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Supplement of

Amines in boreal forest air at SMEAR II station in Finland

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Table S1. 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	Temperature (°C)		Wind speed (m/s)		Main wind direction	Humidity (%)		Rain (mm)		Soil temp. (°C)		Soil humidity (m ³ /m ³)	
	Mean	StDev	Mean	StDev		Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
Mar	0.4	1.3	2.6	0.7	SSE	87	23	0.04	0.09	0.5	0.05	0.4	0.03
Apr	3.7	3.3	2.4	0.9	W	75	20	0.01	0.07	2.0	0.9	0.4	0.02
May	9.7	3.9	1.8	0.7	SSE	69	21	0.00	0.01	6.0	1.1	0.4	0.02
Jul	13.8	3.1	1.5	0.5	NW	75	17	0.01	0.03	12.2	0.9	0.3	0.01
Aug	17.8	3.7	1.4	0.6	SW	74	18	0.00	0.007	14.5	0.9	0.2	0.02
Nov	2.7	2.1	2.9	1.0	SSW	95	3.9	0.04	0.08	3.2	0.4	0.2	0.01
Dec	-0.1	1.7	1.9	0.5	NWW	94	4.3	0.01	0.06	2.6	0.3	0.2	0.03

Table S2. The settings of mass spectrometric analysis

Item	Setting	Unit
Nebulizing Gas (N ₂) Flow	1.5	l min ⁻¹
DL Temperature	210	°C
Heat Block Temperature	400	°C
Detector Voltage	1.25	kV
IG Vaguuum	9.8*10 ⁻⁴	Pa
PG Vacuum	5.4*10 ⁴	Pa

Table S3. Monthly mean and median (med.) of gas and aerosol phase amines and ammonia. N is number of data points.

ng m ⁻³	March		April		May		July		August		November		December	
	mean	med.	mean	med.	mean	med.	mean	med.	mean	med.	mean	med.	mean	med.
<u>Gas</u>														
<u>N</u>	117		112		163		91		113		128		54	
DEA	<DL	<DL	<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	<DL	<DL
DMA	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
TMA	0.4	<DL	0.4	<DL	0.3	<DL	0.4	0.4	0.3	<DL	<DL	<DL	<DL	<DL
PA	<DL	<DL	<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	<DL	<DL
MMA	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
NH ₃	52	19	52	<DL	81	22	45	<DL	66	<DL	<DL	<DL	<DL	<DL
<u>Aerosol</u>														
<u>N</u>	117		112		163		91		113		128		54	
DEA	0.3	<DL	<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	<DL	<DL
DMA	1.5	<DL	3.1	3.0	2.7	<DL	8.4	4.9	1.3	<DL	<DL	<DL	<DL	<DL
TMA	1.1	<DL	0.7	<DL	0.5	<DL	1.8	1.4	0.6	0.6	0.5	<DL	<DL	<DL
PA	<DL	<DL	<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	<DL	<DL
MMA	6.8	<DL	2.9	<DL	<DL	<DL	3.0	<DL	<DL	<DL	<DL	<DL	<DL	<DL
NH ₄ ⁺	425	90	144	64	145	97	136	92	88	28	85	18	8.4	<DL

Table S4. Regression statistics ($y = \beta_1x + \beta_0$) 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; $t = \beta_1/\text{s.e.}$; 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	\pm 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	\pm 0.03	106	11.4	4.4E-20
RH	DMA(g)	0.36	-0.071	\pm 0.009	106	-7.7	7.6E-12
WS	DMA(g)	0.30	-0.99	\pm 0.15	106	-6.8	6.3E-10
soil T	DMA(g)	0.31	0.28	\pm 0.04	115	7.2	6.2E-11
soil Hum	DMA(g)	0.63	25	\pm 2	113	13.9	3.7E-26
air T	EA(g)	0.08	-0.015	\pm 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	\pm 0.04	57	-2.8	0.0064
soil Hum	EA(g)	0.11	9	\pm 4	54	2.6	0.013
air T	TMA(g)	0.06	-0.036	\pm 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	\pm 0.01	309	-4.5	1.2E-05
soil Hum	TMA(g)	0.09	5.1	\pm 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	\pm 0.04	79	-1.9	0.066
soil Hum	DEA(g)	0.04			67		0.11
air T	BA(g)	0.11	-0.006	\pm 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	\pm 0.004	31	-2.0	0.056
soil Hum	BA(g)	0.17	1.1	\pm 0.5	28	2.4	0.024
air T	NH ₃	0.07	0.00142	\pm 0.00023	527	6.3	6.8E-10
RH	NH ₃	0.04	-0.00040	\pm 0.00008	527	-4.9	1.3E-06
WS	NH ₃	0.00			527		0.39
soil T	NH ₃	0.01	0.00075	\pm 0.00029	605	2.6	0.010
soil Hum	NH ₃	0.00			541		0.60

Table S5. Regression statistics ($y = \beta_1x + \beta_0$) of amine concentrations in the aerosol phase vs. ambient conditions. Detailed column description as in Table S4.

x	y	R ²	$\beta_1 \pm \text{s.e.}$	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
soil Hum	NH ₄ ⁺	0.0221	0.58 ± 0.15	668	3.9	1.1E-04

Table S6. Regression statistics ($y = \beta_1x + \beta_0$) of aerosol number concentrations vs. amine and ammonia concentrations in the gas phase. Detailed column description as in Table 5. N_{tot} : aerosol number concentration integrated from the size distributions measured with the DMPS; $N_{1.1-2\text{nm}}$ and $N_{2-3\text{nm}}$: aerosol number concentrations in the size ranges 1.2 – 2 nm and 2 – 3 nm, measured with the PSM; $N_{3-25\text{nm}}$: aerosol 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	$\beta_1 \pm \text{s.e.}$	d.f.	t	p
MMA(g)	N_{tot}	0.11		21		0.12
MMA(g)	$N_{1.1-2\text{nm}}$			0		
MMA(g)	$N_{2-3\text{nm}}$			0		
MMA(g)	$N_{3-25\text{nm}}$	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)	$N_{1.1-2\text{nm}}$	0.06	229 ± 166	31	1.4	0.18
<i>DMA(g) (*</i>	<i>$N_{1.1-2\text{nm}}$</i>	0.63	481 ± 130	8	3.7	0.0061
DMA(g)	$N_{2-3\text{nm}}$	0.00		34		0.95
DMA(g)	$N_{3-25\text{nm}}$	0.04	58 ± 27	115	2.1	0.034
EA(g)	N_{tot}	0.01		57		0.58
EA(g)	$N_{1.1-2\text{nm}}$	0.05		41		0.16
EA(g)	$N_{2-3\text{nm}}$	0.07	-80 ± 44	43	-1.8	0.08
EA(g)	$N_{3-25\text{nm}}$	0.03		57		0.23
TMA(g)	N_{tot}	0.00		309		0.23
TMA(g)	$N_{1.1-2\text{nm}}$	0.01		187		0.12
TMA(g)	$N_{2-3\text{nm}}$	0.00		207		0.58
TMA(g)	$N_{3-25\text{nm}}$	0.00		309		0.66
PA(g)	N_{tot}	0.03		18		0.45
PA(g)	$N_{1.1-2\text{nm}}$	0.18		3		0.48
PA(g)	$N_{2-3\text{nm}}$	0.01		6		0.84
PA(g)	$N_{3-25\text{nm}}$	0.04		18		0.40
DEA(g)	N_{tot}	0.00		73		0.96
DEA(g)	$N_{1.1-2\text{nm}}$			1		
DEA(g)	$N_{2-3\text{nm}}$			1		
DEA(g)	$N_{3-25\text{nm}}$	0.00		79		0.59
BA(g)	N_{tot}	0.10	2234 ± 1230	31	1.8	0.08
BA(g)	$N_{1.1-2\text{nm}}$	0.01		16		0.74
BA(g)	$N_{2-3\text{nm}}$	0.16		17		0.09
BA(g)	$N_{3-25\text{nm}}$	0.01		31		0.63
NH ₃	N_{tot}	0.00		605		0.93
NH ₃	$N_{1.1-2\text{nm}}$	0.13	10853 ± 1710	272	6.3	9.1E-10
NH ₃	$N_{2-3\text{nm}}$	0.03	2154 ± 656	336	3.3	0.0011
NH ₃	$N_{3-25\text{nm}}$	0.00		605		0.33

Table S7. 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 S4 – S6. The line of DMA(a) (* was calculated by using only those data that were measured when RH > 90%.

x	y	R ²	$\beta_1 \pm \text{s.e.}$	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
<i>DMA(a)</i> (*)	<i>N</i> _{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

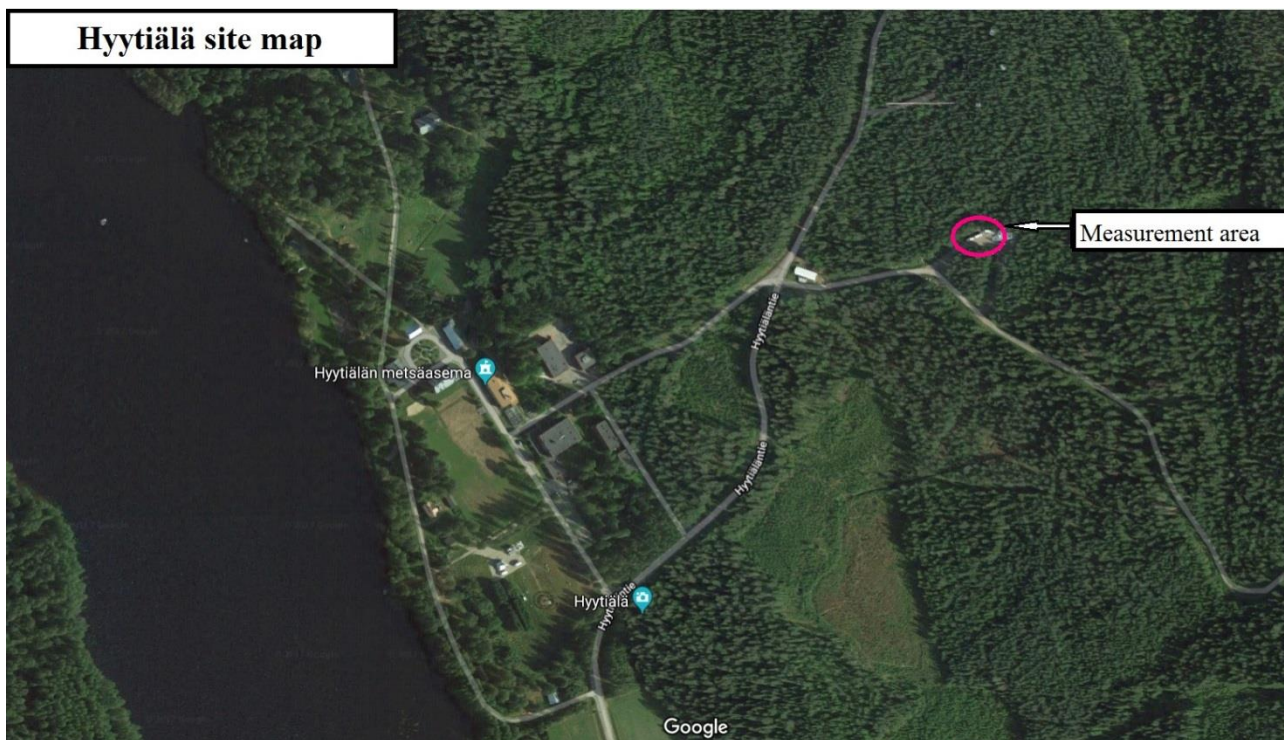


Figure S1. Hyytiälä site map. Imagery ©2017 Google, Map data ©2017 Google.

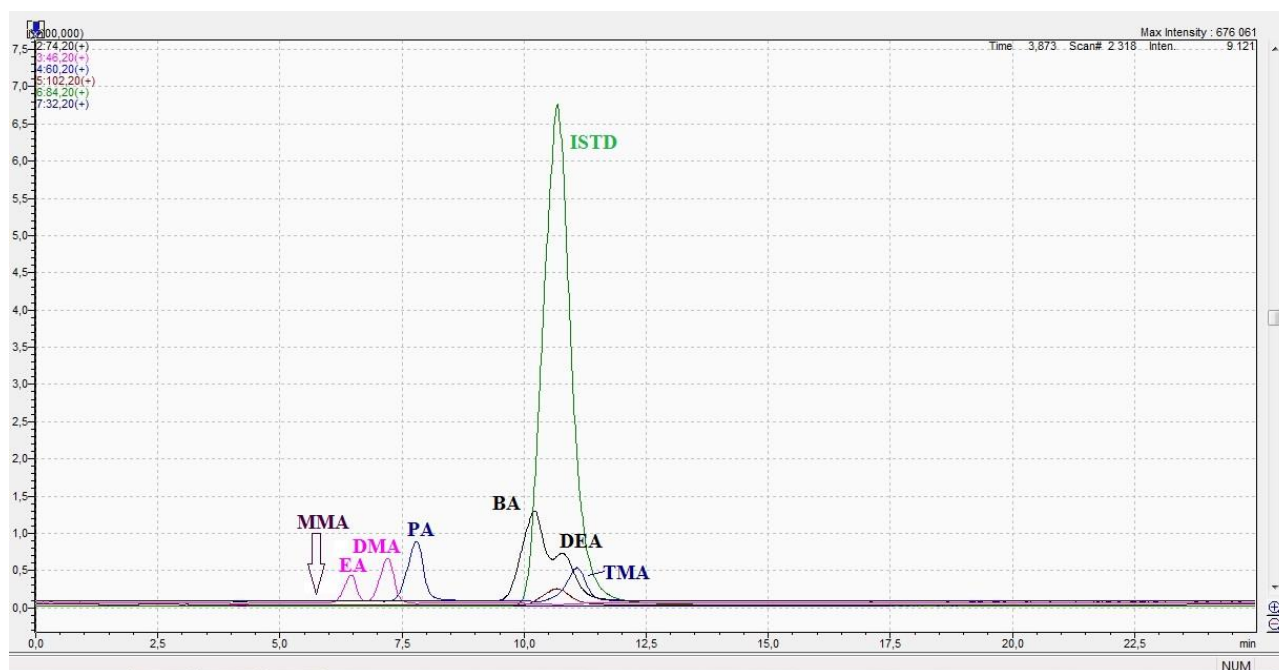


Figure S2. The chromatogram of standard level 50 ng m^{-3} . Other amines than BA and DEA are separating well. Mass 84.20 is the internal standard (ISTD), deuterated diethyl-d10-amine. We were originally also developing method for triethylamine (mass 102.20), but we could not see it. In this chromatogram mass 102.20 is an impurity.

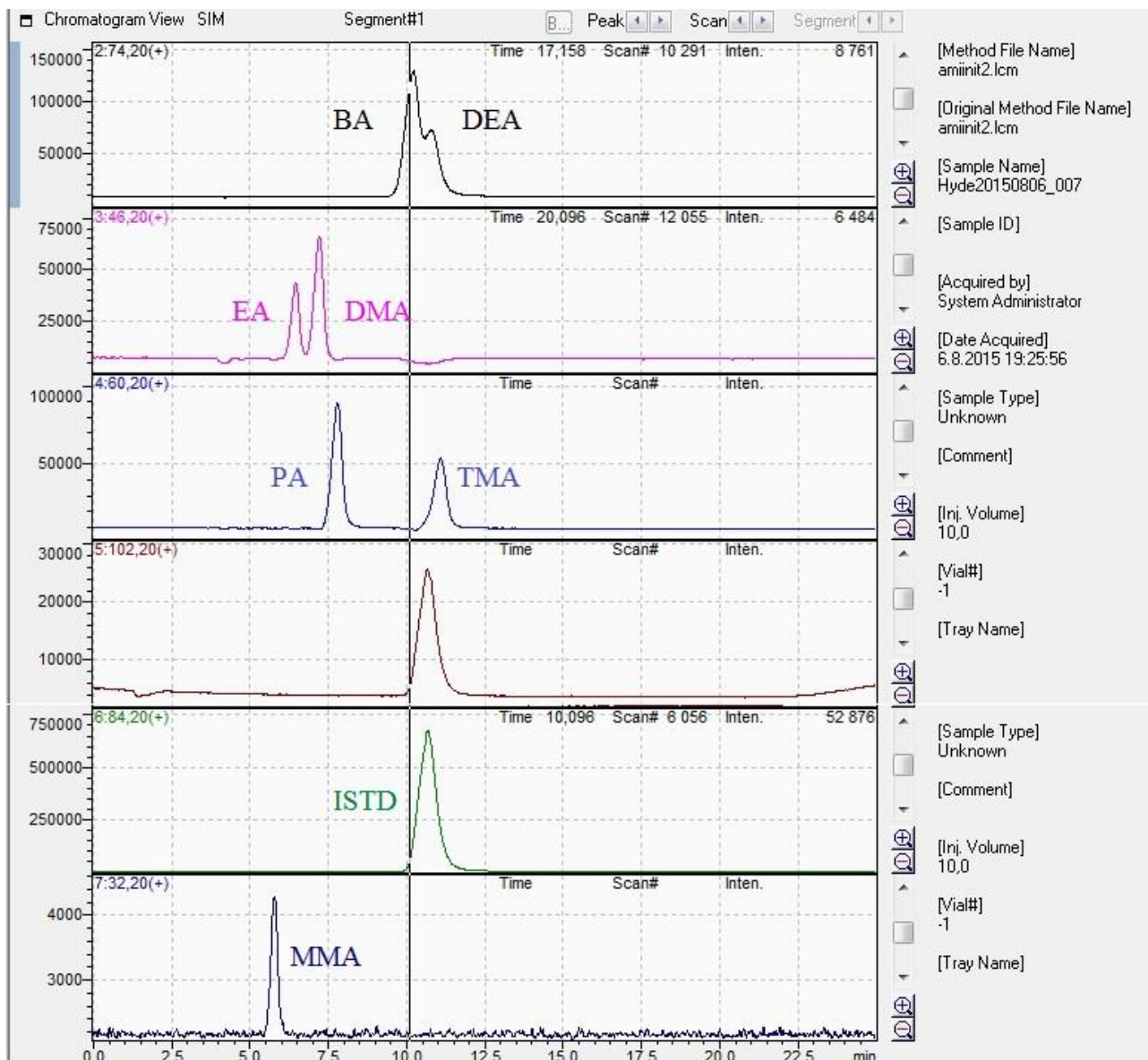


Figure S3. The same chromatogram than in Fig. S2, but different masses are separated.

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. S4) 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 $10\,000\text{ cm}^{-3}$, its geometric mean diameter $D_g = 4\text{ nm}$, and the geometric standard deviation $\sigma_g = 1.5$. Assuming that the density of particles is 1.5 g cm^{-3} the mass of that mode is $\sim 1.05\text{ ng m}^{-3}$. The diffusion losses in the denuder result in a growth of the geometric mean of the size distribution and decrease of mass concentration to $\sim 0.69\text{ ng m}^{-3}$ 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 $D_g = 10\text{ nm}$ and $\sigma_g = 1.5$ the penetrated mass fraction is 95%.

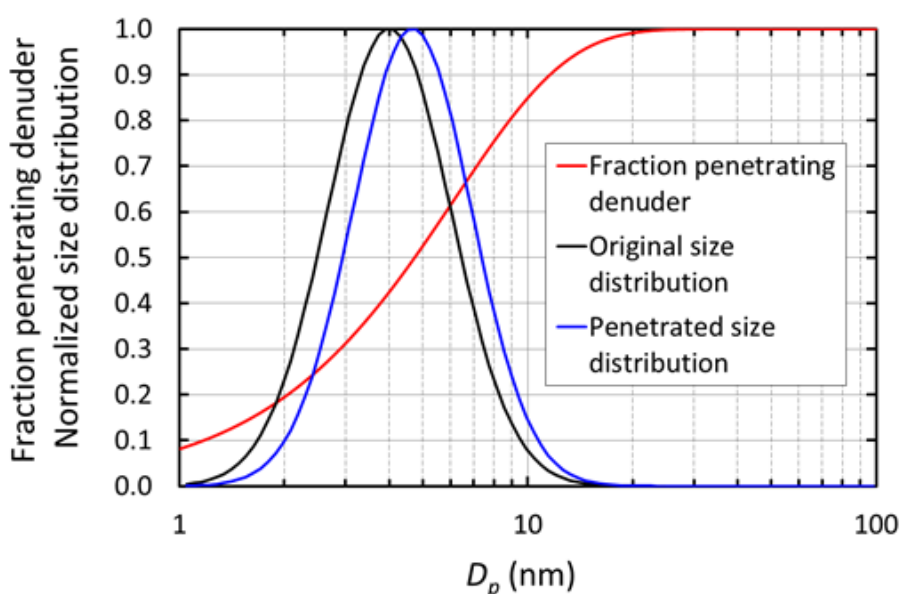


Figure S4. Size-dependent particle penetration probability in the annular denuder of the MARGA and a normalized number size distribution ($dN/d\log D_p$, $D_g = 4\text{ nm}$, $\sigma_g = 1.5$) of a nucleation mode before and after penetrating the denuder.

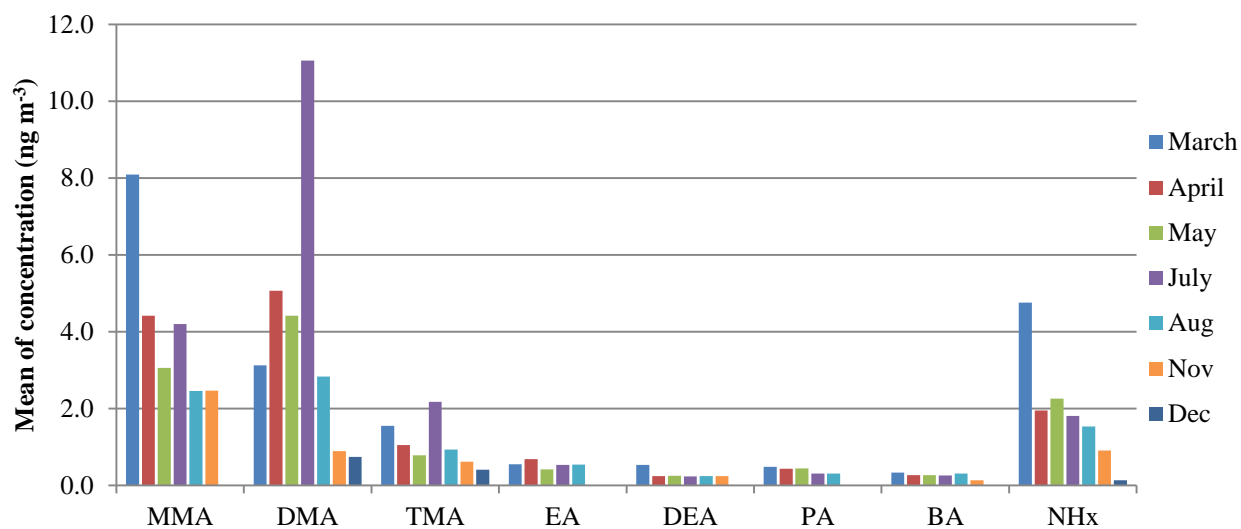


Figure S5. Monthly means of total amine and summed up ammonia and ammonium (NH_x) concentrations (ng/m³). NH₃+NH₄⁺ concentrations have been divided by 100, to fit the scale.

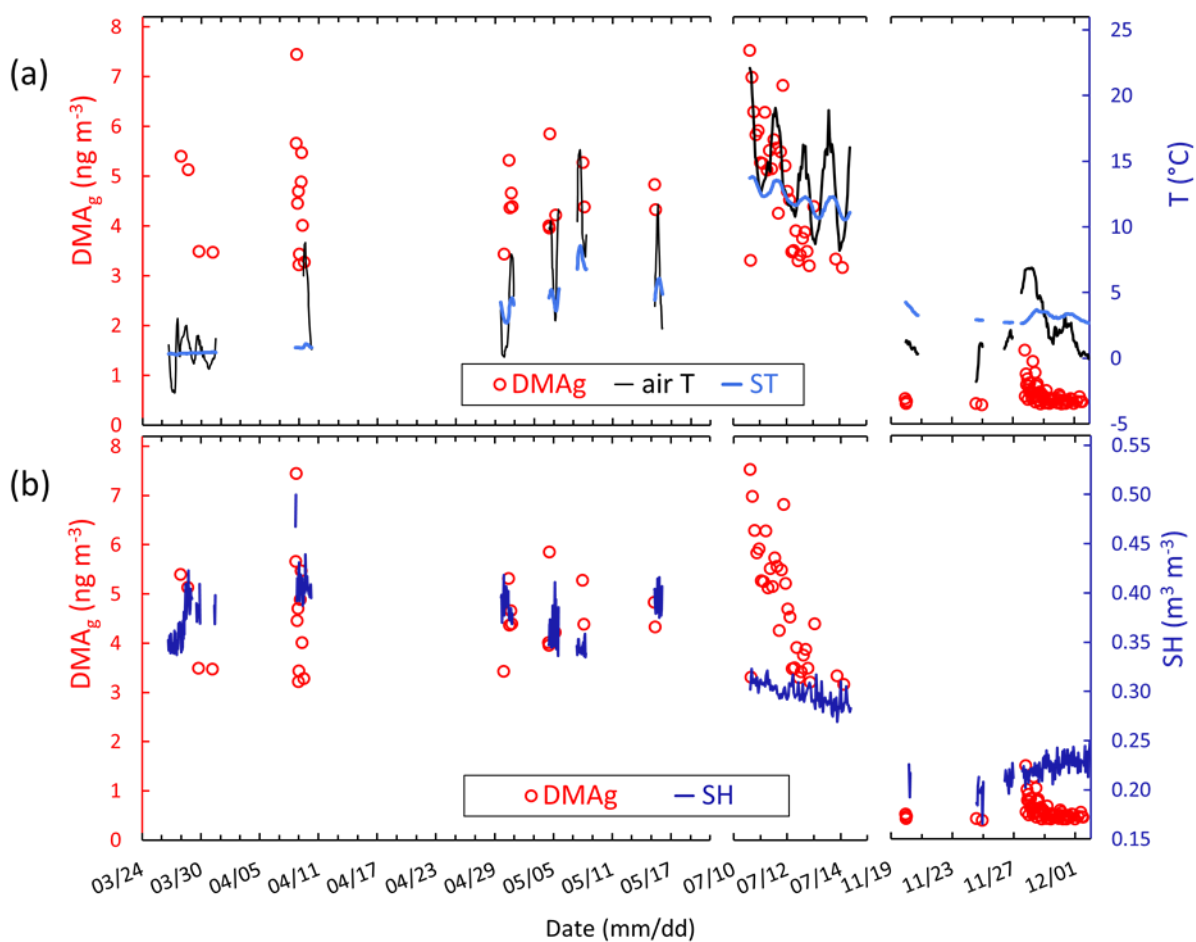


Figure S6. Time series of DMA(g), air temperature (air T), soil temperature (ST) and soil humidity (SH) during the whole measurement period.

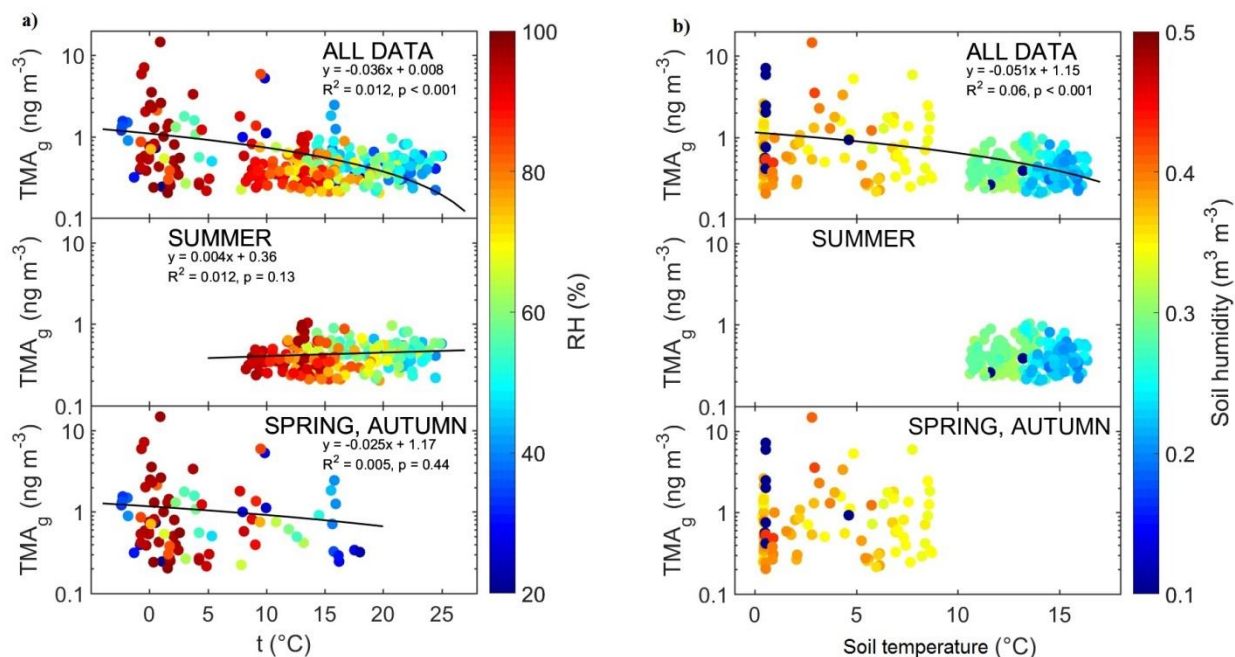


Figure S7. TMA(g) concentration as a function of a) temperature (RH = relative humidity) and b) Soil temperature.

References

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