1.5 to 6.0 ng m^{-3}, so melting snow and ground could also be the sources of TMA as discussed in 3.2.1. During summer TMA(tot) concentrations increased again concomitant with the sum of NH_3 and NH_4^+ in July. The share of the gas phase was ~~throughout the measurements~~ roughly half of the aerosol phase concentration throughout the measurements (Table ~~3~~2 and S2). TMA(tot) did not show a clear diurnal variation (Fig. ~~4~~5).

~~TMA(tot) had higher concentrations in March after which they declined, before increasing again in July to their maximum concentrations suggesting biogenic sources (Fig. 21). TMA(tot) concentrations also peaked at the end of March during rain simultaneously with MMA(tot) and the sum of NH_3 and NH_4^+ increasing from about 1.5 to 6.0 ng m^{-3}. , so melting snow could also be the source of TMA. During summer measurements TMA(tot) increased again concomitant with the sum of NH_3 and NH_4^+ in July. This increase was not due to rain, and it happened simultaneously with the increase in nucleation mode particle concentration.. The share of the gas phase was throughout the measurements roughly half of the particleaerosol phase concentration (Table 3 and 4S2). TMA did not show a clear diurnal variation (Fig. 4).~~

Kieloaho et al. (2013) collected filter samples of gaseous amines from the same boreal forest as we did from May to October 2011 and they also measured low concentrations for the sum of TMA(g) and PA(g) in July. In their measurements the concentrations increased during ~~fall~~autumn. You et al. (2014) measured gaseous C_3-amines (TMA and PA) with CIMS in a forest in Alabama from June to early July in 2013 and their highest concentration (~15 ppt$_v$, ca. 36 ng m^{-3}) was ~10 times higher than ours (3.5 ng m^{-3}). Dawson et al. (2014) collected TMA-samples in ion resin cartridges from late August to middle September near a cattle farm in Chino, California, and ~~analysed~~analyzed the samples with IC. Their results varied from 1.3-6.8 ~~ppm$_v$~~ ppb$_v$ (ca. 3.1–~~-~~16.4 µg m^{-3}), so they measured ~1000 times higher concentrations than we did. This is not surprising, because cattle are a known source of amines. Sellegri et al. (2014) measured amines in March 2002 with CIMS in same boreal forest ~~than~~ that we did. They found TMA(g) with mixing ratios 34–~~-~~80 ppt$_v$ (ca. 82–~~-~~193 ng m^{-3}), so their results are ~30 times higher than ours. Ambient conditions were different than ours when they measured TMA, and ~~that~~ this could be one reason for the higher concentrations they observed.

3.2.3 Dimethylamine

DMA(tot) concentrations also increased from about 3 to 6 ng m^{-3} during the MMA episode in April. Moreover, both particulate and gas phase DMA had maximum concentrations in July suggesting a biogenic source (the highest value was 14.5 ng m^{-3} in the aerosol phase and 7.5 ng m^{-3} in the gas phase). The particle fraction was again generally more abundant than the gaseous fraction~~ average~~. Because amines can be expected to partition in the aqueous aerosols (Ge et al. 2010), it is not surprising to find them mostly in the aerosol phase, considering the high average relative humidity measured (>68%). In August the concentrations decreased, and they were the lowest during early the winter. Kieloaho et al. (2013) measured also high gas phase concentrations of the sum of DMA and EA in July, reaching a maximum of ~75 ppt$_v$ (ca. 138 ng m^{-3}). In their measurements the concentration levels decreased in August similar to our measurements. High DMA and TMA concentrations in summer could indicate biogenic sources. However, these amines concentrations did not correlate with monoterpene concentrations like EA~~, although they react faster with OH radicals than~~ ~~EA~~ (see section 3.~~1.3~~2.4). VandenBoer et al. (2011) measured both DMA(g) and DMA(a) with AIM-IC from late June to early July 2009 in an urban area, with highest concentration of 2.7 ppt$_v$ (ca. 4.6 ng m^{-3}) and 2.7 ng m^{-3} which were at the same level as our DMA(g) in July (7.5 ng m^{-3}). Hanson et al. (2011) also measured DMA concentrations with AmPMS in an urban area with a little higher gas phase concentrations (maximum of 10 ppt$_v$, ca. 19 ng m^{-3}) than in the studies mentioned earlier. Ge et al. (2010) gives DMA also urban sources (e.g. tobacco smoke, automobiles), so that can explain results from Hanson et al. (2011). Youn et al. (2015) measured DMA aerosols and cloud water, and they noticed that DMA concentrations in PM1-aerosols peaked in September. We were also expecting high concentrations in autumn, but due to instrumental problems we unfortunately missed the season. In July we measured from PM10 particles the average concentration of 8.4 ng m^{-3}, and Youn et al. (2015) measured from PM1 particles about twice as high concentration. Different measurement sites could explain the difference. Youn et al. also noticed that DMA(a) displays a unimodal size distribution with dominant peak between 0.18 and 0.56 µm, and concluded that it indicates aminium salt formation with sulphate..

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In August, DMA(tot) had a diurnal variation with a daytime maximum (Fig. 5), but during some nights the concentrations also increased slightly. The DMA(tot) afternoon maxima could be caused by re-emission of DMA that has earlier deposited on surfaces and evaporates when temperature increases during the afternoon. The maximum could also be related to direct biogenic emission. Usually ambient concentrations of biogenic volatile organic compounds, which have temperature dependent emissions, peak during night-time due to weak atmospheric mixing and lack of hydroxyl radical reactions which only take place during daytime (Hakola et al. 2012). The concentrations of light dependent BVOC emissions such as isoprene have daytime maxima because they are emitted only during daytime. Thus, the DMA source could be light dependent. DMA(tot) peaks also at night. Because the atmospheric mixing in the night is weak and there are no OH-reactions, even small emissions can be trapped in a shallower atmospheric boundary layer and cause the increase in concentrations.

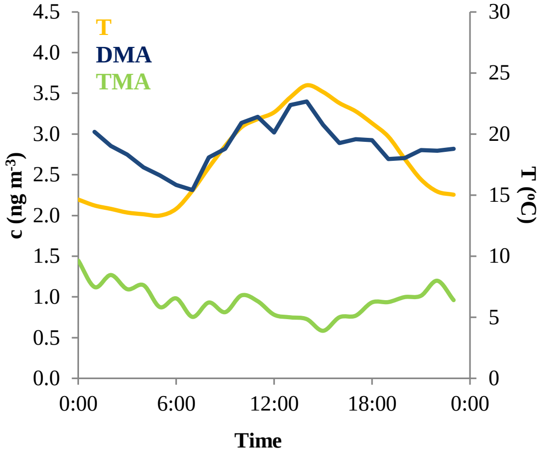

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Figure 5. Mean diurnal variation of total DMA (blue), total TMA (green) concentrations and temperature (yellow) in August 2015.

3.~~1~~2.~~3~~ 4 ~~EA~~Ethylamine

EA(tot) concentrations were low throughout the measurements, but showed a clear diurnal variation in July with a maximum at night (Fig. ~~5~~6). Monoterpene concentrations were measured simultaneously at the same site and had similar diurnal pattern. This type of diurnal variation is typical for many reactive compounds having local sources in boreal forest (Hakola et al. 2012). Low daytime concentrations are due to ~~efficient~~ strong atmospheric mixing and reactions with OH radicals~~ sink reactions~~. The rate coefficients of alkyl amines are slightly lower, but comparable to monoterpene reactions with OH radical. The most common monoterpenes in the boreal forest are α-pinene, 3-carene and β-pinene (Hakola et al. 2012). Their ~~OH radical~~ rate coefficients for reaction with OH are $53.7\cdot10^{-12}$, $88\cdot10^{-12}$, and $78.9\cdot10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively (Atkinson 1994), whereas MMA, EA, DMA and TMA rate coefficients with OH ~~radicals~~ are $22.26\cdot10^{-12}$, $29.85\cdot10^{-12}$, $65.53\cdot10^{-12}$, and $69.75\cdot10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively (U.S. EPA, 2017). Similar diurnal patterns and reactivities ~~indicates~~indicate that EA has a biogenic source. Kürten et al. (2016) measured C_2-amines (i.e. DMA and EA) with CI-APi-TOF in Germany near 3 dairy farms and forest from May to June 2014. They did not observe clear diurnal variation for C_2-amines. In our measurements, EA and DMA had opposite diurnal variations (see ~~chapter~~ section 3.~~1.4~~2.3). That could be the ~~one reason~~ an explanation for ~~results~~ the observations of Kürten et al. (2016), where both C_2-amines were measured together. Aküez (2007) measured EA(g) 0.35 ng m^{-3} (mean concentration) in an urban area in Turkey during winters 2005-2006, and the concentrations were at the same level as ours.

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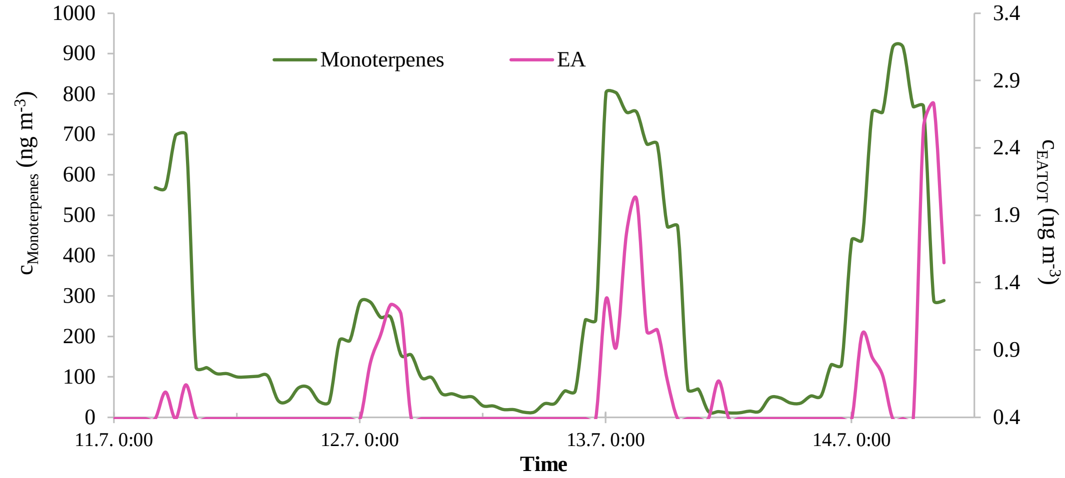

Figure ~~5~~6. ~~Total~~ EA(tot) and monoterpene concentrations in Hyytiälä in July 2015. The EA(tot)~~TOT~~ concentration axis starts from 0.36 ng m^{-3}, because values under that are below the detection limit.

~~3.1.4 DMA~~

~~DMA concentrations also increased from about 3 to 6 ng m^{-3} during the MMA episode in April. Moreover, both particulate and gas phase DMA had maximum concentrations in July (highest value in particle phase 14.5 ng m^{-3} and in gaseous phase 7.5 ng m^{-3}). The particulate fraction was again generally more abundant than the gaseous fraction average. Because amines can be expected to partition in the aqueous aerosols (Ge et al. 2010), it is not surprising to find them mostly in the particle phase, considering the high average relative humidity measured (<68%). In August the concentrations decreased, and they were lowest during early winter. Kieloaho et al. (2013) measured also high gas phase concentrations of the sum of DMA and EA in July, reaching a maximum of ~75 ppt$_v$ (ca. 138 ng m^{-3}). In their measurements the concentration levels decreased in August similar to our measurements. High DMA and TMA concentrations in summer could indicate biogenic sources. However, these amines concentrations did not correlate with monoterpene concentrations like EA, although they react faster with OH radicals than EA (see chapter 3.1.3). VandenBoer et al. (2011) measured gaseous DMA with AIM-IC from late June to early July 2009 in an urban area, with highest concentration of 2.5 ppt$_v$ (ca. 4.6 ng m^{-3}) which was at the same level as our gaseous DMA in July (7.5 ng m^{-3}). Hanson et al. (2011) also measured DMA concentrations with AmPMS in an urban area with a little higher gas phase concentrations (maximum of 10 ppt$_v$, ca. 19 ng m^{-3}) than in the studies mentioned earlier.~~

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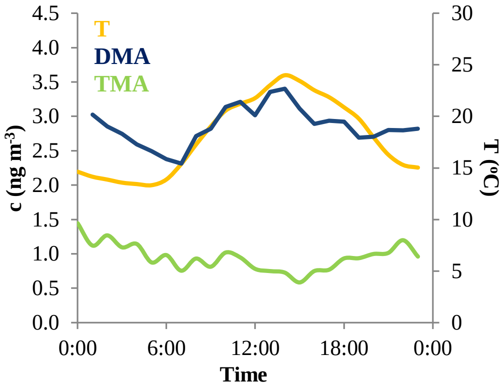
~~Ge et al. (2010) gives DMA also urban sources (e.g. tobacco smoke, automobiles), so that can explain results from Hanson et al. (2011).~~

~~In August DMA had diurnal variation with a daytime maximum (Fig. 6), but during some nights the concentrations also increased a bit. The DMA afternoon maxima could be caused by re-emission of DMA that has earlier deposited on surfaces and evaporates when temperature increases during afternoon. The maximum could also be related to direct biogenic emission. Usually ambient concentrations of biogenic volatile organic compounds peak during nighttime due to inefficient mixing and lack of hydroxyl radical reactions which only take place during daytime (Hakola et al. 2012). The concentrations of light dependent BVOC emissions such as isoprene have daytime maxima because they are emitted only during daytime. Thus, DMA source could be light dependent.~~

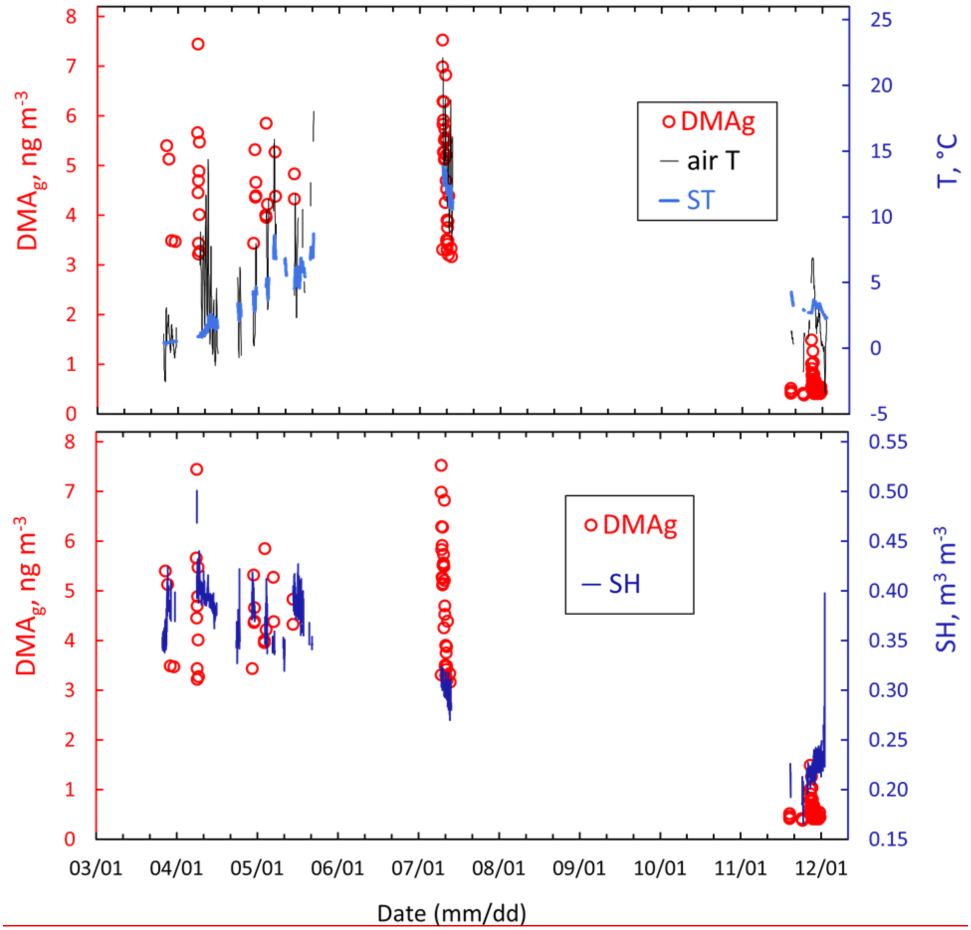


~~Figure 6. Average diurnal variation of total DMA (blue), total TMA (green) concentrations and temperature (yellow) in August 2015.~~

3.~~2~~ 3 Correlations ~~with~~ between meteorological ~~parameters~~ quantities and ~~nano-particle concentrations~~amines

We noticed that ~~especially~~ the concentrations of DMA(g) ~~vary with~~followed, although vaguely, the variations of both air and soil temperature (Fig. S5~~7~~), so it was reasonable to study whether there are any clear relationships between the amine concentrations and parameters describing ambient conditions. ~~we~~We ~~decided to~~ calculated linear regressions of amines, ammonia and ammonium ~~with different ambient conditions (~~ vs. air relative humidity (RH) and temperature (T) as well as soil temperature (ST) and soil humidity (SH)~~)~~. The results of the linear regression analyses of the amines, ammonia, ammonium, and the ambient conditions are presented in Tables S4 and S5 for the gas and aerosol phase, respectively.

In the gas phase DMA had the strongest correlation with ambient condition parameters, suggesting that DMA(g) concentrations increase with increasing air temperature, soil temperature and soil humidity but decrease with increasing atmospheric humidity and wind speed. The scatter plots of DMA(g) vs these parameters (Fig. 7) shows, however, that the relationships are different in different seasons. The most consistent relationships of DMA(g) are with air and soil temperature, the slopes of the linear regressions are positive for the whole data and for summer alone (Fig. 8). ~~Gas phase DMA had the strongest correlation with ambient conditions (Table 5).~~



~~Figure 7. Time series of DMA(g), air temperature (air T), soil temperature (ST) and soil humidity (SH) during the whole measurement period.~~ 1400

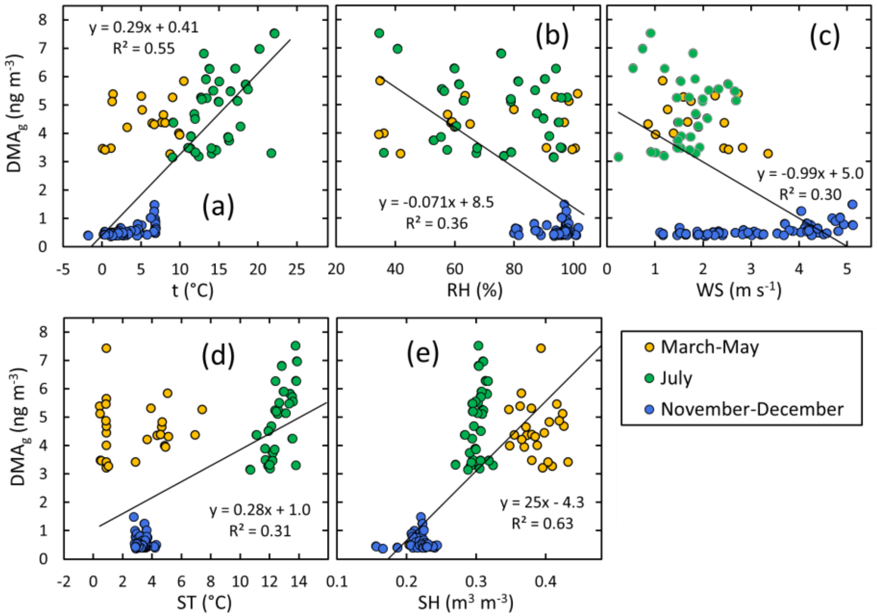


Figure 7. DMA in the gas phase vs selected ambient condition parameters: a) air temperature, b) relative humidity, c) wind speed, d) soil temperature, and e) soil humidity in spring, summer, and early winter. The linear regressions shown in the plots were calculated using the data points of all seasons.

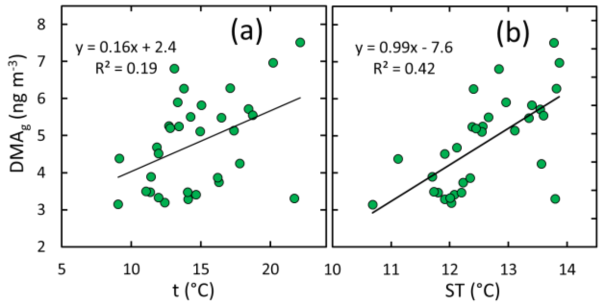


Figure 8. DMA in the gas phase vs a) air temperature, b) soil temperature in summer.

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~~Table 5. Regression statistics ($y = \beta_1 x + \beta_0$) of amine and ammonia concentrations in the gas phase vs. ambient conditions. R^2: the square of the Pearson's correlation coefficient; s.e.: standard error of β_1; d.f.: degrees of freedom; t = β_1/s.e.; p: p-value of the Student's t distribution; air T: air temperature; RH: relative humidity of air; WS: wind speed at 16.8 m; soil T: soil temperature; soil Hum: soil humidity. The slopes, standard errors and t-values are shown only for those regressions that have a p-value < 0.1. Very low p-values are highlighted by bold font.~~

~~x~~	~~y~~	~~R^2~~	~~β_1 ± s.e.~~	~~d.f.~~	~~t~~	~~p~~
~~air T~~	~~MMA(g)~~	~~0.01~~		~~11~~		~~0.82~~
~~RH~~	~~MMA(g)~~	~~0.16~~		~~11~~		~~0.17~~
~~WS~~	~~MMA(g)~~	~~0.17~~		~~11~~		~~0.16~~
~~soil T~~	~~MMA(g)~~	~~0.00~~		~~21~~		~~0.94~~
~~soil Hum~~	~~MMA(g)~~	~~0.00~~		~~19~~		~~0.85~~
~~air T~~	~~DMA(g)~~	~~**0.55**~~	~~0.29 ± 0.03~~	~~106~~	~~11.4~~	~~**4.4E-20**~~
~~RH~~	~~DMA(g)~~	~~**0.36**~~	~~-0.071 ± 0.009~~	~~106~~	~~-7.7~~	~~**7.6E-12**~~
~~WS~~	~~DMA(g)~~	~~**0.30**~~	~~-0.99 ± 0.15~~	~~106~~	~~-6.8~~	~~**6.3E-10**~~
~~soil T~~	~~DMA(g)~~	~~**0.31**~~	~~0.28 ± 0.04~~	~~115~~	~~7.2~~	~~**6.2E-11**~~
~~soil Hum~~	~~DMA(g)~~	~~**0.63**~~	~~25 ± 2~~	~~113~~	~~13.9~~	~~**3.7E-26**~~
~~air T~~	~~EA(g)~~	~~0.08~~	~~-0.015 ± 0.007~~	~~49~~	~~-2.0~~	~~0.051~~
~~RH~~	~~EA(g)~~	~~0.00~~		~~49~~		~~0.83~~
~~WS~~	~~EA(g)~~	~~0.02~~		~~49~~		~~0.38~~
~~soil T~~	~~EA(g)~~	~~0.12~~	~~-0.12 ± 0.04~~	~~57~~	~~-2.8~~	~~0.0064~~
~~soil Hum~~	~~EA(g)~~	~~0.11~~	~~9 ± 4~~	~~54~~	~~2.6~~	~~0.013~~
~~air T~~	~~TMA(g)~~	~~0.06~~	~~-0.036 ± 0.009~~	~~297~~	~~-4.2~~	~~**3.3E-05**~~
~~RH~~	~~TMA(g)~~	~~0.01~~		~~297~~		~~0.18~~
~~WS~~	~~TMA(g)~~	~~0.01~~		~~297~~		~~0.038~~
~~soil T~~	~~TMA(g)~~	~~0.06~~	~~-0.05 ± 0.01~~	~~309~~	~~-4.5~~	~~**1.2E-05**~~
~~soil Hum~~	~~TMA(g)~~	~~0.09~~	~~5.1 ± 1.0~~	~~297~~	~~5.3~~	~~**2.3E-07**~~
~~air T~~	~~PA(g)~~	~~0.02~~		~~12~~		~~0.66~~
~~RH~~	~~PA(g)~~	~~0.11~~		~~12~~		~~0.25~~
~~WS~~	~~PA(g)~~	~~0.00~~		~~12~~		~~0.84~~
~~soil T~~	~~PA(g)~~	~~0.00~~		~~18~~		~~0.91~~
~~soil Hum~~	~~PA(g)~~	~~0.12~~		~~12~~		~~0.22~~
~~air T~~	~~DEA(g)~~	~~0.00~~		~~79~~		~~0.67~~
~~RH~~	~~DEA(g)~~	~~0.00~~		~~78~~		~~0.57~~
~~WS~~	~~DEA(g)~~	~~0.03~~		~~79~~		~~0.10~~
~~soil T~~	~~DEA(g)~~	~~0.04~~	~~-0.07 ± 0.04~~	~~79~~	~~-1.9~~	~~0.066~~
~~soil Hum~~	~~DEA(g)~~	~~0.04~~		~~67~~		~~0.11~~
~~air T~~	~~BA(g)~~	~~0.11~~	~~-0.006 ± 0.003~~	~~29~~	~~-1.9~~	~~0.07~~
~~RH~~	~~BA(g)~~	~~0.05~~		~~29~~		~~0.24~~
~~WS~~	~~BA(g)~~	~~0.04~~		~~29~~		~~0.31~~
~~soil T~~	~~BA(g)~~	~~0.11~~	~~-0.009 ± 0.004~~	~~31~~	~~-2.0~~	~~0.056~~
~~soil Hum~~	~~BA(g)~~	~~0.17~~	~~1.1 ± 0.5~~	~~28~~	~~2.4~~	~~0.024~~
~~air T~~	~~NH_3~~	~~0.07~~	~~0.00142 ± 0.00023~~	~~527~~	~~6.3~~	~~**6.8E-10**~~
~~RH~~	~~NH_3~~	~~0.04~~	~~-0.00040 ± 0.00008~~	~~527~~	~~-4.9~~	~~**1.3E-06**~~
~~WS~~	~~NH_3~~	~~0.00~~		~~527~~		~~0.39~~
~~soil T~~	~~NH_3~~	~~0.01~~	~~0.00075 ± 0.00029~~	~~605~~	~~2.6~~	~~0.010~~
~~soil Hum~~	~~NH_3~~	~~0.00~~		~~541~~		~~0.60~~

~~The results of the linear regression analyses of the amines, ammonia, ammonium, and the ambient conditions are presented in Tables 5 and 6. In the gas phase the p values are especially low for DMA vs. any of the ambient condition parameters, suggesting that DMA concentrations increase with increasing air temperature, soil temperature and soil humidity but decrease with increasing atmospheric humidity and wind speed. T~~In the gas phase the second strongest correlations – even though weak – are those of TMA ~~vs~~ against environmental conditions (Table S4).~~.~~ Interestingly, when looking at all data, TMA(g) concentration seems to decrease with increasing air and soil temperature (Fig. S6), opposite to the relationship of DMA ~~vs.~~and temperature. As already mentioned TMA concentrations were high in spring and they are likely to originate partly from melting snow and ground, whereas DMA might have biogenic sources in summer, which could explain different correlation ~~behavior~~behavior. The scatter plot of TMA(g) vs. temperature (Fig. S6) also reveals that the relationship is not consistent in all seasons: in summer it is even a vaguely positive, statistically not significant positivel relationship. The ammonia concentration increased with ~~the~~ air temperature ~~in line~~consistent with Makkonen et al. (2014) and decreased with increasing relative humidity. The latter suggests that at high humidity surfaces are moist and ammonia gets ~~adsorbed~~ absorbed onto the water.

All the gas phase amines except MMA were found to have a positive correlation with soil water content. The studied amines are water soluble and therefore negative correlation would be expected if the soil would act only as a sink. However, our results suggest that soil processes are producing amines and they may be enhanced with increasing humidity. Forest soils are a reservoir of the alkyl amines (Kieloaho et al. 2016) and modelling studies have shown that they can act as a source of alkyl amines to the atmosphere (Kieloaho et al. 2017). With their model Kieloaho et al. (2017) found a positive correlation with soil temperature for soil-to atmosphere flux of DMA, but correlation with soil water content was opposite to our observation.

~~Table 6. Regression statistics (y = β_1x + β_0) of amine concentrations in the aerosol phase vs. ambient conditions. Detailed column description as in Table 5.~~

~~x~~	~~y~~	~~R^2~~	~~β_1 ± s.e.~~	~~d.f.~~	~~t~~	~~p~~
~~air T~~	~~MMA(a)~~	~~0.10~~	~~-0.42 ± 0.08~~	~~235~~	~~-5.2~~	~~**3.5E-07**~~
~~RH~~	~~MMA(a)~~	~~0.09~~	~~0.11 ± 0.02~~	~~235~~	~~4.8~~	~~**2.7E-06**~~
~~WS~~	~~MMA(a)~~	~~0.05~~	~~1.8 ± 0.5~~	~~235~~	~~3.6~~	~~**4.2E-04**~~
~~soil T~~	~~MMA(a)~~	~~0.10~~	~~-0.47 ± 0.09~~	~~248~~	~~-5.3~~	~~**2.6E-07**~~
~~soil Hum~~	~~MMA(a)~~	~~0.05~~	~~26 ± 8~~	~~226~~	~~3.3~~	~~**0.0012**~~
~~air T~~	~~DMA(a)~~	~~0.04~~	~~0.12 ± 0.03~~	~~486~~	~~4.3~~	~~**2.4E-05**~~
~~RH~~	~~DMA(a)~~	~~0.02~~		~~486~~		~~**0.0020**~~
~~WS~~	~~DMA(a)~~	~~0.03~~	~~-0.9 ± 0.2~~	~~486~~	~~-3.9~~	~~**1.2E-04**~~
~~soil T~~	~~DMA(a)~~	~~0.04~~	~~0.17 ± 0.04~~	~~521~~	~~4.6~~	~~**4.6E-06**~~
~~soil Hum~~	~~DMA(a)~~	~~0.00~~		~~487~~		~~0.15~~
~~air T~~	~~EA(a)~~	~~0.11~~	~~-0.055 ± 0.02~~	~~70~~	~~-3.0~~	~~**0.0040**~~
~~RH~~	~~EA(a)~~	~~0.03~~		~~70~~		~~0.14~~
~~WS~~	~~EA(a)~~	~~0.07~~	~~0.4 ± 0.2~~	~~70~~	~~2.2~~	~~0.030~~
~~soil T~~	~~EA(a)~~	~~0.06~~	~~-0.12 ± 0.05~~	~~75~~	~~-2.2~~	~~0.029~~
~~soil Hum~~	~~EA(a)~~	~~0.16~~	~~18 ± 5~~	~~66~~	~~3.6~~	~~**5.9E-04**~~
~~air T~~	~~TMA(a)~~	~~0.01~~	~~-0.03 ± 0.01~~	~~372~~	~~-2.3~~	~~0.019~~
~~RH~~	~~TMA(a)~~	~~0.00~~		~~372~~		~~0.90~~
~~WS~~	~~TMA(a)~~	~~0.00~~		~~372~~		~~0.85~~
~~soil T~~	~~TMA(a)~~	~~0.01~~		~~383~~		~~0.028~~
~~soil Hum~~	~~TMA(a)~~	~~0.09~~	~~5.5 ± 1.0~~	~~342~~	~~5.8~~	~~**1.7E-08**~~
~~air T~~	~~PA(a)~~	~~0.01~~		~~24~~		~~0.64~~
~~RH~~	~~PA(a)~~	~~0.01~~		~~24~~		~~0.67~~
~~WS~~	~~PA(a)~~	~~0.01~~		~~24~~		~~0.57~~
~~soil T~~	~~PA(a)~~	~~0.05~~		~~28~~		~~0.24~~
~~soil Hum~~	~~PA(a)~~	~~0.10~~		~~19~~		~~0.16~~
~~air T~~	~~DEA(a)~~	~~0.18~~	~~-0.05 ± 0.02~~	~~22~~	~~-2.2~~	~~0.038~~
~~RH~~	~~DEA(a)~~	~~0.09~~		~~22~~		~~0.15~~
~~WS~~	~~DEA(a)~~	~~0.07~~		~~22~~		~~0.22~~
~~soil T~~	~~DEA(a)~~	~~0.18~~	~~-0.07 ± 0.03~~	~~24~~	~~-2.3~~	~~0.028~~
~~soil Hum~~	~~DEA(a)~~	~~0.03~~		~~18~~		~~0.47~~
~~air T~~	~~BA(a)~~	~~0.24~~	~~-0.020 ± 0.008~~	~~18~~	~~-2.4~~	~~0.028~~
~~RH~~	~~BA(a)~~	~~0.08~~		~~18~~		~~0.23~~
~~WS~~	~~BA(a)~~	~~0.02~~		~~18~~		~~0.58~~
~~soil T~~	~~BA(a)~~	~~0.21~~	~~-0.03 ± 0.01~~	~~19~~	~~-2.2~~	~~0.038~~
~~soil Hum~~	~~BA(a)~~	~~0.07~~		~~14~~		~~0.32~~
~~air T~~	~~NH_4^+~~	~~0.0382~~	~~-0.007 ± 0.001~~	~~654~~	~~-5.1~~	~~**4.5E-07**~~
~~RH~~	~~NH_4^+~~	~~0.0610~~	~~0.0031 ± 0.0005~~	~~654~~	~~6.5~~	~~**1.4E-10**~~
~~WS~~	~~NH_4^+~~	~~0.0355~~	~~0.055 ± 0.011~~	~~654~~	~~4.9~~	~~**1.2E-06**~~
~~soil T~~	~~NH_4^+~~	~~0.0665~~	~~-0.012 ± 0.002~~	~~732~~	~~-7.2~~	~~**1.3E-12**~~

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~~soil Hum~~	~~NH_4^+~~	~~0.0221~~	~~0.58 ± 0.15~~	~~668~~	~~3.9~~	~~**1.1E-04**~~

3.4 Correlations of amines with nano-particle concentrations

In addition to the dependency of amine concentrations on ambient conditions, the relationships between ~~particle~~aerosol number and amine concentrations were studied with a similar regression analysis. The amine concentrations were compared with the total number concentration integrated from the size distributions measured with the DMPS (N_{tot}), with the ~~particle~~aerosol number concentrations in the size ranges 1.1-2 nm and 2-3 nm, measured with the PSM ($N_{1.1\text{-}2nm}$ and $N_{2\text{-}3nm}$, respectively) and with the ~~particle~~aerosol particle and cluster number concentrations between 3 and 25 nm measured with the DMPS ($N_{3\text{-}25\ nm}$). The regression analysis results for the gas-phase amines and aerosol phase amines are presented in Tables ~~7~~ S6 and ~~8~~S7, respectively.

The period during which both the MARGA-MS detected ~~gas-phase~~ DMA(g) concentrations above the detection limit and the PSM detected cluster-mode ~~particle~~aerosols simultaneously was short. There were 33 data points for the regression analysis. There was a weak positive correlation between them (Fig. ~~8~~9) even though the correlation was statistically not significant (R^2 = 0.06, p = 0.18, Table ~~7~~S6). The correlation had some dependence on the ambient conditions: air relative humidity (RH) and temperature (T) as well as soil temperature (ST) and soil humidity (SH). The correlation was more significant when both soil and air were humid (RH > 90 %, SH > 0.3 $m^3\ m^{-3}$). The linear regression calculated by using only those data that were measured RH>90% has a higher correlation coefficient and slope is statistically significant (R^2 = 0.63, p = 0.006, Table S6, Fig. 9b) but it has to be noted that there were only 10 simultaneous data points at the high RH.

There was no correlation between the slightly larger ~~particle~~aerosols ($N_{2\text{-}3nm}$) and DMA~~ in the gas phase~~(g) (Table ~~7~~S6), suggesting that DMA(g) took part in the initial steps of secondary ~~particle~~aerosol formation namely clustering. This is qualitatively in agreement with an experimental CLOUD chamber study where it has been demonstrated that even very small amounts of DMA greatly enhance the formation of nano-particles (Almeida et al. 2013, Lehtipalo et al.~~,~~ 2016). In the aerosol phase DMA was the only amine that had a statistically significant correlation with the cluster-mode ~~particle~~ number concentrations and as for the gas-phase the correlation coefficient was higher at high relative humidity (Table ~~8~~S7~~, Fig. 9~~). Other ambient condition ~~parameters~~ quantities apparently did not affect this relationship (Fig. ~~8~~9).

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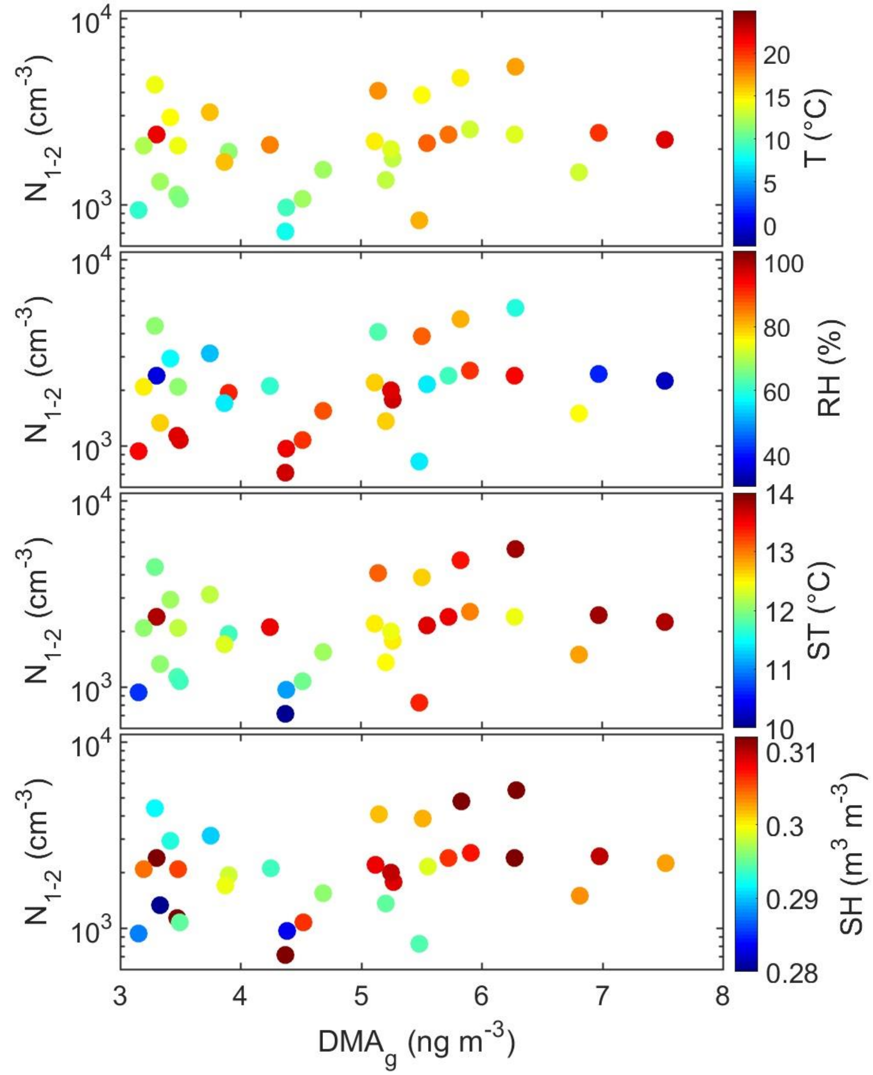
N_{1-2} (cm^{-3})
10^4
10^3
T (°C)
0
5
10
15
20
RH (%)
40
60
80
100
ST (°C)
10
11
12
13
14
SH (m^3 m^{-3})
0.28
0.29
0.3
0.31
3
4
5
6
7
8
DMA$_g$ (ng m^{-3})

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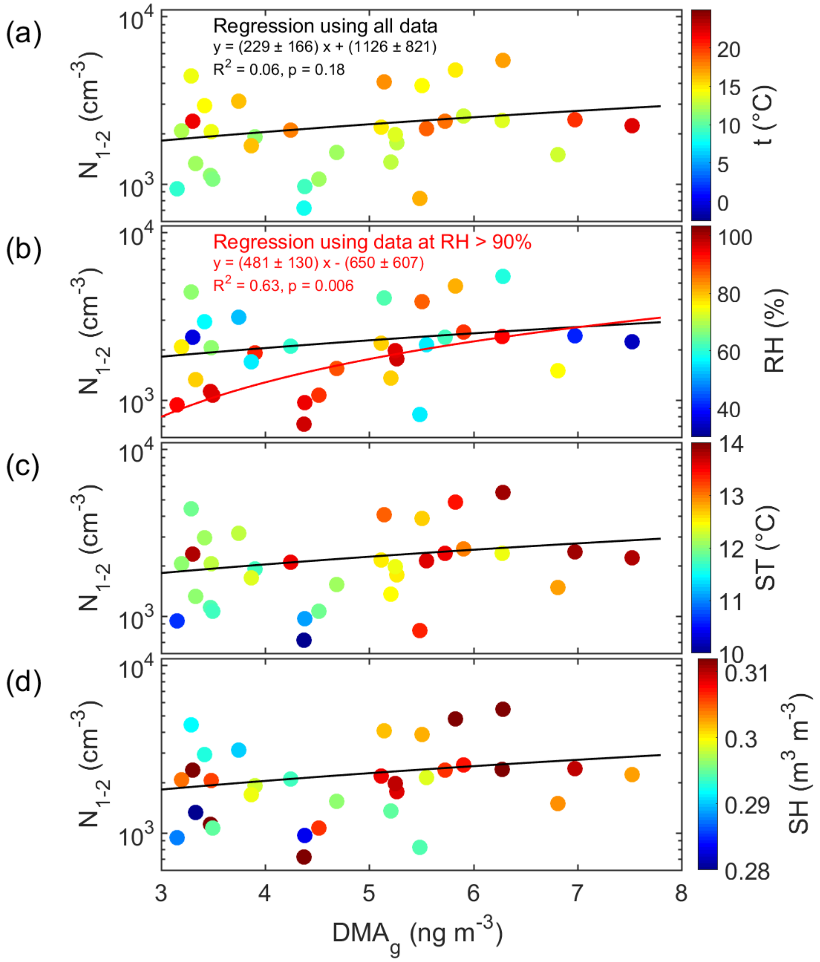

Figure ~~8~~9. Cluster-mode ~~particle~~aerosol number concentration ~~–~~($N_{1.1\text{-}2nm}$) as a function of dimethyl amine (DMA) concentration in the gas phase and color-coded with a)~~,~~ air temperature (T), b) air relative humidity (RH), c) soil temperature (ST) and d) soil humidity (SH). In all subplots the black line shows the linear regression calculated by using all data and in b) the red line shows in addition the linear regression by using only those data that were measured at RH > 90%.

~~Table 7. Regression statistics ($y = \beta_1 x + \beta_0$) of aerosol number concentrations vs. amine and ammonia concentrations in the gas phase. Detailed column description as in Table 5. N_{tot}: particle number concentration integrated from the size distributions measured with the DMPS; $N_{1.1-2nm}$ and N_{2-3nm}: particle number concentrations in the size ranges 1.2 – 2 nm and 2 – 3 nm, measured with the PSM; $N_{3-25\ nm}$: particle number concentrations between 3 and 25 nm of the DMPS. The line of DMA(g) (* was calculated by using only those data that were measured when RH > 90%.~~

~~x~~	~~y~~	~~R^2~~	~~$\beta_1 \pm$ s.e.~~	~~d.f.~~	~~t~~	~~p~~
~~MMA(g)~~	~~N_{tot}~~	~~0.11~~		~~21~~		~~0.12~~
~~MMA(g)~~	~~$N_{1.1-2\ nm}$~~			~~0~~		
~~MMA(g)~~	~~$N_{2-3\ nm}$~~			~~0~~		
~~MMA(g)~~	~~$N_{3-25\ nm}$~~	~~0.13~~	~~145 ± 83~~	~~21~~	~~1.7~~	~~0.097~~
~~DMA(g)~~	~~N_{tot}~~	~~0.16~~	~~222 ± 47~~	~~115~~	~~4.7~~	~~**6.1E-06**~~
~~DMA(g)~~	~~$N_{1.1-2\ nm}$~~	~~**0.06**~~	~~229 ± 166~~	~~31~~	~~1.4~~	~~0.18~~
~~*DMA(g) (**~~	~~$N_{1.1-2\ nm}$~~	~~***0.63***~~	~~*481 ± 130*~~	~~*8*~~	~~*3.7*~~	~~***0.0061***~~
~~DMA(g)~~	~~$N_{2-3\ nm}$~~	~~0.00~~		~~34~~		~~0.95~~
~~DMA(g)~~	~~$N_{3-25\ nm}$~~	~~0.04~~	~~58 ± 27~~	~~115~~	~~2.1~~	~~0.034~~
~~EA(g)~~	~~N_{tot}~~	~~0.01~~		~~57~~		~~0.58~~
~~EA(g)~~	~~$N_{1.1-2\ nm}$~~	~~0.05~~		~~41~~		~~0.16~~
~~EA(g)~~	~~$N_{2-3\ nm}$~~	~~0.07~~	~~-80 ± 44~~	~~43~~	~~-1.8~~	~~0.08~~
~~EA(g)~~	~~$N_{3-25\ nm}$~~	~~0.03~~		~~57~~		~~0.23~~
~~TMA(g)~~	~~N_{tot}~~	~~0.00~~		~~309~~		~~0.23~~
~~TMA(g)~~	~~$N_{1.1-2\ nm}$~~	~~0.01~~		~~187~~		~~0.12~~
~~TMA(g)~~	~~$N_{2-3\ nm}$~~	~~0.00~~		~~207~~		~~0.58~~
~~TMA(g)~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~309~~		~~0.66~~
~~PA(g)~~	~~N_{tot}~~	~~0.03~~		~~18~~		~~0.45~~
~~PA(g)~~	~~$N_{1.1-2\ nm}$~~	~~0.18~~		~~3~~		~~0.48~~
~~PA(g)~~	~~$N_{2-3\ nm}$~~	~~0.01~~		~~6~~		~~0.84~~
~~PA(g)~~	~~$N_{3-25\ nm}$~~	~~0.04~~		~~18~~		~~0.40~~
~~DEA(g)~~	~~N_{tot}~~	~~0.00~~		~~73~~		~~0.96~~
~~DEA(g)~~	~~$N_{1.1-2\ nm}$~~			~~1~~		
~~DEA(g)~~	~~$N_{2-3\ nm}$~~			~~1~~		
~~DEA(g)~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~79~~		~~0.59~~
~~BA(g)~~	~~N_{tot}~~	~~0.10~~	~~2234 ± 1230~~	~~31~~	~~1.8~~	~~0.08~~
~~BA(g)~~	~~$N_{1.1-2\ nm}$~~	~~0.01~~		~~16~~		~~0.74~~
~~BA(g)~~	~~$N_{2-3\ nm}$~~	~~0.16~~		~~17~~		~~0.09~~
~~BA(g)~~	~~$N_{3-25\ nm}$~~	~~0.01~~		~~31~~		~~0.63~~
~~NH_3~~	~~N_{tot}~~	~~0.00~~		~~605~~		~~0.93~~
~~NH_3~~	~~$N_{1.1-2\ nm}$~~	~~0.13~~	~~10853 ± 1710~~	~~272~~	~~6.3~~	~~**9.1E-10**~~
~~NH_3~~	~~$N_{2-3\ nm}$~~	~~0.03~~	~~2154 ± 656~~	~~336~~	~~3.3~~	~~**0.0011**~~
~~NH_3~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~605~~		~~0.33~~

~~Table 8. Regression statistics ($y = \beta_1 x + \beta_0$) of aerosol number concentrations vs. amine concentrations in the aerosol phase. Detailed column description as in Tables 5 – 7. The line of DMA(a) (* was calculated by using only those data that were measured when RH > 90%.~~

~~x~~	~~y~~	~~R^2~~	~~β_1 ± s.e.~~	~~d.f.~~	~~t~~	~~p~~
~~MMA(a)~~	~~N_{tot}~~	~~0.04~~	~~53 ± 15~~	~~248~~	~~3.4~~	**~~7.9E-04~~**
~~MMA(a)~~	~~$N_{1.1-2\ nm}$~~	~~0.05~~	~~-335 ± 159~~	~~77~~	~~-2.1~~	~~0.038~~
~~MMA(a)~~	~~$N_{2-3\ nm}$~~	~~0.03~~		~~77~~		~~0.16~~
~~MMA(a)~~	~~$N_{3-25\ nm}$~~	~~0.02~~		~~247~~		~~0.019~~
~~DMA(a)~~	~~N_{tot}~~	~~0.00~~		~~521~~		~~0.48~~
~~DMA(a)~~	~~$N_{1.1-2\ nm}$~~	~~0.10~~	~~99 ± 20~~	~~215~~	~~4.9~~	**~~1.8E-06~~**
~~DMA(a)(~~*	~~$N_{1.1-2\ nm}$~~	~~0.14~~	~~59 ± 23~~	~~43~~	~~2.6~~	**~~0.013~~**
~~DMA(a)~~	~~$N_{2-3\ nm}$~~	~~0.00~~		~~217~~		~~0.93~~
~~DMA(a)~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~519~~		~~0.21~~
~~EA(a)~~	~~N_{tot}~~	~~0.01~~		~~75~~		~~0.42~~
~~EA(a)~~	~~$N_{1.1-2\ nm}$~~	~~0.03~~		~~46~~		~~0.22~~
~~EA(a)~~	~~$N_{2-3\ nm}$~~	~~0.01~~		~~37~~		~~0.51~~
~~EA(a)~~	~~$N_{3-25\ nm}$~~	~~0.32~~	~~103 ± 17~~	~~75~~	~~6.0~~	**~~7.1E-08~~**
~~TMA(a)~~	~~N_{tot}~~	~~0.00~~		~~383~~		~~0.91~~
~~TMA(a)~~	~~$N_{1.1-2\ nm}$~~	~~0.00~~		~~232~~		~~0.75~~
~~TMA(a)~~	~~$N_{2-3\ nm}$~~	~~0.00~~		~~204~~		~~0.32~~
~~TMA(a)~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~382~~		~~0.74~~
~~PA(a)~~	~~N_{tot}~~	~~0.00~~		~~28~~		~~0.93~~
~~PA(a)~~	~~$N_{1.1-2\ nm}$~~			~~1~~		
~~PA(a)~~	~~$N_{2-3\ nm}$~~			~~0~~		
~~PA(a)~~	~~$N_{3-25\ nm}$~~	~~0.01~~		~~28~~		~~0.53~~
~~DEA(a)~~	~~N_{tot}~~	~~0.02~~		~~24~~		~~0.47~~
~~DEA(a)~~	~~$N_{1.1-2\ nm}$~~			~~1~~		
~~DEA(a)~~	~~$N_{2-3\ nm}$~~			~~1~~		
~~DEA(a)~~	~~$N_{3-25\ nm}$~~	~~0.02~~		~~24~~		~~0.54~~
~~BA(a)~~	~~N_{tot}~~	~~0.03~~		~~19~~		~~0.44~~
~~BA(a)~~	~~$N_{1.1-2\ nm}$~~			~~4~~		
~~BA(a)~~	~~$N_{2-3\ nm}$~~			~~2~~		
~~BA(a)~~	~~$N_{3-25\ nm}$~~	~~0.00~~		~~19~~		~~0.80~~
~~NH_4^+~~	~~N_{tot}~~	~~0.04~~	~~1194 ± 224~~	~~732~~	~~5.3~~	**~~1.3E-07~~**
~~NH_4^+~~	~~$N_{1.1-2\ nm}$~~	~~0.00~~				~~0.99~~
~~NH_4^+~~	~~$N_{2-3\ nm}$~~	~~0.00~~				~~0.40~~
~~NH_4^+~~	~~$N_{3-25\ nm}$~~	~~0.03~~	~~-703 ± 147~~	~~732~~	~~-4.8~~	**~~2.12-06~~**

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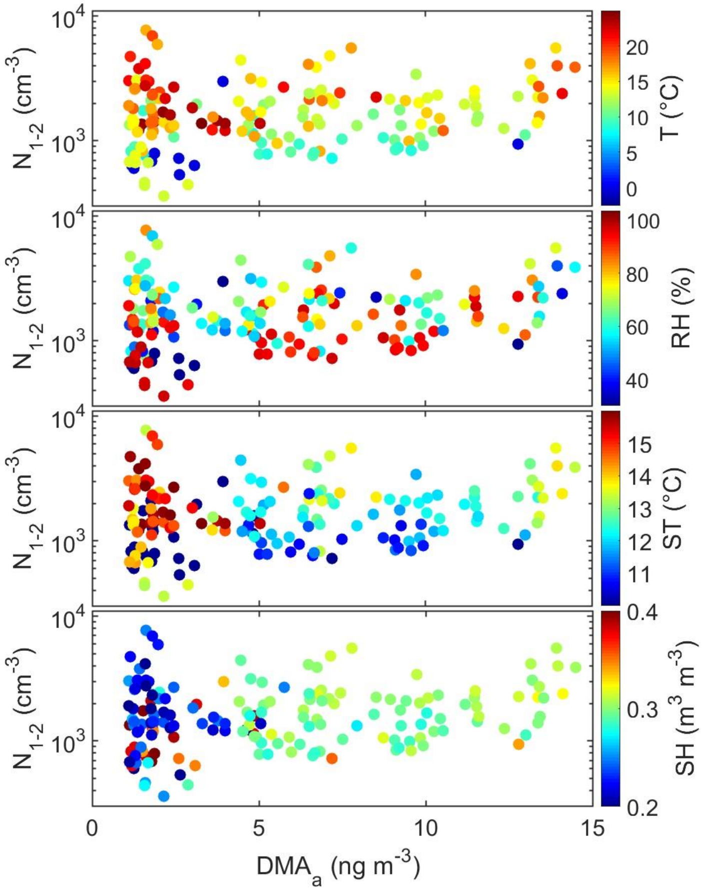

~~Figure 9. Cluster-mode particle number concentration ($N_{1.1-2nm}$) as a function of dimethyl amine (DMA(a) concentration in the aerosol phase, air temperature (T), air relative humidity (RH), soil temperature (ST) and soil humidity (SH).~~

There were considerably more simultaneous data points of the cluster-mode ~~particle~~aerosol number concentration and ammonia (NH_3). The correlation $N_{1.1-2nm}$ vs. NH_3 was statistically significant ($R^2 = 0.13$, p~~$= 9.1*10^{-10}$~~<0.001, Table ~~7~~S6). In addition, this correlation apparently also depended on the ambient conditions so that in warm (T >15°C, ST > 14°C) and dry (RH < 60%, SH < 0.25 m^3 m^{-3}) conditions the positive correlation was more obvious (Fig. ~~10~~10). In the aerosol phase ammonium (NH_4^+) did not correlate at all with the cluster mode particle number concentration~~s~~ but positively with the total

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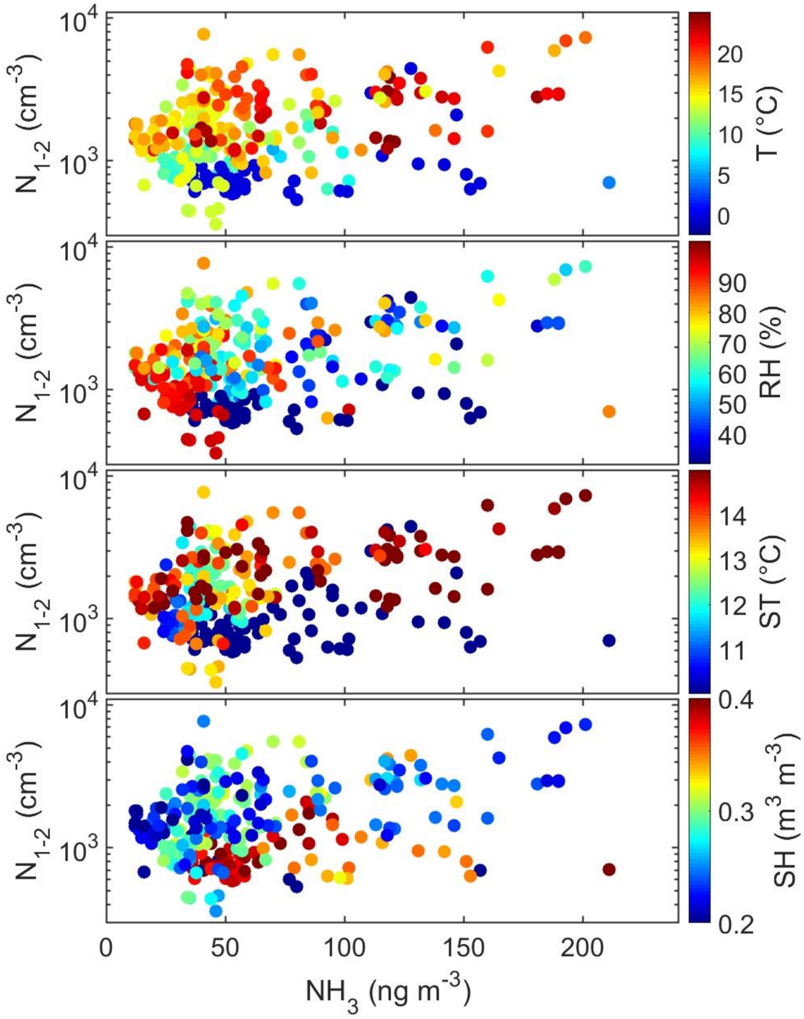

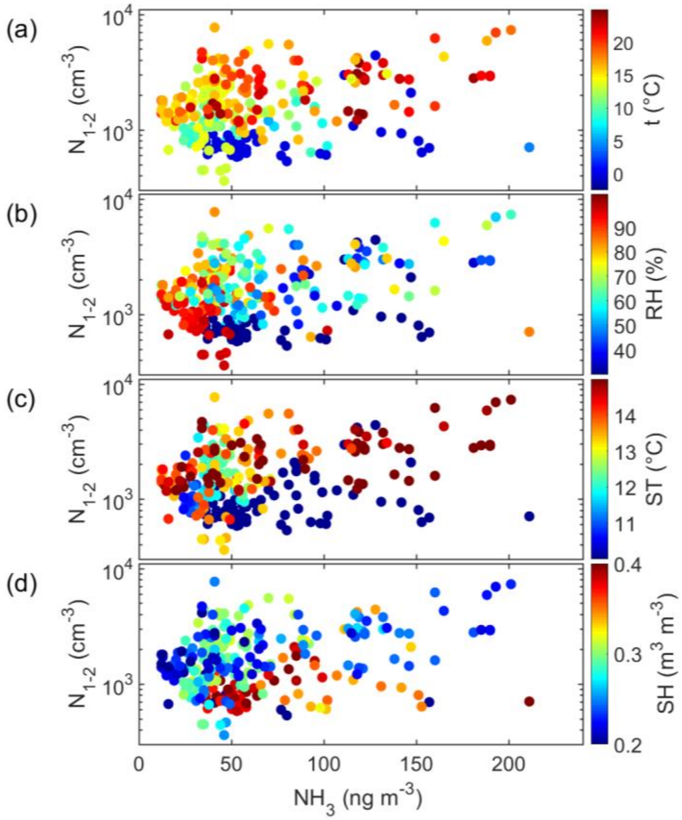

Figure ~~10~~10. Cluster-mode ~~particle~~aerosol number concentration ($N_{1.1\text{-}2nm}$) as a function of ammonia (NH_3) concentration and color-coded with~~,~~ a) air temperature (t), b) air relative humidity (RH), c) soil temperature (ST) and d) soil humidity (SH).

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~~The other amines did not have any significant correlations with the particles in the smallest particle size ranges.~~

4. Conclusions

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An on-line method using in-situ ion-chromatograph with mass-spectrometric detection for~~ sampling, separating and detecting~~ measuring amines in low concentrations from the ambient air both in the gas and aerosol phase was developed. In situ amine and ammonia measurements were conducted in SMEAR II station (Hyytiälä, Finland) from March 2015 to

December 2015, covering altogether about 8 weeks. Concentrations of 7 different amines and ammonia in ~~particle~~aerosol- and gas-phase were measured with 1-hour time resolution.

The developed MARGA-MS method was suitable for field measurements of amines. The DLs were low (0.2–11.4 ng m^{-3}), and the accuracy and precision of IC-MS analysis were moderately good. With the method amines with same masses or same retention time were separated, only DEA and BA were incompletely separated. However, MARGA-MS had some technical drawbacks (e.g. consumption of ~40 l of solutions per week).

The amines turned out to be a heterogeneous group of compounds; different amines are likely to have different sources. All amines had higher concentrations in the aerosol phase than in the gas phase. MMA and TMA concentrations were the highest in spring concomitant with ammonia and ammonium. Melting of snow and ground can be the source of these compounds. The decomposing litter and organic soil layer beneath snow can release organic compounds to snow cover and to the atmosphere. ~~Measured concentrations of summed up ammonia and ammonium were also highest in spring and the share of ammonia increased towards summer.~~

TMA ha~~s~~d an additional maximum simultaneously with DMA during summer, ~~which could indicate biogenic source~~and EA was only detected in July. The summer maxima could indicate biogenic sources. However, unlike EA, ~~they~~ DMA and TMA did not show similar diurnal variation as monoterpenes. The diurnal variation is determined by the balance between emissions, reactivity and mixing in the atmosphere. Usually ambient concentrations of biogenic volatile organic compounds, which have temperature dependent emissions, peak during nighttime due to inefficient mixing and lack of hydroxyl radical reactions which only take place during daytime. The~~is~~ missing daytime minima of DMA and TMA ~~um~~ can be due to light dependent biogenic source, or TMA and DMA might be re-emitted from surfaces during daytime, when temperature increases.

All amines except MMA ~~are positively~~ correlated positively with soil humidity, which could indicate a humidity dependent production mechanism. ~~Gas-~~ Gas-phase DMA correlated positively with small 1.1-2 nm ~~particle~~aerosols, when both soil and air were humid. It did not correlate~~d~~ with slightly ~~bigger~~ larger ~~particle~~aerosols at all, suggesting that gas phase DMA may be important in new ~~particle~~aerosol formation.

Data availability. The datasets can be accessed by contacting the corresponding author.

Competing interests. The authors declare that they have no conflict of interest.

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