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 measurements covered about 8 weeks between March

15 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 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}

20 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, NH$_3$ and NH$_4^+$, were <2.4 ng m^{-3}, 19 ng m^{-3} and 90 ng m^{-3} respectively. DMA and TMA had summer maxima indicating biogenic sources. We observed diurnal variation for DMA but not for TMA. The highest concentrations of these compounds were measured in July. 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

25 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 new particle formation. 0.63 EA concentrations were low all the time, July means were <0.36 ng m^{-3} and 0.4 ± 0.4 ng m^{-3} in gas and aerosol phase respectively, but they 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

Amines are gaseous bases, whose general formula is RNH_2, R_2NH or R_3N. Models based on quantum chemistry data have
35 shown that they could participate in aerosol particle formation with sulfuric acid even at very low mixing ratios (Kurtén et al. 2008, Paasonen et al. 2012). Also the recent laboratory experiments at CLOUD chamber shows that already minute concentrations of dimethylamine (DMA) are able to produce new particles with sulphuric acid (Almeida et al. 2013, Kürten et al. 2016) Atmospheric aerosol particles affect the climate, because they can act as cloud condensation nuclei (IPCC 2014). They also scatter and absorb sun radiation. Amines also affect hydroxyl radical (OH) reactivity and therefore atmospheric
40 chemistry (Hellén et al. 2014, Kieloaho et al. 2013).

Ambient gas phase amines have been measured earlier using different methods. Samples have been collected in phosphoric acid-impregnated fiberglass filters (Kieloaho et al., 2013), to solid phase micro extraction fiber (Parshintsev et al. 2015) and to ion exchange resin (Dawson et al. 2014) and they have been percolated through acidic solution (Akyüz M., 2007).
45 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 liquid chromatography coupled to mass spectrometry (HPLC-MS) (Kieloaho et al. 2013). The mentioned techniques have various shortcomings: quantitation based on collection on fibers is problematic, collecting in filters requires long sampling times (usually several days), percolating in acidic solutions requires intensive sample pre-
50 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 novel in-situ methods for measuring ambient air gas-phase amines have been developed, usually based on mass-
55 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
60 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 phase amines have been sampled to filters and analyzed later in 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
65 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 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 detection limits remain too high for measurements in the boreal forest.

70 These methods have been utilized in short campaigns from couple of days to couple of weeks. Only Kieloaho et al. (2013) measured longer period, but their sampling time was long (24 – 72 h). Most of the measurements discussed previously were made in urban or sub-urban area, and only some (Sellegri et al. 2005, Kieloaho et al. 2013, Kulmala et al. 2013 and Sipilä et al. 2015) were made in boreal forest site.

75 The in-situ method developed in this study for atmospheric amine measurements was used in the boreal forest, where amines are expected to affect aerosol particle formation even at extremely low concentrations (Kurtén et al. 2008, Paasonen et al. 2012). We report seasonal and diurnal variations of amines in boreal forest air and their partitioning between gas and particle phase. 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

2.1 Measurement site

Measurements were performed in a Scots pine forest at the SMEAR II station (Station for Measuring Forest Ecosystem-
85 Atmosphere Relations) in Hyytiälä, Southern Finland (61°510′N, 24°170′E, 180 m a.s.l., Hari and Kulmala, 2005). The largest nearby city is Tampere, situated 60 km southwest from the station with approximately 364 000 inhabitants. The instrument was located in a container about 4 meters outside the forest in a small opening. In addition to pines, also small spruces (Picea abies) were growing 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.

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2.2 Meteorological conditions

Data for the meteorological parameters were obtained from the SmartSmear AVAA portal (Junninen et al. 2009). Table 1 shows the meteorological conditions during measurements periods.

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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

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2.3 Measurement methods

In the present study we used MARGA (instrument for Measuring AeRosols and Gases in Ambient air, Metrohm-Applikon, Schiedam, Netherlands) (ten Brink et al. 2007) for sampling and measuring. MARGA is an online ion chromatograph (IC)
105 connected to a sampling system. In addition, this system was connected to an electrospray ionization quadrupole MS (Shimadzu LCMS-2020, Shimadzu Corporation, Kyoto, Japan) to improve sensitivity of amine measurements. 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).

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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) were calculated from signal-to-noise ratios (3:1) for most of the compounds
115 and they were similar in gas and particle phase (Table 2). 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 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 (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

125 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.

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In the figures we used moving average for DMA, because every other measured DMA concentration was a little higher than the other 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.

135 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 ($N_{3-25\ nm}$), referred to as 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

140 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 ($N_{1.1-2nm}$) was used. In addition, the particle concentration between 2 and 3 nm (N_{2-3nm}), was obtained by subtracting

145 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

150 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 = β_1/s.e.). The test statistics were compared with the Student's t distribution on n - 2 (sample size - number of

155 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

160 humidity.

3. Results

3.1 Variability of the concentrations

Figure 1 shows the monthly means and medians of total amine concentrations (sum of gas and aerosol phases) and Figure 2 shows the box and whisker plots to describe the statistics of the measured concentrations. Amines were mainly in aerosol phase (Table 3 and 4). Different seasonal patterns were found for different amines and they are described below.

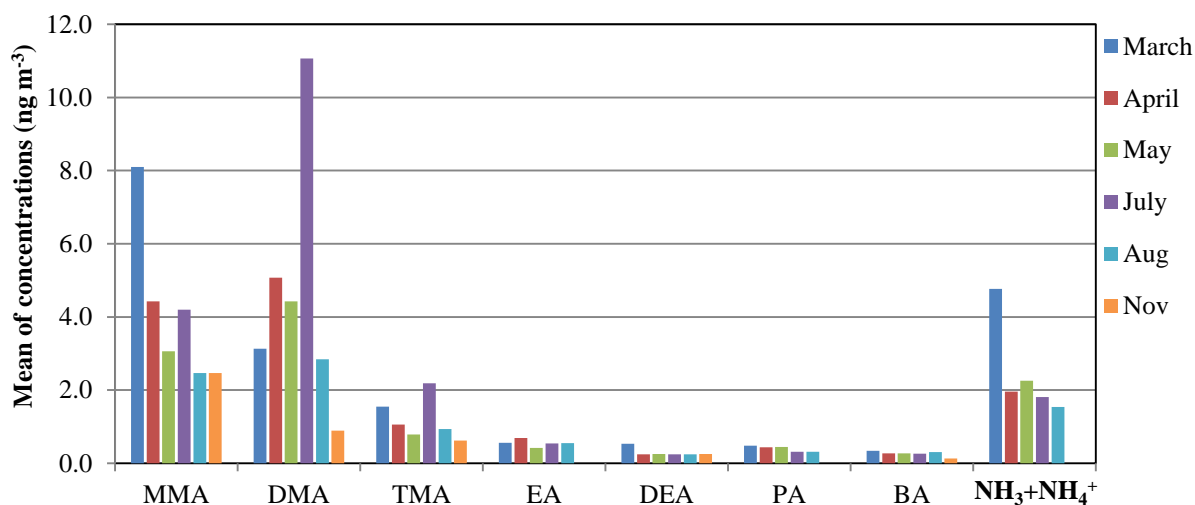
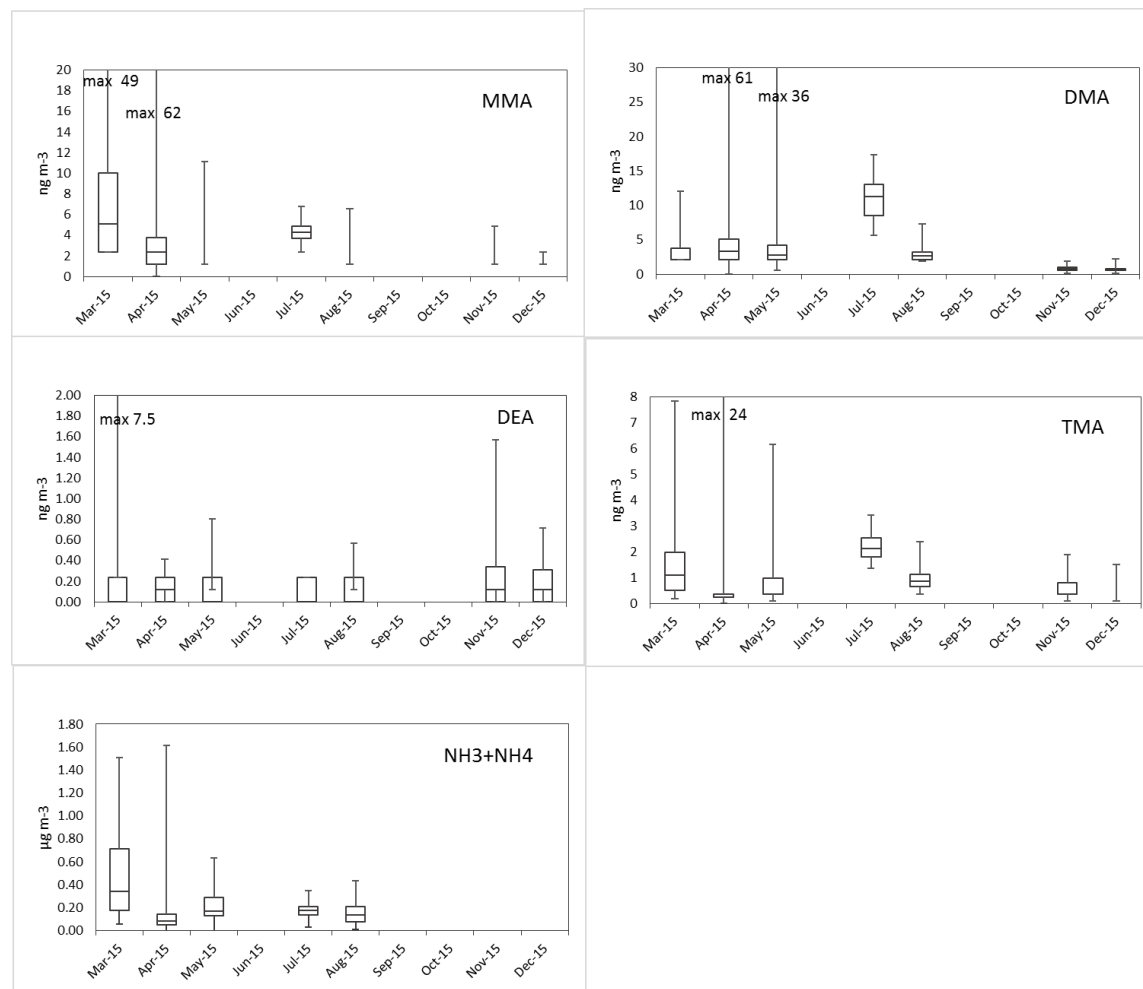



Figure 1. Monthly means of total amine and summed up ammonia and ammonium ($NH_3+NH_4^+$) concentrations (ng/m^3). $NH_3+NH_4^+$ concentrations have been divided by 100, to fit the scale.

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

180 Table 3. Ratio of gas and aerosol phases. N=number of data above detection limit, ratio=gas/(gas+aerosol).

	DEA	BA	DMA	TMA	PA	EA	MMA	NH$_3$
N	6	3	53	208	5	21	9	596
Average ratio	-	-	0.44	0.29	-	0.48	0.41	0.35
Min ratio	-	-	0.09	0.10	-	0.05	0.18	0.05
Max ratio	-	-	0.83	0.90	-	0.95	0.52	0.84

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		

3.1.1 MMA

185   A spring maximum was observed for MMA (max. 50 ng m^{-3}) and the concentrations correlated with the sum of NH$_3$ and

NH$_4^+$ (R^2=0.52, Fig. 3). During spring we observed two occasions when MMA and the sum of NH$_3$ and NH$_4^+$ concentrations

increased considerably at the same time. 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.

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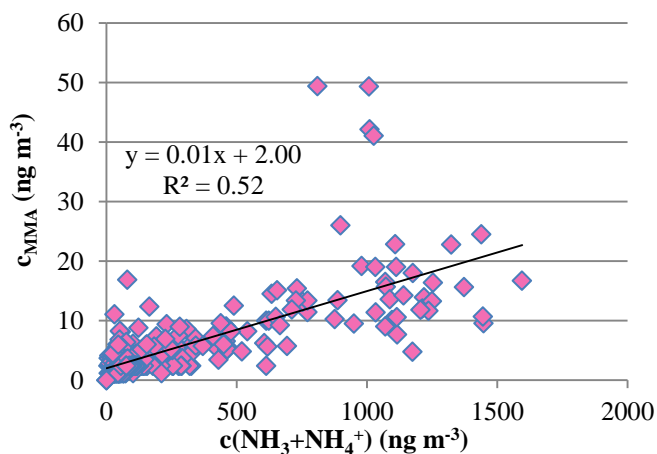
Figure 3. Concentrations (ng/m^3) of total MMA (y-axis) vs concentrations of $NH_3 + NH_4^+$ (x-axis) in March and April 2015.

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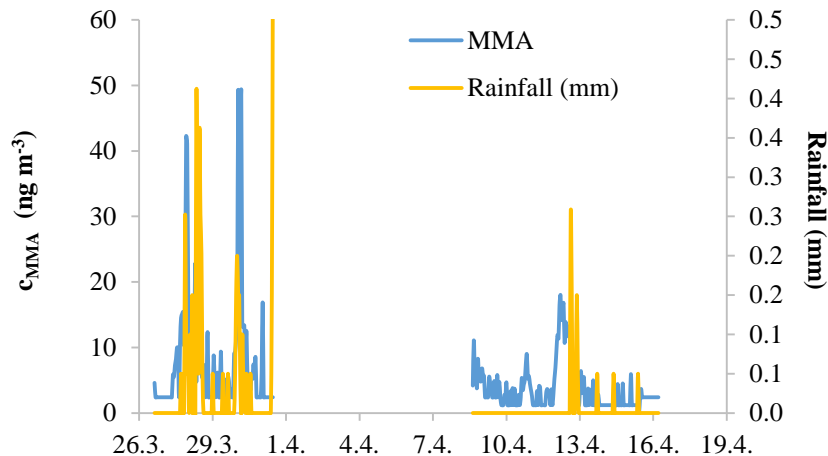


Figure 4: MMA concentrations (gas and aerosol phase) and rainfall measured in Hyytiälä during spring 2015.

Most of the MMA was in particle phase (Table 3 and 4): monthly mean of aerosol phase MMA varied between <2.4 and 6.8
200 ng m^{-3} (Table 4), while monthly means of gas phase MMA were below DL throughout the measurements. In early winter
(late November to early December) MMA was not detected. Ammonia showed similar seasonal variation as MMA with the
maximum in March and lower concentrations towards the end of summer. During spring ammonia was also mainly in
aerosol phase. In earlier studies You et al. (2014) detected gaseous MMA with CIMS in Alabama forest in summer, at about

the same level as our measurements (maximum ~3.8 ng m^{-3}). Also Freshour et al. (2014) measured MMA with AmPMS in 3

205   different sites in USA, and their mean concentrations were at the same level than 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 mean results were 0.26 and 1.30 ng m^{-3}, respectively. Values are in same level with our measurements. That is surprising, because in urban area there are lots of MMA-sources (e.g. industry and automobiles, Ge et al. 2011), so higher mean concentrations would have been expected.

210   **3.1.2 TMA**

TMA had higher concentrations in March after which they declined, before increasing again in July to their maximum concentrations (Fig. 2). TMA concentrations also peaked at the end of March during rain simultaneously with MMA and the sum of NH_3 and NH_4^+ increasing from about 1.5 to 6.0 ng m^{-3}. During summer measurements TMA 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

215   the increase in nucleation mode particle concentration. The share of the gas phase was throughout the measurements roughly half of the particle phase concentration (Table 3 and 4). TMA did not show a clear diurnal variation.

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 and PA in July. In their measurements the

220   concentrations increased during fall. 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 cattle farm in Chino, California, and analysed the samples wit IC. Their results varied from 1.3-6.8 ppm$_v$ (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

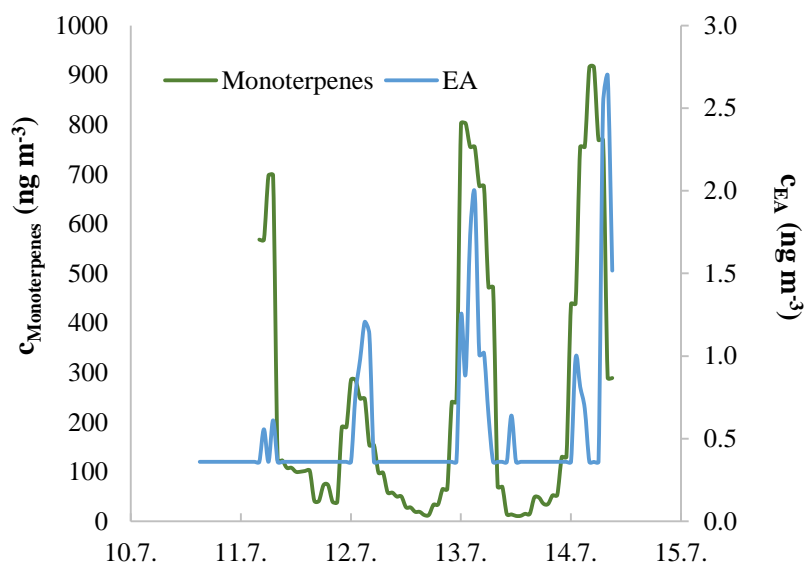
225   source of amines. Sellegri et al. (2014) measured amines in March 2002 with CIMS in same boreal forest than we did. They found TMA with mixing ratios 34-80 ppt$_v$ (ca. 82-193 ng m^{-3}), so their results are ~30 times higher than ours. Ambient conditions were different than ours when they measured TMA, and that could be one reason for higher concentrations they observed.

3.1.3 EA

230   EA concentrations were low throughout the measurements, but showed a clear diurnal variation in July with a maximum at night (Fig. 5). 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 mixing and OH radical sink reactions. The rate coefficients of alkyl amines are slightly lower, but comparable to monoterpene reactions with OH radical. The most common monoterpenes in

235   the boreal forest are α-pinene, 3-carene and β-pinene (Hakola et al. 2012). Their OH radical rate coefficients are 53.7·10^{-12},

$88 \cdot 10^{-12}$, and $78.9 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively (Atkinson 1994), whereas MMA, EA, DMA and TMA rate coefficients with OH radicals are $22.26 \cdot 10^{-12}$, $29.85 \cdot 10^{-12}$, $65.53 \cdot 10^{-12}$, and $69.75 \cdot 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively (U.S. EPA, 2017). Similar diurnal patterns and reactivities indicates 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

240   not observe clear diurnal variation for C_2-amines. In our measurements, EA and DMA had opposite diurnal variations (see chapter 3.1.4). That could be the one reason for results of Kürten et al. (2016).

245   Figure 5. Total EA and monoterpene concentrations in Hyytiälä in July 2015.

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

250   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

255   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

260   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).

In August DMA had diurnal variation with a daytime maximum (Fig. 6), but during some nights the concentrations also

265   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.

270   Thus, DMA source could be light dependent.

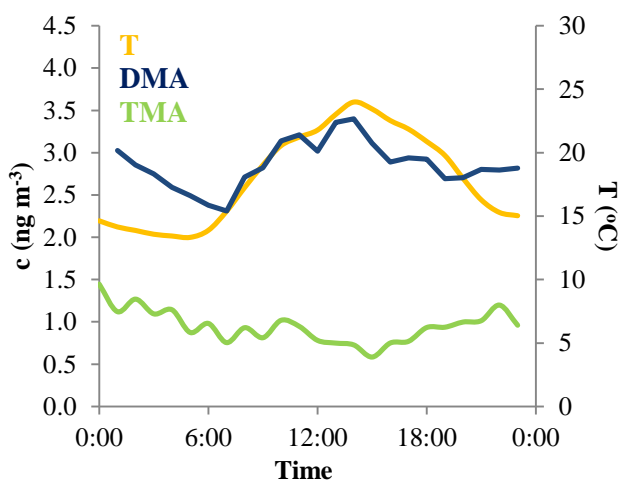



Figure 6. Average diurnal variation of total DMA (blue), total TMA (green) concentrations and temperature (yellow) in

275   August 2015.

3.2 Correlation with meteorological parameters and nano-particle concentrations

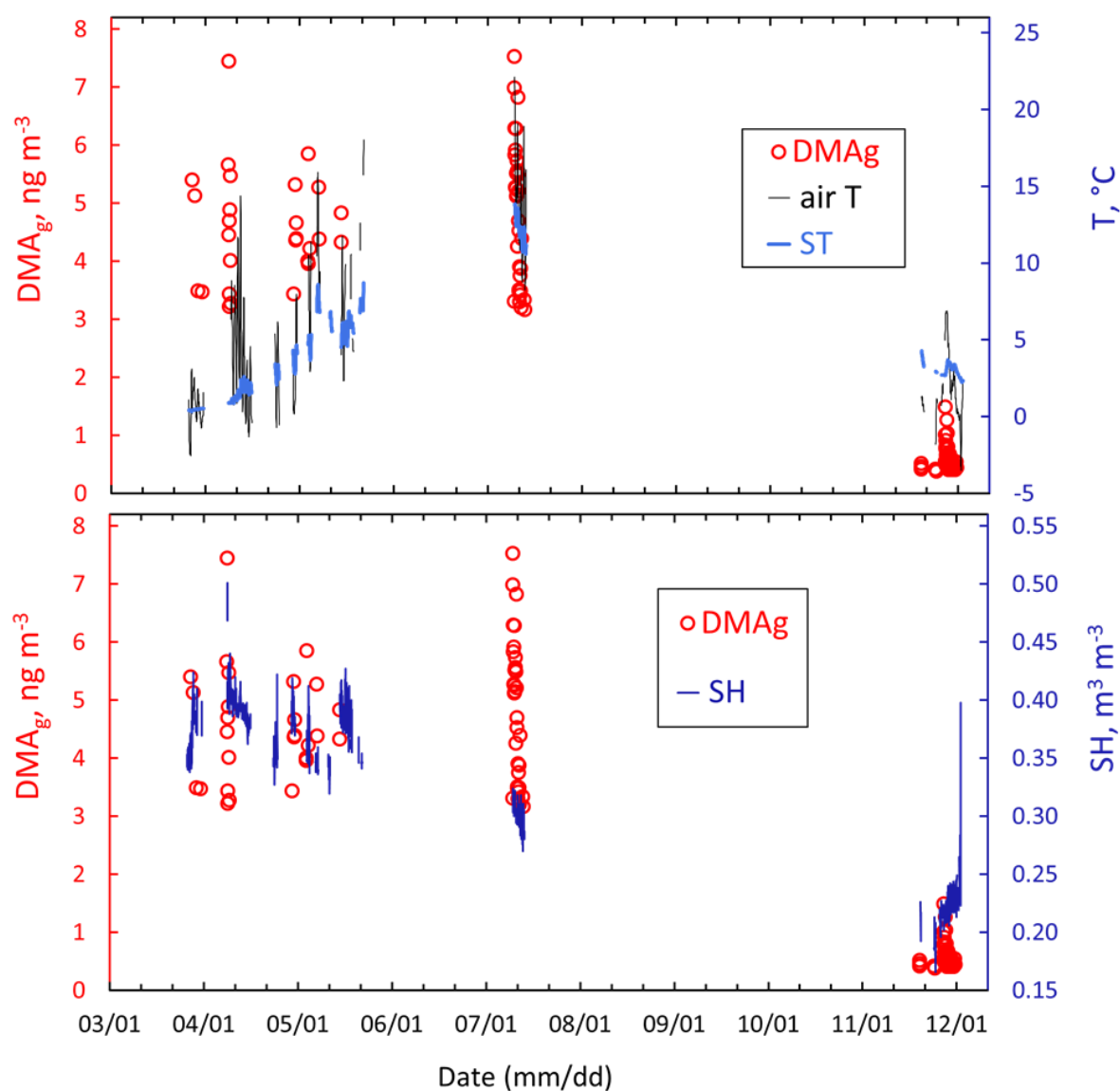
We noticed that especially concentrations of DMA vary with temperature (Fig. 7), so we decided to calculate linear
280   regressions of amines, ammonia and ammonium with different ambient conditions (air relative humidity (RH) and
temperature (T) as well as soil temperature (ST) and soil humidity (SH)). Gas phase DMA had the strongest correlation with
ambient conditions (Table 5).

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

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	$\beta_1 \pm$ s.e.	d.f.	t	p
air T	MMA	0.01		11		0.82
RH	MMA	0.16		11		0.17
WS	MMA	0.17		11		0.16
soil T	MMA	0.00		21		0.94
soil Hum	MMA	0.00		19		0.85
air T	DMA	**0.55**	0.29 ± 0.03	106	11.4	**4.4E-20**
RH	DMA	**0.36**	-0.071 ± 0.009	106	-7.7	**7.6E-12**
WS	DMA	**0.30**	-0.99 ± 0.15	106	-6.8	**6.3E-10**
soil T	DMA	**0.31**	0.28 ± 0.04	115	7.2	**6.2E-11**
soil Hum	DMA	**0.63**	25 ± 2	113	13.9	**3.7E-26**
air T	EA	0.08	-0.015 ± 0.007	49	-2.0	0.051
RH	EA	0.00		49		0.83
WS	EA	0.02		49		0.38
soil T	EA	0.12	-0.12 ± 0.04	57	-2.8	0.0064
soil Hum	EA	0.11	9 ± 4	54	2.6	0.013
air T	TMA	0.06	-0.036 ± 0.009	297	-4.2	**3.3E-05**
RH	TMA	0.01		297		0.18
WS	TMA	0.01		297		0.038
soil T	TMA	0.06	-0.05 ± 0.01	309	-4.5	**1.2E-05**
soil Hum	TMA	0.09	5.1 ± 1.0	297	5.3	**2.3E-07**
air T	PA	0.02		12		0.66
RH	PA	0.11		12		0.25
WS	PA	0.00		12		0.84
soil T	PA	0.00		18		0.91
soil Hum	PA	0.12		12		0.22
air T	DEA	0.00		79		0.67
RH	DEA	0.00		78		0.57
WS	DEA	0.03		79		0.10
soil T	DEA	0.04	-0.07 ± 0.04	79	-1.9	0.066
soil Hum	DEA	0.04		67		0.11
air T	BA	0.11	-0.006 ± 0.003	29	-1.9	0.07
RH	BA	0.05		29		0.24
WS	BA	0.04		29		0.31
soil T	BA	0.11	-0.009 ± 0.004	31	-2.0	0.056
soil Hum	BA	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,
295 suggesting that DMA concentrations increase with increasing air temperature, soil temperature and soil humidity but decrease with increasing atmospheric humidity and wind speed. The second strongest correlations are those of TMA vs environmental conditions. Interestingly, TMA concentration seems to decrease with increasing air and soil temperature, opposite to the relationship of DMA vs. 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,
300 which could explain different correlation behavior. The ammonia concentration increased with the air temperature in line 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 on the water.

All the gas phase amines except MMA were found to have positive correlation with soil water content. The studied amines
305 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 positive correlation with soil temperature for soil-to atmosphere flux of DMA, but correlation with soil water content was opposite.
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Table 6. Regression statistics ($y = \beta_1 x + \beta_0$) of amine concentrations in the aerosol phase vs. ambient conditions. Detailed column description as in Table 5.

x	y	R^2	$\beta_1 \pm$ s.e.	d.f.	t	p
air T	MMA	0.10	-0.42 ± 0.08	235	-5.2	**3.5E-07**
RH	MMA	0.09	0.11 ± 0.02	235	4.8	**2.7E-06**
WS	MMA	0.05	1.8 ± 0.5	235	3.6	**4.2E-04**
soil T	MMA	0.10	-0.47 ± 0.09	248	-5.3	**2.6E-07**
soil Hum	MMA	0.05	26 ± 8	226	3.3	**0.0012**
air T	DMA	0.04	0.12 ± 0.03	486	4.3	**2.4E-05**
RH	DMA	0.02		486		**0.0020**
WS	DMA	0.03	-0.9 ± 0.2	486	-3.9	**1.2E-04**
soil T	DMA	0.04	0.17 ± 0.04	521	4.6	**4.6E-06**
soil Hum	DMA	0.00		487		0.15
air T	EA	0.11	-0.055 ± 0.02	70	-3.0	**0.0040**
RH	EA	0.03		70		0.14
WS	EA	0.07	0.4 ± 0.2	70	2.2	0.030
soil T	EA	0.06	-0.12 ± 0.05	75	-2.2	0.029
soil Hum	EA	0.16	18 ± 5	66	3.6	**5.9E-04**
air T	TMA	0.01	-0.03 ± 0.01	372	-2.3	0.019
RH	TMA	0.00		372		0.90
WS	TMA	0.00		372		0.85
soil T	TMA	0.01		383		0.028
soil Hum	TMA	0.09	5.5 ± 1.0	342	5.8	**1.7E-08**
air T	PA	0.01		24		0.64
RH	PA	0.01		24		0.67
WS	PA	0.01		24		0.57
soil T	PA	0.05		28		0.24
soil Hum	PA	0.10		19		0.16
air T	DEA	0.18	-0.05 ± 0.02	22	-2.2	0.038
RH	DEA	0.09		22		0.15
WS	DEA	0.07		22		0.22
soil T	DEA	0.18	-0.07 ± 0.03	24	-2.3	0.028
soil Hum	DEA	0.03		18		0.47
air T	BA	0.24	-0.020 ± 0.008	18	-2.4	0.028
RH	BA	0.08		18		0.23
WS	BA	0.02		18		0.58
soil T	BA	0.21	-0.03 ± 0.01	19	-2.2	0.038
soil Hum	BA	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**
soil Hum	NH_4^+	0.0221	0.58 ± 0.15	668	3.9	**1.1E-04**

330   In addition to the dependency of amine concentrations on ambient conditions, the relationships between particle 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 number concentrations in the size ranges 1.1-2 nm and 2-3 nm, measured with the PSM ($N_{1.1-2nm}$ and N_{2-3nm}, respectively) and with the particle number concentrations between 3 and 25 nm measured with the DMPS ($N_{3-25\ nm}$). The regression analysis results

335   for the gas-phase amines and aerosol phase amines are presented in Tables 7 and 8, respectively.

The period during which both the MARGA-MS detected gas-phase DMA concentrations above detection limit and the PSM detected cluster-mode particles simultaneously was short. There were 33 data points for the regression analysis. There was a weak positive correlation between them (Fig. 8) even though the correlation was statistically not significant ($R^2 = 0.06$, p =

340   0.18, Table 7). 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 $m^3\ m^{-3}$) 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 particles (N_{2-3nm}) and DMA in the gas phase (Table 7), suggesting that DMA took part in the initial steps of particle formation. This is qualitatively in agreement with an experimental CLOUD

345   chamber study where it has been demonstrated that even very small amounts of DMA greatly enhance the formation of nano-particles (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, Fig. 9). Other ambient condition parameters apparently did not affect this relationship (Fig. 8).

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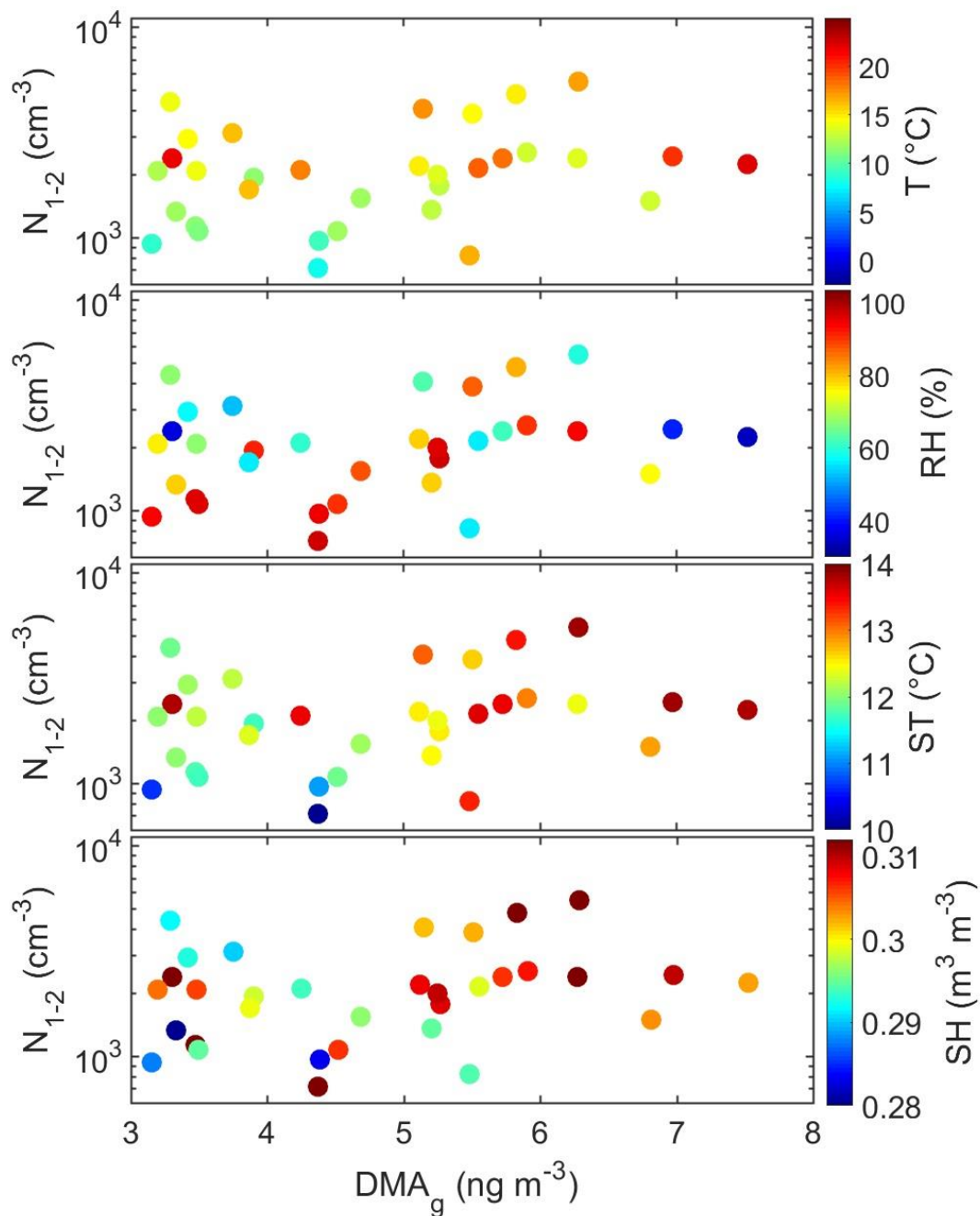
Figure 8. Cluster-mode particle number concentration ($N_{1.1-2nm}$) as a function of dimethyl amine (DMA) concentration in the
355 gas phase, air temperature (T), air relative humidity (RH), soil temperature (ST) and soil humidity (SH).

360   Table 7. Regression statistics (y = β₁x + β₀) 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(* 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	N_{tot}	0.11		21		0.12
MMA	$N_{1.1-2\ nm}$			0		
MMA	$N_{2-3\ nm}$			0		
MMA	$N_{3-25\ nm}$	0.13	145 ± 83	21	1.7	0.097
DMA	N_{tot}	0.16	222 ± 47	115	4.7	**6.1E-06**
DMA	$N_{1.1-2\ nm}$	**0.06**	229 ± 166	31	1.4	0.18
*DMA(**	*$N_{1.1-2\ nm}$*	*0.63*	*481 ± 130*	*8*	*3.7*	*0.0061*
DMA	$N_{2-3\ nm}$	0.00		34		0.95
DMA	$N_{3-25\ nm}$	0.04	58 ± 27	115	2.1	0.034
EA	N_{tot}	0.01		57		0.58
EA	$N_{1.1-2\ nm}$	0.05		41		0.16
EA	$N_{2-3\ nm}$	0.07	-80 ± 44	43	-1.8	0.08
EA	$N_{3-25\ nm}$	0.03		57		0.23
TMA	N_{tot}	0.00		309		0.23
TMA	$N_{1.1-2\ nm}$	0.01		187		0.12
TMA	$N_{2-3\ nm}$	0.00		207		0.58
TMA	$N_{3-25\ nm}$	0.00		309		0.66
PA	N_{tot}	0.03		18		0.45
PA	$N_{1.1-2\ nm}$	0.18		3		0.48
PA	$N_{2-3\ nm}$	0.01		6		0.84
PA	$N_{3-25\ nm}$	0.04		18		0.40
DEA	N_{tot}	0.00		73		0.96
DEA	$N_{1.1-2\ nm}$			1		
DEA	$N_{2-3\ nm}$			1		
DEA	$N_{3-25\ nm}$	0.00		79		0.59
BA	N_{tot}	0.10	2234 ± 1230	31	1.8	0.08
BA	$N_{1.1-2\ nm}$	0.01		16		0.74
BA	$N_{2-3\ nm}$	0.16		17		0.09
BA	$N_{3-25\ nm}$	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

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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.

x	y	R^2	$\beta_1 \pm$ s.e.	d.f.	t	p
MMA	N_{tot}	0.04	53 ± 15	248	3.4	**7.9E-04**
MMA	$N_{1.1-2\ nm}$	0.05	-335 ± 159	77	-2.1	0.038
MMA	$N_{2-3\ nm}$	0.03		77		0.16
MMA	$N_{3-25\ nm}$	0.02		247		0.019
DMA	N_{tot}	0.00		521		0.48
DMA	$N_{1.1-2\ nm}$	0.10	99 ± 20	215	4.9	**1.8E-06**
DMA(*	$N_{1.1-2\ nm}$	0.14	59 ± 23	43	2.6	**0.013**
DMA	$N_{2-3\ nm}$	0.00		217		0.93
DMA	$N_{3-25\ nm}$	0.00		519		0.21
EA	N_{tot}	0.01		75		0.42
EA	$N_{1.1-2\ nm}$	0.03		46		0.22
EA	$N_{2-3\ nm}$	0.01		37		0.51
EA	$N_{3-25\ nm}$	0.32	103 ± 17	75	6.0	**7.1E-08**
TMA	N_{tot}	0.00		383		0.91
TMA	$N_{1.1-2\ nm}$	0.00		232		0.75
TMA	$N_{2-3\ nm}$	0.00		204		0.32
TMA	$N_{3-25\ nm}$	0.00		382		0.74
PA	N_{tot}	0.00		28		0.93
PA	$N_{1.1-2\ nm}$			1		
PA	$N_{2-3\ nm}$			0		
PA	$N_{3-25\ nm}$	0.01		28		0.53
DEA	N_{tot}	0.02		24		0.47
DEA	$N_{1.1-2\ nm}$			1		
DEA	$N_{2-3\ nm}$			1		
DEA	$N_{3-25\ nm}$	0.02		24		0.54
BA	N_{tot}	0.03		19		0.44
BA	$N_{1.1-2\ nm}$			4		
BA	$N_{2-3\ nm}$			2		
BA	$N_{3-25\ nm}$	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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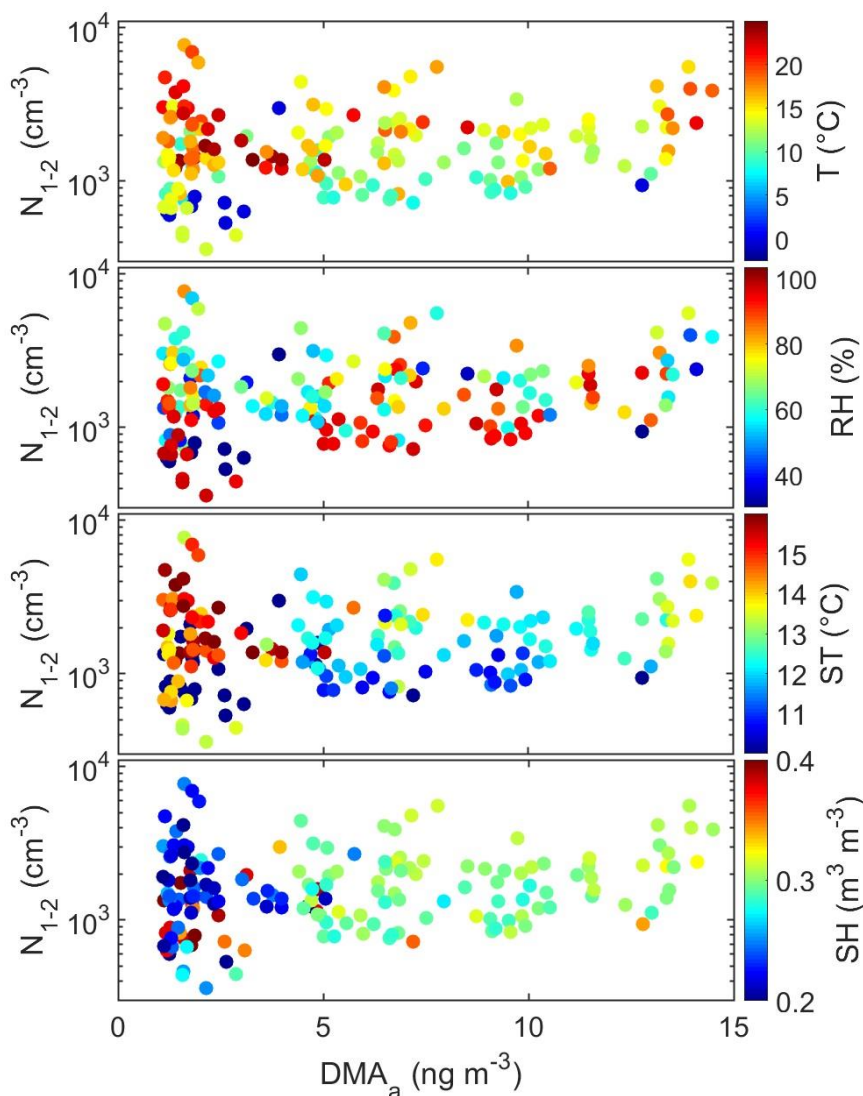
Figure 9. Cluster-mode particle number concentration ($N_{1.1-2nm}$) as a function of dimethyl amine (DMA) concentration in the aerosol phase, air temperature (T), air relative humidity (RH), soil temperature (ST) and soil humidity (SH).

375 There were considerably more simultaneous data points of the cluster-mode particle number concentration and ammonia (NH_3). The correlation $N_{1.1-2nm}$ vs. NH_3 was statistically significant ($R^2 = 0.13$, p = $9.1*10^{-10}$, Table 7). 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). In the aerosol phase ammonium (NH_4^+) did not correlate at all with the cluster mode particles but positively with the total number concentration (Table 8).

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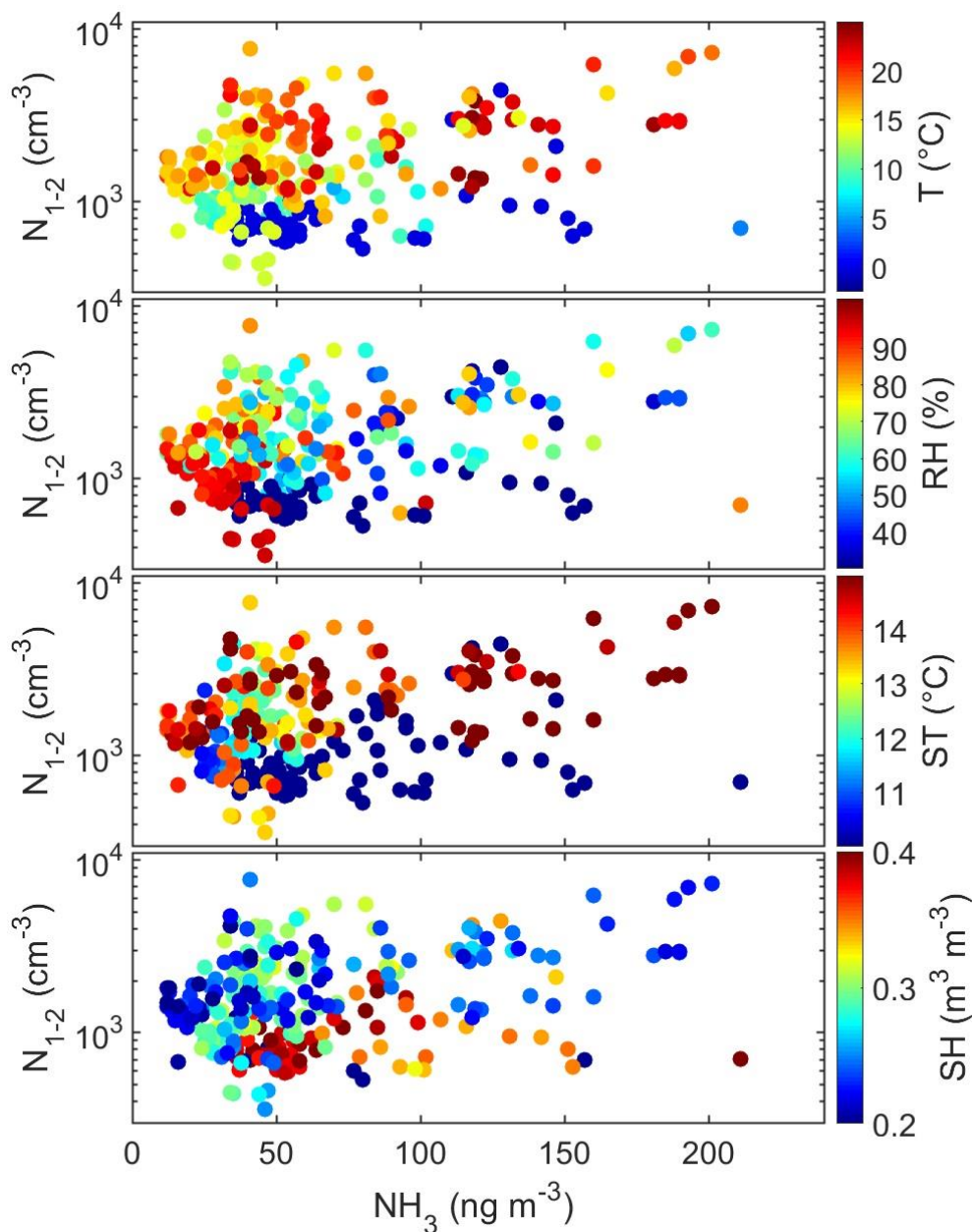
Figure 10. Cluster-mode particle number concentration ($N_{1.1-2nm}$) as a function of ammonia (NH_3) concentration, air temperature (t), air relative humidity (RH), soil temperature (ST) and soil humidity (SH).

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

4. Conclusions

390 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- and gas-phase were measured with 1-hour time resolution.

The amines turned out to be a heterogeneous group of compounds; different amines are likely to have different sources. All
395 amines had higher concentrations in aerosol phase. MMA and TMA concentrations were highest in spring. Melting of snow and ground can be the source of these compounds. Measured concentrations of summed up ammonia and ammonium were also highest in spring and the share of ammonia increased towards summer.

TMA has an additional maximum simultaneously with DMA during summer, which could indicate biogenic source.
400 However, unlike EA, they did not show similar diurnal variation as monoterpenes. This missing daytime minimum 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 with soil humidity, which could indicate humidity dependent production
405 mechanism. Gas phase DMA correlated with small 1.1-2 nm particles, when both soil and air were humid. It did not correlated with slightly bigger particles at all, suggesting that gas phase DMA may be important in new particle formation.

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