Chemical and microbiological characterization of primary biological aerosol particles at the boreal forest

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S1 Materials and reagents

L-Alanine (Ala), L-Aspartic acid (Asp), L-Glutamic acid (Glu), L-Glutamine (Gln), Glycine (Gly), L-Isoleucine (Iso), L-Leucine (Leu), L-Lysine (Lys), L-Methionine (Met), L-Phenylalanine (Phe), L-Proline (Pro), L-Threonine (Thr), L-Tryptophan (Trp), L-Tyrosine (Tyr) and L-Valine (Val) from Seikagaku Kogyo Co. (Tokyo, Japan); L-Arginine (ca. 99 %) (Arg), L-Histidine (≥ 99 %) (His) and Inositol (ca. 99 %) from MERCK (Darmstadt, Germany); L-Serine (ca. 99 %) (Ser) from Ega-Chemie (Steinheim, Germany), Asparagine anhydrous (Asn), Sucrose (≥ 99.5 %), 1,6-Anhydro-b-D-glucose (99 %), D-Arabitol, D-Mannitol, Glycine-2,2-d_2 (Gly-d2), L-Lysine-4,4,5,5-d_4 (98 atom% D, 98% (CP)) (Lys-d4) and L-Phenylalanie-3,3-d_2 (98 atom% D) (Phe-d2) from Sigma-Aldrich (St. Louis, USA); D(+)-Trehalose dihydrate (purity 99 %) from AK Scientic (Union City, USA) and D-Fructose-$13C_6$ from Carbosynth Ltd. (Berkshire, UK) were used for the preparation of amino acids and saccharides stock solutions. All labelled compounds were used as internal standards (ISTD) in the analysis. N-Hexane (purity 98 %) from VWR Chemicals (Fontenay-sous-Bois, France) was used for lipid removal from the extracted samples. Formic acid (≥ 99 %) from VWR, acetonitrile (≥ 99.9 %) from Sigma-Aldrich, and ultra-pure water from a Millipore DirectQ-UV system (Molsheim, France) were used for the preparation of the mobile phase used in the HPLC analysis.

Individual standard solutions of the different analytes under study, including ISTD compounds, were prepared in 0.1% formic acid. Concentrations of stock solutions of the target analytes were 1000 µg mL^{-1}, with the exception of Tyr (200 µg mL^{-1}), Asp (400 µg mL^{-1}) and D-Fructose-$13C_6$ (5000 ng mL^{-1}). Calibration solutions were prepared daily by dilution of the stock standard solutions with 0.1% formic acid. Stock standard solutions were stable at 4 °C for two weeks.

All the tools and glassware used for sample preparation were ultrasonic cleaned, before use, with water and methanol (≥ 99%) from Honeywell Riedel-de Haën (Charlotte, NC, USA) and dried at 150 °C in an oven (Heraeus, Hanau, Germany).

S2. Determination of gas phase volatile organic compounds

Volatile organic compounds (VOCs) were measured by PTR-MS. The application of a non-dissociative proton transfer reaction enables the measurement of most of the common VOCs with a high time-resolution and sensitivity without any sample treatment (Yuan et al., 2017; de Gouw et al., 2003). A disadvantage of PTR-MS is that it only gives information about the molecular mass of protonated compounds but not about their molecular structure. In this study, thirteen masses measured by PTR-MS were identified: 33, 42, 47, 59, 61, 69, 71, 73, 79, 81, 87, 93 and 137 Da. These masses were related to methanol, acetonitrile, ethanol, acetone, acetic acid, isoprene, methacrolein, 2-butanone, benzene, α-pinene fragment, methylbutenol, toluene and monoterpenes respectively (de Gouw and Warneke, 2007; Taipale et al., 2008). However, some of them might be originating from other VOCs. Sampling was conducted at 8.4 m above the ground level (inside the canopy) as described by Rantala et al. (2015). PTR-MS was calibrated with a calibration gas standard (Apel–Riemer Environmental, Inc.) containing 1 ppmv of all the VOCs analyzed in this study with the exception of methanol and acetonitrile, which were quantified based on the relative transmission curve. Calibration, the determination of the relative transmission curve and the calculations of volume mixing ratios, were conducted according to procedures described by Taipale et al. (2008).

Table S1. Aerosol sampling dates and sampling volume.

Sample	Start (day and hour)	Stop (day and hour)	Sampling volume [m^3]
Sample 1 (S1)	04.09.2017 09:07	06.09.2017 09:20	92.27
Sample 2 (S2)	06.09.2017 09:20	08.09.2017 08:45	90.63
Sample 3 (S3)	11.09.2017 08:24	13.09.2017 07:42	90.46
Sample 4 (S4)	13.09.2017 07:42	15.09.2017 08:54	93.94
Sample 5 (S5)	18.09.2017 08:35	20.09.2017 08:27	91.46
Sample 6 (S6)	20.09.2017 08:27	22.09.2017 09:18	93.40
Sample 7 (S7)	25.09.2017 08:35	27.09.2017 08:48	92.33
Sample 8 (S8)	27.09.2017 08:48	29.09.2017 09:31	93.09
Sample 9 (S9)	02.10.2017 08:10	04.10.2017 09:33	94.29
Sample 10 (S10)	04.10.2017 09:33	06.10.2017 08:26	89.56
Sample 11 (S11)	09.10.2017 08:09	11.10.2017 08:59	93.14
Sample 12 (S12)	11.10.2017 08:59	13.10.2017 09:19	92.18
Sample 13 (S13)	23.10.2017 08:49	25.10.2017 09:03	91.99
Sample 14 (S14)	25.10.2017 09:03	27.10.2017 08:49	91.27
Sample 15 (S15)	30.10.2017 09:32	01.11.2017 09:19	91.12
Sample 16 (S16)	01.11.2017 09:19	03.11.2017 10:09	93.11
Sample 17 (S17)	06.11.2017 10:20	08.11.1017 09:35	90.20
Sample 18 (S18)	08.11.2017 09:35	10.11.2017 09:58	92.35
Sample 19 (S19)	13.11.2017 10:08	15.11.2017 10.56	93.11
Sample 20 (S20)	15.11.2017 10:56	17.11.2017 10:23	90.49
Sample 21 (S21)	20.11.2017 10:05	22.11.2017 09:40	90.81

Table S2. Ionization conditions for amino acids and saccharides.

Parameter	Value
Gas temperature (°C)	290
Gas flow (mL min^{-1})	9
Nebulizer pressure (psi)	50
Capillary voltage (V)	3900

Table S3. Multiple reaction monitoring settings (b) for amino acids and saccharides. MS, precursor ion, MS/MS, product ion F, Fragmentor voltage; CE, collision energy; and CAV, cell accelerator voltage. * Ionized as [M+Na]+ adduct.

Compound	MS ion (m/z)	MS^2 ion (m/z)	F (V)	CE(V)	CAV (V)	Ionization
Ala	90	44	61	9	4	+
Arg	175	70	61	25	4	+
Asn	133	74	61	17	4	+
Asp	134	74	61	13	4	+
Glu	148	84	61	17	4	+
Gln	147	84	61	17	4	+
Gly	76	30	61	9	4	+
Gly-d2	78	32	61	9	4	+
His	156	110	61	13	4	+
Iso	132	69	61	9	4	+
Leu	132	44	61	25	4	+
Lys	147	84	61	17	4	+
Lys-d4	151	88	61	17	4	+
Met	150	56	61	17	4	+
Phe	166	120	61	13	4	+
Phe-d2	168	122	61	13	4	+
Pro	116	70	61	17	4	+
Ser	106	60	61	9	4	+
Thr	120	74	61	9	4	+
Trp	205	188	61	5	4	+
Tyr	182	136	61	13	4	+
Val	118	72	61	9	4	+
Sucrose	365	203	181	40	4	–
Trehalose	365	203	181	40	4	–
Arabitol	151	89	105	15	0	–
Fructose	179	89	75	3	0	–
Fructose-$13C_6$	185	92	75	5	0	–
Inositol	179	89	105	20	2	–
Levoglucosan*	185	–	61	0	4	+
Mannitol	181	89	105	15	2	–
Mannose	179	89	105	5	2	–

Table S4. Ancillary data for statistical analysis.

Concentration of atmospheric gases, aerosol, meteorological and environmental parameters			
M01	Total particle concentration (1 cm^{-3})	M22	Daily sum precipitation (mm)
M02	Methane flux (nmol m^{-2} s^{-1})	M23	Ultraviolet A radiation (W m^{-2})
M03	Evapotranspiration (mmol m^{-2} per half hour)	M24	Utraviolet B radiation (W m^{-2})
M04	Carbon dioxide flux (µmol m^{-2} s^{-1})	M25	Global shortwave solar radiation (W m^{-2})
M05	Gross primary production derived from net ecosystem exchange (µmol m^{-2} s^{-1})	M26	Reflected shortwave radiation (W m^{-2})
M06	CO_2 (ppm)	M27	Reflected photosynth. active radiation (µmol m^{-2} s^{-1})
M07	Water vapor concentration (ppth)	M28	Photosynth. active radiation (µmol m^{-2} s^{-1})
M08	CO (ppb)	M29	Diffuse photosynth. active radiation (µmol m^{-2} s^{-1})
M09	O_3 (ppb)	M30	Below canopy photosynth. active rad. (µmol m^{-2} s^{-1})
M10	NO (ppb)	M31	Incoming far-infrared radiation (W/m^{-2})
M11	NO_x (ppb)	M32	Outgoing far-infrared radiation (W m^{-2})
M12	SO_2 (ppb)	M33	Soil temperature in the organic layer (ºC)
M13	Atmospheric pressure (hPa)	M34	Soil temperature in A horizon (ºC)
M14	Air temperature (Celsius)	M35	Soil temperature in B1 horizon (ºC)
M15	Relative humidity (%)	M36	Soil temperature in B2 horizon (ºC)
M16	Horizontal wind speed (m s^{-1})	M37	Vol. soil water content in the organic layer (m^3 m^{-3})
M17	Horizontal wind direction (degree)	M38	Vol. soil water content in A horizon (m^3 m^{-3})
M18	Wind direction, average of above-canopy (degree)	M39	Volumetric soil water content in B1 horizon (m^3 m^{-3})
M19	Visibility (km)	M40	Volumetric soil water content in B2 horizon (m^3 m^{-3})
M20	Cloud base height layer 1 (m)	M41	Soil heat flux (W m^{-2})
M21	Daily sum of snowfall accumulated (mm)		

Table S5. Analytical features of the method used for the chemical characterization of PBAPs.

Compound	Calibration	R^2	LOD (ng m^{-3})	LOQ (ng m^{-3})	Linearity (ng m^{-3})
Ala	y = 0.0014x + 0.0265	0.992	0.01	0.03	0.03–20.82
Arg	y = 0.0114x + 0.0938	0.996	0.01	0.02	0.02–25.09
Asn	y = 0.0018x - 0.0054	0.999	0.02	0.05	0.05–11.41
Asp	y = 0.0037x - 0.0032	0.997	0.01	0.03	0.03–18.55
Glu	y = 0.007x - 0.0026	0.999	0.01	0.03	0.03–23.83
Gln	y = 0.0067x - 0.0007	0.999	0.01	0.03	0.03–35.02
Gly	y = 0.0024x + 0.0041	0.999	0.01	0.03	0.03–9.33
His	y = 0.0167x + 0.0903	0.998	0.04	0.12	0.12–11.40
Iso	y = 0.0002x + 0.0016	0.997	0.01	0.03	0.03–2.64
Leu	y = 0.0001x - 0.0008	0.996	0.01	0.03	0.03–12.91
Lys	y = 0.007x + 0.0691	0.999	0.01	0.03	0.03–3. 40
Met	y = 0.0006x + 0.0077	0.996	0.01	0.03	0.02–11.41
Phe	y = 0.0018x + 0.0002	0.999	0.01	0.03	0.03–3.50
Pro	y = 0.0035x + 0.0667	0.993	0.01	0.03	0.03–8.41
Ser	y = 0.0078x - 0.0126	0.999	0.03	0.10	0.10–9.33
Thr	y = 0.0038x + 0.0011	0.999	0.01	0.02	0.02–12.39
Trp	y = 0.0008x + 0.0036	0.999	0.01	0.03	0.03–0.34
Tyr	y = 0.0004x + 0.0045	0.997	0.01	0.03	0.03–5.73
Val	y = 0.0033x + 0.0705	0.991	0.01	0.03	0.03–3.85
Arabitol	y = 0.00005x + 0.0005	0.999	0.05	0.16	0.16–64.15
Fructose	y = 0.0026x - 0.0117	0.998	0.01	0.01	0.02–122.72
Inositol	y = 0.002x + 0.0187	0.996	0.01	0.03	0.03–1.35
Levoglucosan	y = 0.0013x + 0.0261	0.995	0.03	0.10	0.10–64.15
Mannitol	y = 0.004x - 0.0011	0.998	0.02	0.06	0.06–47.36
Mannose	y = 0.0024x - 0.0048	0.999	0.01	0.03	0.03–8.83
Sucrose	y = 0.0023x + 0.0147	0.998	0.02	0.06	0.06–25.77
Trehalose	y = 0.004x - 0.0011	0.995	0.01	0.04	0.04–14.36

Table S6. Extraction recoveries of the method used for the chemical characterization of PBAPs.

Compounds	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Ala	250	261.5	104.6
Arg	250	260.6	104.2
Asn	250	295.2	118.1
Asp	250	289.9	115.9
Glu	250	238.9	95.6
Gln	250	278.0	111.2
Gly	250	238.9	95.6
His	250	254.9	101.9
Iso	250	215.3	86.1
Leu	250	226.0	90.4
Lys	250	246.0	98.4
Met	250	206.8	82.7
Phe	250	215.2	86.1
Pro	250	231.7	92.7
Ser	250	334.9	133.9
Thr	250	194.9	77.9
Trp	250	183.1	73.2
Tyr	250	215.3	86.1
Val	250	219.9	87.9
Arabitol	250	219.8	87.9
Fructose	250	258.9	104.5
Inositol	2500	2387.8	95.5
Levoglucosan	250	313.5	125.4
Mannitol	125	105.1	84.1
Mannose	250	211.9	84.8
Sucrose	125	124.4	99.5
Trehalose	250	248.1	99.3

Table S7. Effect of the sample matrix on the ionization of the different amino acids and saccharides analyzed by the method used for the chemical characterization of PBAPs.

Compounds	Recovery L1 (%)	Recovery L2 (%)	Recovery L3 (%)	Average Recovery (%)
Ala	110.5	102.2	123.0	111.9
Arg	88.5	119.5	126.9	111.6
Asn	134.2	94.8	120.1	116.4
Asp	84.5	100.2	122.3	102.4
Gln	114.3	88.3	78.0	93.5
Glu	85.6	78.3	119.2	94.4
Gly	89.3	104.0	126.7	106.7
His	94.0	112.4	115.9	107.4
Iso	111.7	116.5	117.6	115.3
Leu	70.5	110.3	117.4	99.4
Lys	117.3	55.3	126.3	99.7
Met	78.2	125.9	116.2	106.8
Phe	83.1	118.3	117.8	106.4
Pro	79.2	100.0	116.7	98.7
Ser	105.4	92.4	132.7	110.1
Thr	72.8	97.7	122.1	97.5
Trp	87.6	114.4	116.9	106.3
Tyr	79.8	97.1	118.8	98.6
Val	80.7	139.2	117.5	112.5
Arabitol	78.3	79.1	93.7	83.7
Fructose	90.1	73.3	77.5	80.3
Inositol	77.1	93.1	128.7	99.6
Mannitol	74.2	86.6	83.5	81.5
Mannose	81.2	70.3	108.3	86.6
Sucrose	78.7	87.3	128.6	98.2
Trehalose	79.8	86.1	118.8	94.9

L1, addition of 8 ng from each compound; L2, addition of 77 ng from each compound; L3, addition of 111 ng from each compound.

Table S8. Summary statistics for the determination of amino acids in PBAPs. N, Number of observations; Av., Average concentration (ng m^{-3}); SD, Standard deviation (ng m^{-3}); CV, Coefficient of variation (%); Min., Minimum (ng m^{-3}); Max, Maximum (ng m^{-3}).

	Size	N	Av.	SD	CV	Min	Max	Range	Std. Skewness*	Std. Kurtosis*
Ala	PM 1	21	0.5	1.3	37.4	0.3	0.9	0.6	0.1	-0.3
	PM 2.5	15	0.5	1.3	34.4	0.3	0.8	0.5	-0.3	-0.3
	PM10	18	1.8	1.4	57.8	1.1	3.0	2.0	-0.6	-1.1
	PM >10	18	1.2	1.9	153.1	0.4	3.7	3.4	-0.2	-0.4
Arg	PM 1	11	0.4	1.1	8.5	0.4	0.5	0.1	-1.0	-0.1
	PM 2.5	16	0.7	1.5	98.3	0.3	1.2	0.9	-1.9	0.3
	PM10	20	1.9	1.5	67.5	0.6	3.6	3.0	-1.7	1.4
	PM >10	20	1.3	1.9	120.3	0.4	4.1	3.6	-0.9	-0.5
Asn	PM 1									
	PM 2.5									
	PM10	17	1.1	1.7	165.3	0.5	2.0	1.5	-1.2	-0.9
	PM >10	21	0.7	1.9	159.2	0.2	2.9	2.7	0.5	-0.2
Asp	PM 1									
	PM 2.5									
	PM10	10	1.6	1.4	61.2	1.0	2.5	1.5	-0.5	-0.5
	PM >10	7	1.6	1.5	90.2	1.0	3.6	2.5	1.7	1.7
Gln	PM 1	12	0.5	1.3	38.1	0.3	0.8	0.5	0.2	-0.4
	PM 2.5	19	0.8	1.7	94.9	0.3	1.3	1.0	-1.2	-1.0
	PM10	20	1.9	1.9	100.5	0.4	3.9	3.5	-1.9	0.4
	PM >10	21	1.3	1.8	132.1	0.4	4.7	4.3	-0.3	0.3
Glu	PM 1	20	0.4	1.3	82.4	0.3	0.6	0.4	0.5	-0.4
	PM 2.5	18	0.6	1.5	24.5	0.3	1.0	0.7	-1.3	-0.8
	PM10	20	1.7	1.5	76.9	0.7	2.7	2.0	-1.3	-0.8
	PM >10	21	1.1	1.8	171.6	0.5	4.0	3.5	0.7	-0.3
Gly	PM 1	17	0.7	1.5	144.7	0.3	1.6	1.3	-1.4	1.1
	PM 2.5									
	PM10	8	1.0	1.5	188.9	0.6	1.6	1.1	0.0	-1.2
	PM >10	13	0.9	1.8	191.3	0.4	2.6	2.2	0.6	-0.8
His	PM 1									
	PM 2.5	11	0.3	1.1	8.4	0.3	0.4	0.1	-0.5	-1.2
	PM10	11	1.5	1.3	65.4	0.9	2.0	1.1	-1.2	-0.3
	PM >10	13	1.2	1.6	137.4	0.5	2.7	2.2	-0.6	-0.3
Ile	PM 1									
	PM 2.5									
	PM10	17	0.7	1.3	81.4	0.5	1.1	0.6	0.4	-1.2
	PM >10	11	0.7	1.4	119.5	0.4	1.5	1.1	0.4	0.7
Leu	PM 1									
	PM 2.5									
	PM10	18	2.0	1.5	58.4	0.9	3.0	2.2	-1.1	-0.7

	PM >10	17	1.7	1.4	67.1	0.9	2.9	2.0	-0.2	-0.8
Lys	PM 1									
	PM 2.5									
	PM10	13	0.9	1.2	101.9	0.7	1.2	0.5	1.6	0.4
	PM >10	13	0.7	1.6	127.1	0.3	1.7	1.4	0.0	-0.1
Phe	PM 1									
	PM 2.5	14	0.3	1.5	27.9	0.1	0.6	0.5	0.9	0.7
	PM10	19	0.6	1.8	57.4	0.2	1.2	1.0	-1.5	-0.4
	PM >10	18	0.4	2.0	81.6	0.1	1.7	1.6	-0.1	-0.6
Pro	PM 1	15	0.3	1.3	21.4	0.2	0.5	0.3	0.1	-0.8
	PM 2.5	14	0.3	1.3	22.9	0.2	0.4	0.3	-0.8	-0.8
	PM10	18	1.2	1.3	96.9	0.5	1.7	1.2	-1.6	1.1
	PM >10	21	1.2	1.7	177.9	0.4	2.5	2.1	-0.4	-0.9
Ser	PM 1									
	PM 2.5									
	PM10	20	1.7	1.3	57.8	0.9	2.6	1.7	-1.0	-0.5
	PM >10	16	1.3	1.6	74.6	0.5	2.3	1.8	-0.7	-0.4
Thr	PM 1									
	PM 2.5									
	PM10	20	1.4	1.4	116.3	0.7	2.2	1.5	-0.8	-1.1
	PM >10	19	0.8	2.0	131.7	0.2	3.0	2.8	-0.6	-0.1
Trp	PM 1									
	PM 2.5									
	PM10	11	0.4	1.2	25.1	0.3	0.6	0.3	-1.4	0.5
	PM >10	10	0.4	1.5	36.2	0.2	0.6	0.4	-0.5	-0.1
Tyr	PM 1									
	PM 2.5									
	PM10	14	0.9	1.2	52.5	0.7	1.2	0.6	-0.4	-0.9
	PM >10	15	0.8	1.6	78.8	0.3	2.1	1.9	-0.1	1.5
Val	PM 1	18	0.3	1.2	14.7	0.3	0.5	0.2	1.2	0.4
	PM 2.5									
	PM10	13	0.5	1.5	64.1	0.2	0.8	0.6	-1.7	0.1

* Calculated after logarithmic transformation of the original data

Table S9. Summary statistics for the determination of saccharides in PBAPs. N, Number of observations; Av., Average concentration (ng m^{-3}); SD, Standard deviation (ng m^{-3}); CV, Coefficient of variation (%); Min., Minimum (ng m^{-3}); Max, Maximum (ng m^{-3}).

	Size	N	Av.	SD	CV	Min	Max	Range	Std. skewness*	Std. kurtosis*
Arabitol (Ara)	PM 1	10	0.9	1.7	58.4	0.4	2.7	2.3	-0.3	0.4
	PM 2.5	18	1.4	1.8	41.5	0.4	3.8	3.4	-0.6	-1.1
	PM10	15	4.4	1.7	33.7	1.8	10.4	8.6	-1.8	0.6
	PM >10	9	2.3	1.3	35.2	1.2	3.7	2.4	-0.9	0.0
Fructose (Fru)	PM 1		0.7	2.0	192.5	0.1	2.0	1.9		
	PM 2.5		0.9	2.1	197.3	0.1	2.8	2.7		
	PM10	16	6.0	1.8	32.1	1.9	13.5	11.6	0.7	1.3
	PM >10	13	1.3	1.6	170.7	0.6	2.9	2.3	0.7	1.3
Inositol (Ino)	PM 1		0.2	1.5	28.5	0.1	0.5	0.4		
	PM 2.5		0.3	1.6	41.5	0.1	0.5	0.4		
	PM10	15	1.3	1.3	115.0	1.0	2.1	1.2	-0.6	-0.2
	PM >10	14	1.4	1.4	105.5	0.9	2.2	1.3	1.6	0.8
Mannitol (Mnt)	PM 1	10	0.9	1.7	58.4	0.4	2.7	2.3	1.3	1.2
	PM 2.5	18	1.4	1.8	41.5	0.4	3.8	3.4	-1.0	-1.1
	PM10	20	4.4	1.7	33.7	1.8	10.4	8.6	-1.1	-0.2
	PM >10	21	2.3	1.3	35.2	1.2	3.7	2.4	-0.2	-0.3
Mannose (Mns)	PM 1		0.7	2.0	192.5	0.1	2.0	1.9		
	PM 2.5		0.9	2.1	197.3	0.1	2.8	2.7		
	PM10	16	6.0	1.8	32.1	1.9	13.5	11.6	-1.6	-0.3
	PM >10	15	1.3	1.6	170.7	0.6	2.9	2.3	-1.4	0.9
Sucrose (Suc)	PM 1		0.2	1.5	28.5	0.1	0.5	0.4		
	PM 2.5		0.3	1.6	41.5	0.1	0.5	0.4		
	PM10	20	1.3	1.3	115.0	1.0	2.1	1.2	-1.5	-0.1
	PM >10	17	1.4	1.4	105.5	0.9	2.2	1.3	0.3	-0.3
Trehalose (Tre)	PM 1		0.9	1.7	58.4	0.4	2.7	2.3		
	PM 2.5	17	1.4	1.8	41.5	0.4	3.8	3.4	-0.8	-1.0
	PM10	11	4.4	1.7	33.7	1.8	10.4	8.6	0.2	-1.0
	PM >10	19	2.3	1.3	35.2	1.2	3.7	2.4	-1.1	-0.8

* Calculated after logarithmic transformation of the original data.

Table S10. Summary statistics for the determination of number of gene copies for microbes in PBAPs. N, Number of observations; Av., Average number of gene copies (gene copies m^{-3}); SD, Standard deviation (gene copies m^{-3}); CV, Coefficient of variation (%); Min., Minimum (gene copies m^{-3}); Max, Maximum (gene copies m^{-3}).

	Size	N	Av.	SD	CV	Min	Max	Range	Std. skewness*	Std. kurtosis*
Bacteria	PM 1	21	0.9	1.7	58.4	0.4	2.7	2.3	1.0	-0.7
(Bac)	PM 2.5	21	1.4	1.8	41.5	0.4	3.8	3.4	0.2	-0.7
	PM10	21	4.4	1.7	33.7	1.8	10.4	8.6	-0.5	-0.8
	PM >10	20	2.3	1.3	35.2	1.2	3.7	2.4	-0.2	-0.5
Fungi	PM 1	20	0.7	2.0	192.5	0.1	2.0	1.9	-1.2	0.2
(Fun)	PM 2.5	21	0.9	2.1	197.3	0.1	2.8	2.7	-1.7	0.7
	PM10	21	6.0	1.8	32.1	1.9	13.5	11.6	-0.6	-0.8
	PM >10	20	1.3	1.6	170.7	0.6	2.9	2.3	-0.2	-1.2
Pseudomonas	PM 1	10	0.2	1.5	28.5	0.1	0.5	0.4	0.1	-0.2
(Pse)	PM 2.5	11	0.3	1.6	41.5	0.1	0.5	0.4	-0.8	-0.6
	PM10	8	1.3	1.3	115.0	1.0	2.1	1.2	0.9	-0.6
	PM >10	7	1.4	1.4	105.5	0.9	2.2	1.3	0.1	-1.1

* Calculated after logarithmic transformation of the original data.

Table S11. Summary statistics for the determination of total DNA in PBAPs. N, Number of observations; Av., Average concentration (ng m^{-3}); SD, Standard deviation (ng m^{-3}); CV, Coefficient of variation (%); Min., Minimum (ng m^{-3}); Max, Maximum (ng m^{-3}).

	Size	N	Aver.	SD	CV	Min	Max	Range	Std. skewness*	Std. kurtosis*
DNA	PM 1									
	PM 2.5	11	0.2	1.2	9.8	0.1	0.2	0.1	0.2	-1.1
	PM10	21	0.2	1.2	8.5	0.1	0.2	0.1	-1.0	1.4
	PM >10	21	0.2	1.2	11.1	0.1	0.2	0.1	1.5	-0.3

* Calculated after logarithmic transformation of the original data.

Table S12. Membership table for the cluster classification of the samples based on variations in atmospheric gases concentration, aerosol, meteorological and environmental parameters.

	Number of clusters (N) and membership			
Sample	**N=2**	**N=3**	**N=4**	**N=5**
S1	1	1	1	1
S2	1	1	1	1
S3	1	2	2	2
S4	1	2	2	2
S5	1	2	3	3
S6	1	2	3	3
S7	1	2	2	2
S8	1	2	2	2
S9	1	2	2	2
S10	1	2	2	2
S11	1	2	2	2
S12	1	2	2	2
S13	2	3	3	3
S14	2	3	3	3
S15	2	3	3	3
S16	2	3	3	3
S17	2	3	3	3
S18	2	3	3	3
S19	2	3	3	3
S20	2	3	3	3
S21	2	3	3	5

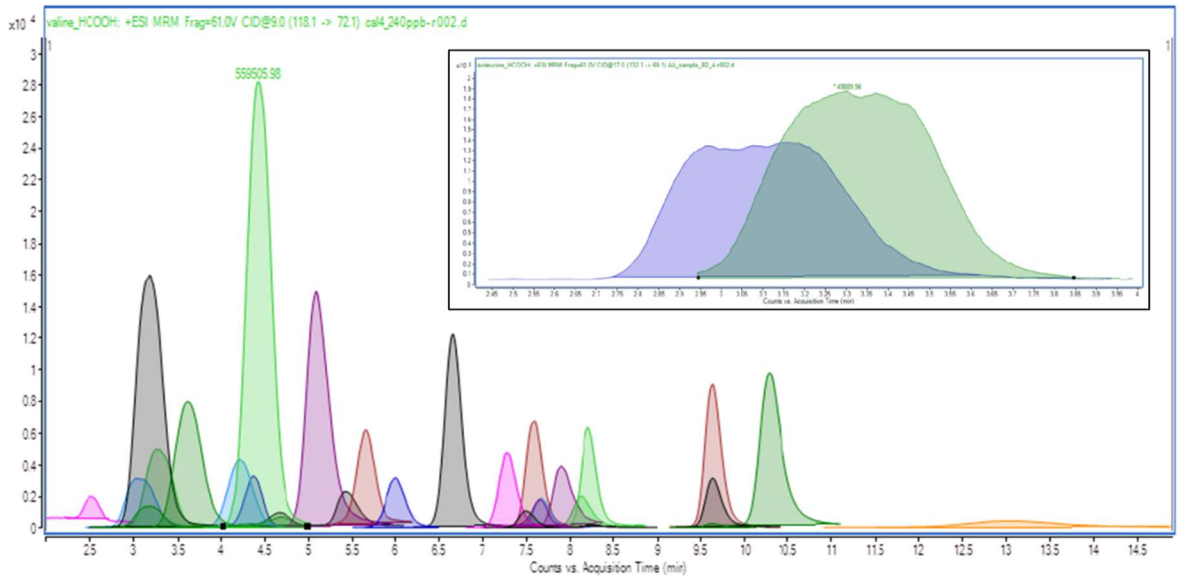
Table S13. Statistical features of the MLR models used for the potential elucidation of chemical signals from microbes in aerosol particles. N, number of samples in the model; R2, correlation coefficient adjusted by degree of freedom; SEE, standard error of the estimate; MAE, mean absolute error; and D-W, Durbin Watson statistic P-value.

	Size	N	P-value	R2	SEE	MAE	D-W
Bacteria	**PM 1**	19	0.001	0.91	0.15	0.09	0.40
	PM 2.5	19	0.021	0.98	0.09	0.02	0.11
	PM10	18	0.008	0.95	0.17	0.07	0.50
	PM >10	18	0.007	0.99	0.03	0.01	0.91
Total DNA	**PM 1**	19	0.001	0.92	0.27	0.12	0.13
	PM 2.5	19	0.002	0.96	0.19	0.07	0.39
	PM10	19	0.002	0.96	0.02	0.01	0.33
	PM >10	18	0.023	0.97	0.03	0.01	0.19
Fungi	**PM 1**	19	0.001	0.97	0.12	0.04	1.00
	PM 2.5	19	0.007	0.92	0.21	0.07	0.27
	PM10	19	0.008	0.94	0.26	0.17	0.86
	PM >10	19	0.005	0.97	0.08	0.02	0.60
Pseudomonas	**PM 1**	18	0.004	0.95	0.29	0.13	0.06
	PM 2.5	18	0.005	0.98	0.09	0.03	0.30
	PM10	19	0.002	0.99	0.01	0.01	0.20
	PM >10	18	0.017	0.99	0.01	0.01	0.56

Table S14. Statistical features of the MLR models used for the elucidation of potential connections between gas phase VOCs and the microbiological composition of the aerosol particles. N, number of samples in the model; R2, correlation coefficient adjusted by degree of freedom; SEE, standard error of the estimate; MAE, mean absolute error; and D-W, Durbin Watson statistic P-value.

	Size	N	P-value	R^2	SEE	MAE	D-W
Bacteria	**PM 1**	18	0.002	0.92	0.13	0.06	0.28
	PM 2.5	18	0.028	0.95	0.12	0.05	0.50
	PM10	18	0.003	0.95	0.11	0.04	0.18
	PM >10	20	0.004	0.96	0.11	0.05	0.50
Fungi	**PM 1**	19	0.001	0.94	0.16	0.06	0.43
	PM 2.5	18	0.006	0.93	0.20	0.07	0.41
	PM10	19	0.003	0.92	0.17	0.07	0.34
	PM >10	18	0.003	0.98	0.06	0.02	0.46
Pseudomonas	**PM 1**	18	0.016	0.90	0.24	0.10	0.13
	PM 2.5	18	0.041	0.93	0.17	0.05	0.21
	PM10	18	0.002	0.98	0.02	0.01	0.07
	PM >10	18	0.004	0.94	0.05	0.02	0.37

A



B

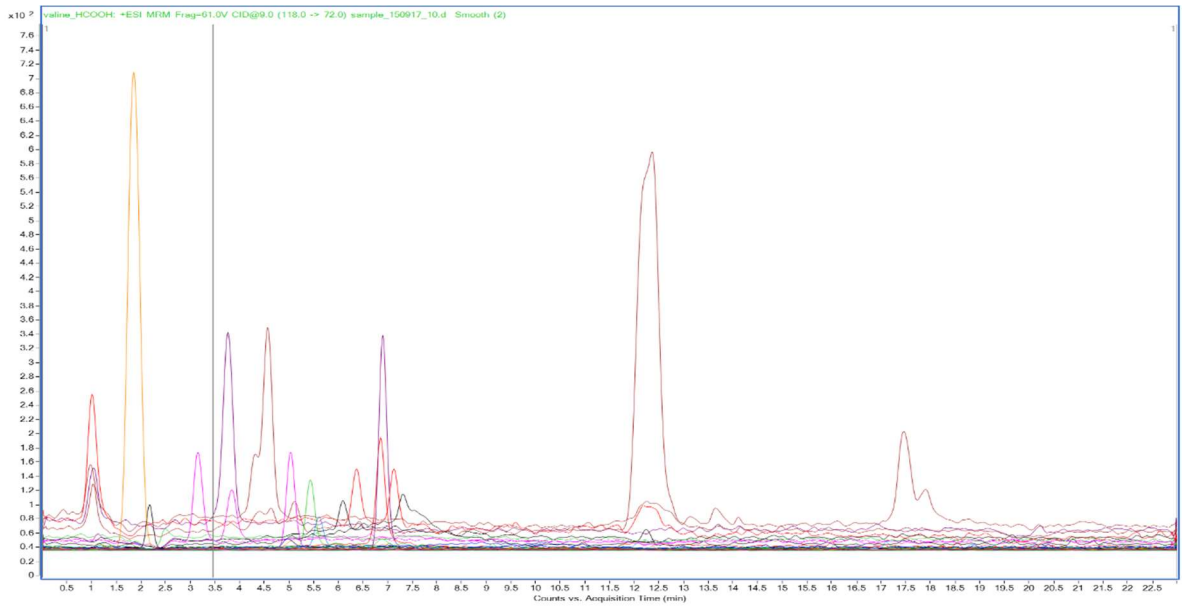


Figure S1. Typical HILIC chromatograms for a standard solution containing 250 ng mL^{-1} of each analyte (A) and an aerosol sample (B). Detailed separation between Ile and Leu is provided as insert in the chromatogram provided for standard solutions.

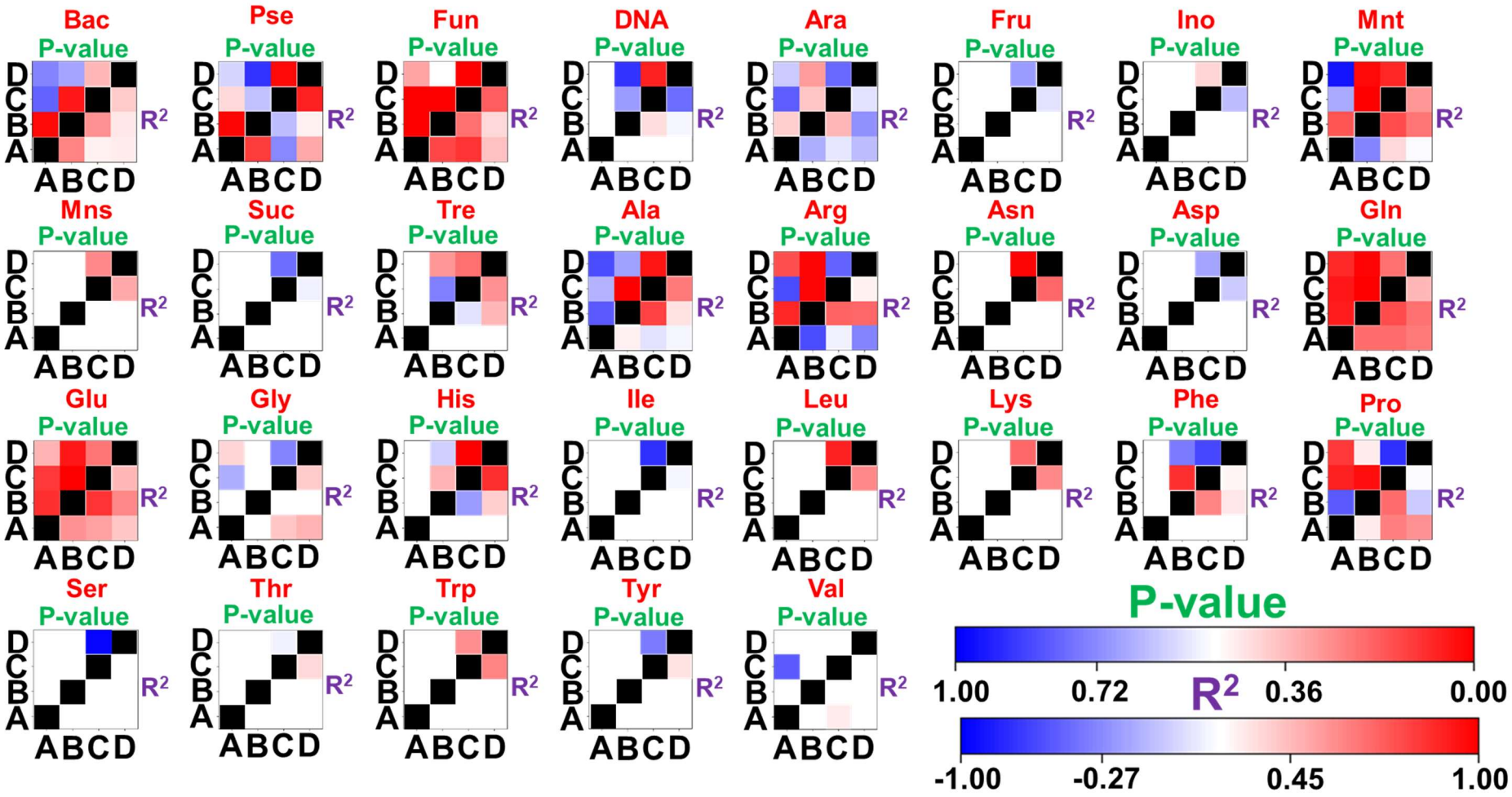


Figure S2. Pearson correlation for the individual microbial groups and chemical compounds detected in PBAPs as a function of the particle size. P- and R2 values are shown in the upper and lower part of the heat map, respectively. Negative R^2 values are used in the figure to show negative correlations. **A**, < 1.0 µm particles 1; **B**, 1.0–2.5 µm particles; **C**, 2.5–10.0 µm particles; and **D**, 10 > µm particles. Bac, bacteria; Pse, *Pseudomonas*; and Fun, fungi.

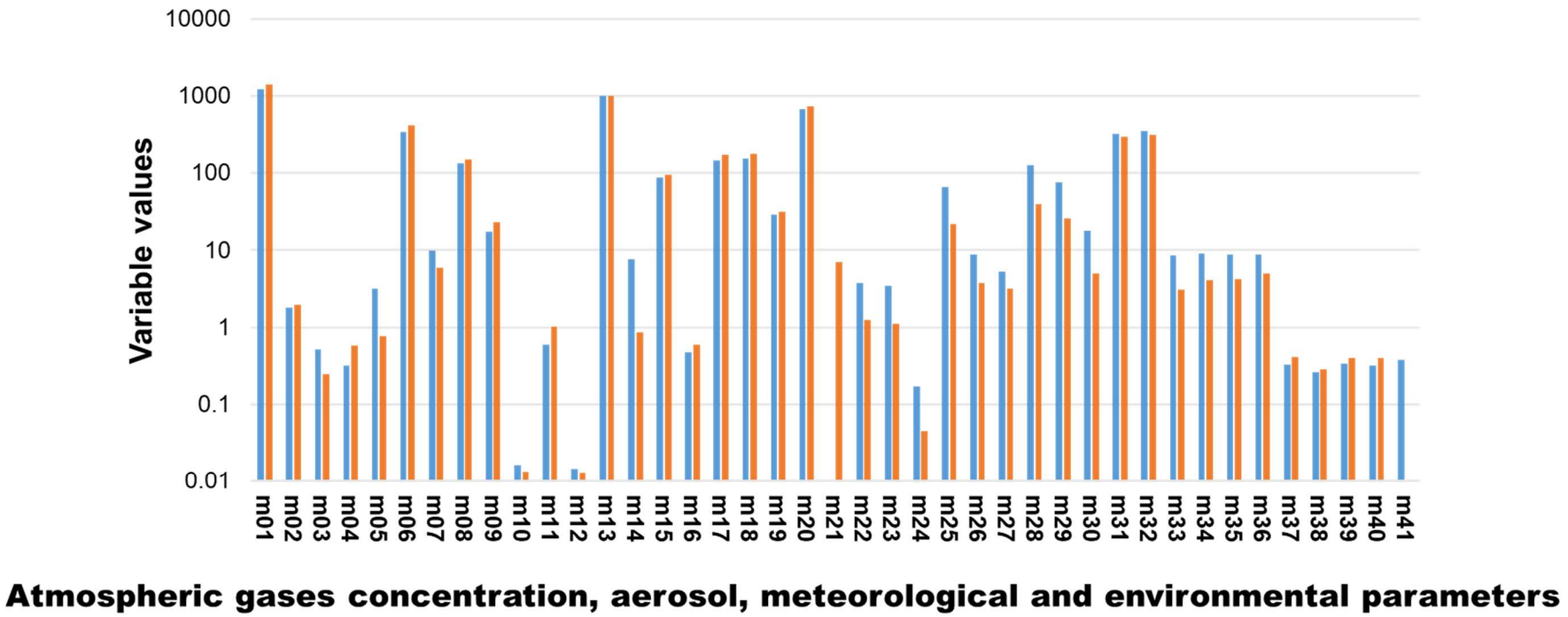


Figure S3. Differences between clusters according to the ancillary data. Variable values are shown in logarithmic scale. ■ Sampling period 1(04.09.2017 to 13.10.2017) and ■ Sampling period 2 (23.10.2017 to 22.11.2017). Variable names are coded in Table S4.

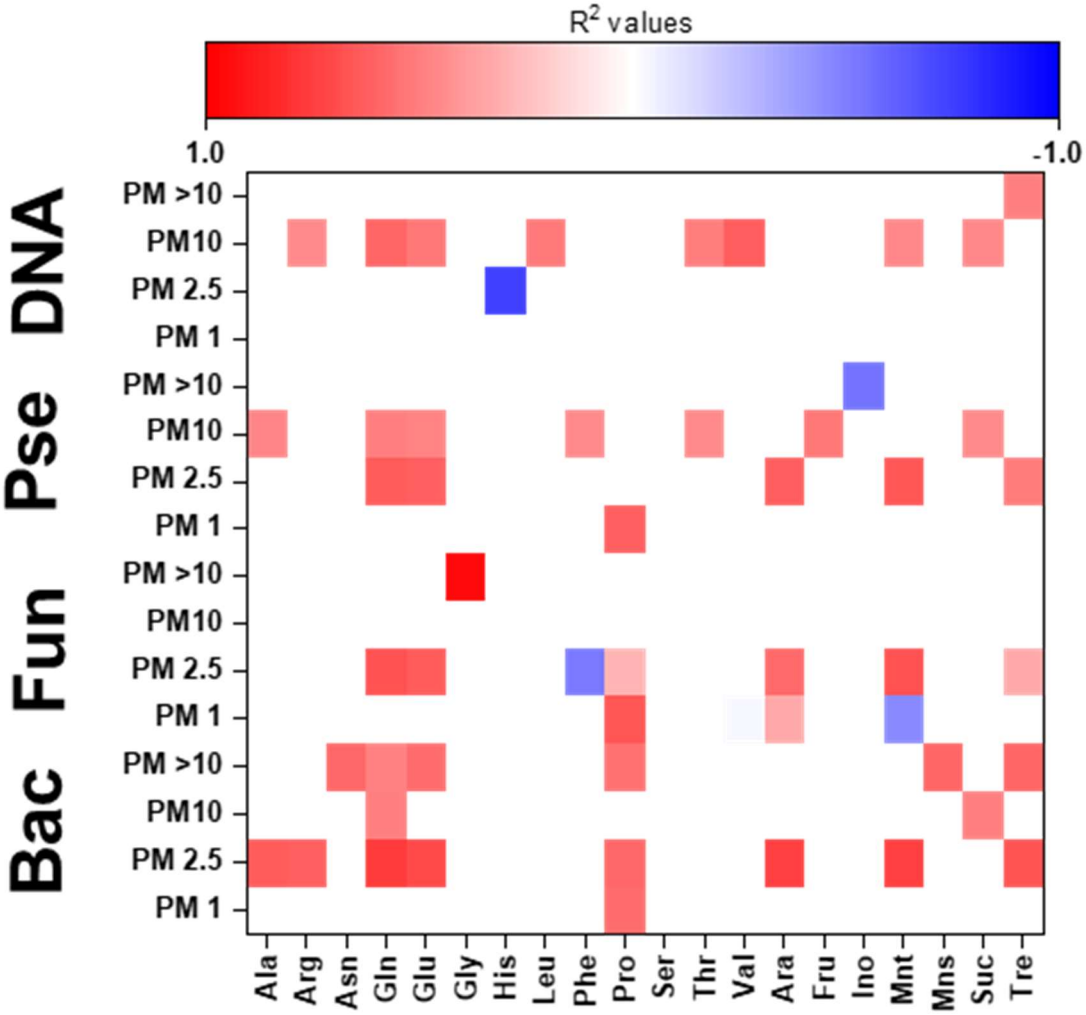


Figure S4. Pearson correlation results between the chemical compounds and the microbial groups, including total DNA, for the different particle sizes. Correlations with P-values > 0.05 are not shown in this figure. Negative R^2 values are used in the figure to show negative correlations between the microbial groups and the chemical species. Bac, bacteria; Pse, *Pseudomonas*; and Fun, fungi.

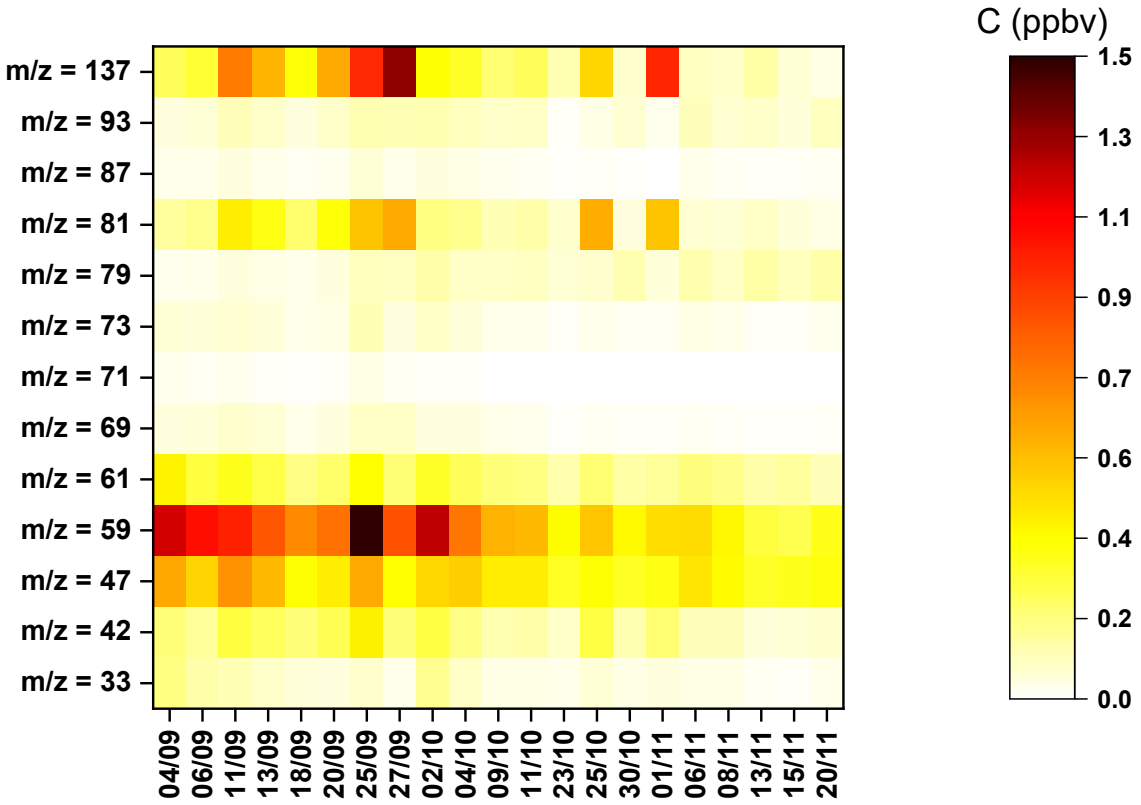


Figure S5. Gas phase VOCs in samples expressed with different m/z ions. Initial date of collection is shown in x-axis for the different samples. Concentration is expressed as ppbv.

Fig. S6 A

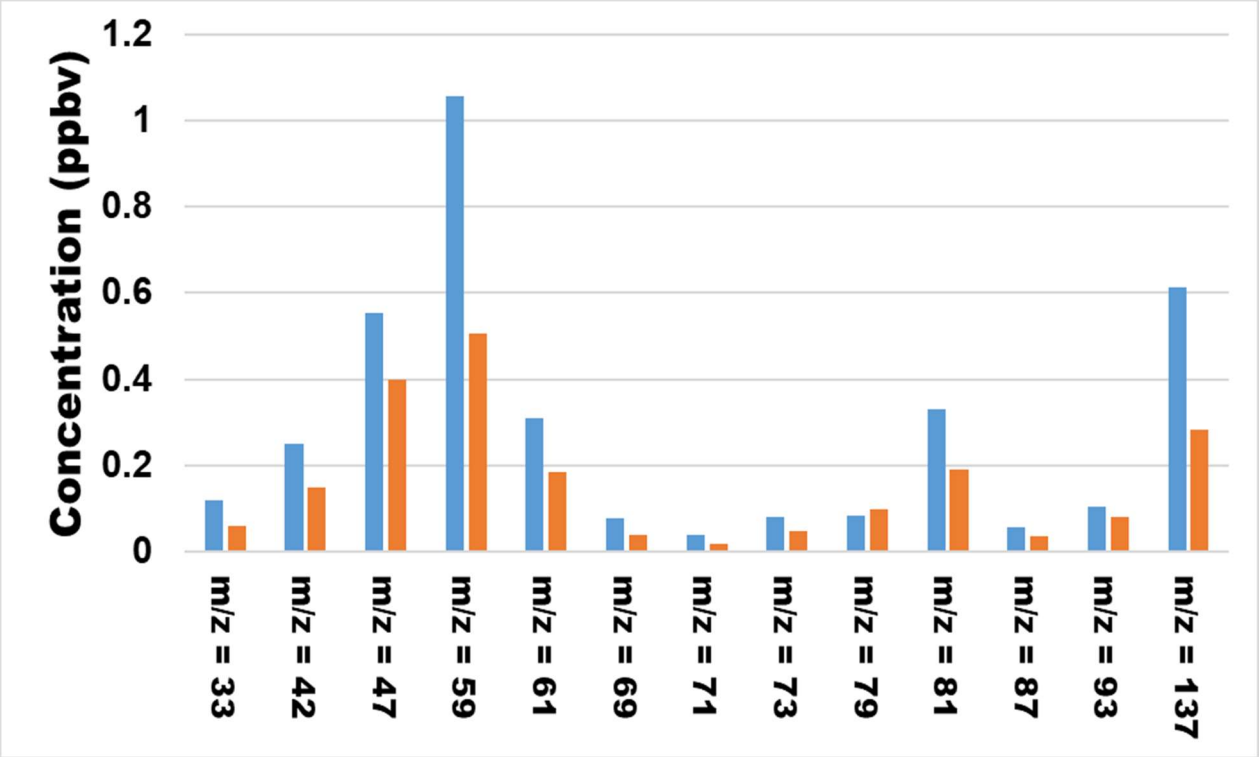

Concentration (ppbv)
1.2
1
0.8
0.6
0.4
0.2
0
m/z = 33
m/z = 42
m/z = 47
m/z = 59
m/z = 61
m/z = 69
m/z = 71
m/z = 73
m/z = 79
m/z = 81
m/z = 87
m/z = 93
m/z = 137

Fig. S6 B

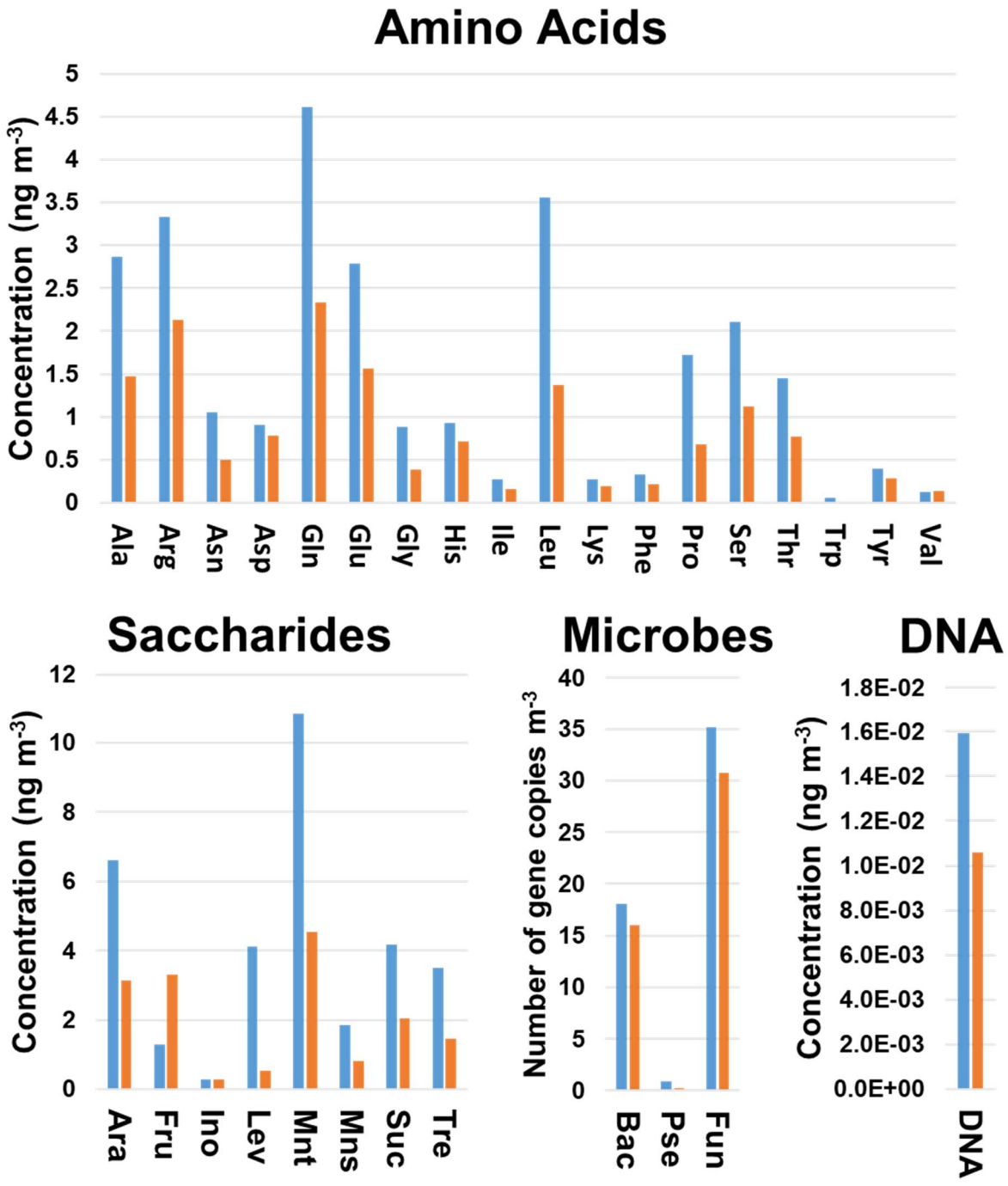


Figure S6. Potential connections between gas phase VOCs and the microbiological composition of PBAPs. A) Differences between clusters based on the gas phase VOCs; B) differences in the chemical and microbiological composition of PBAPs based on the groups established by gas phase VOCs. Average concentrations were calculated for all filter sizes analyzed. ■ Group 1 (04.09.2017–15.9.2017 and 25.09.2017–06.10.2017) and ■ Group 2 (18.09.2017–22.09.2017 and 09.10.2017–22.11.2017). Bac, bacteria; Pse, *Pseudomonas*; and Fun, fungi.

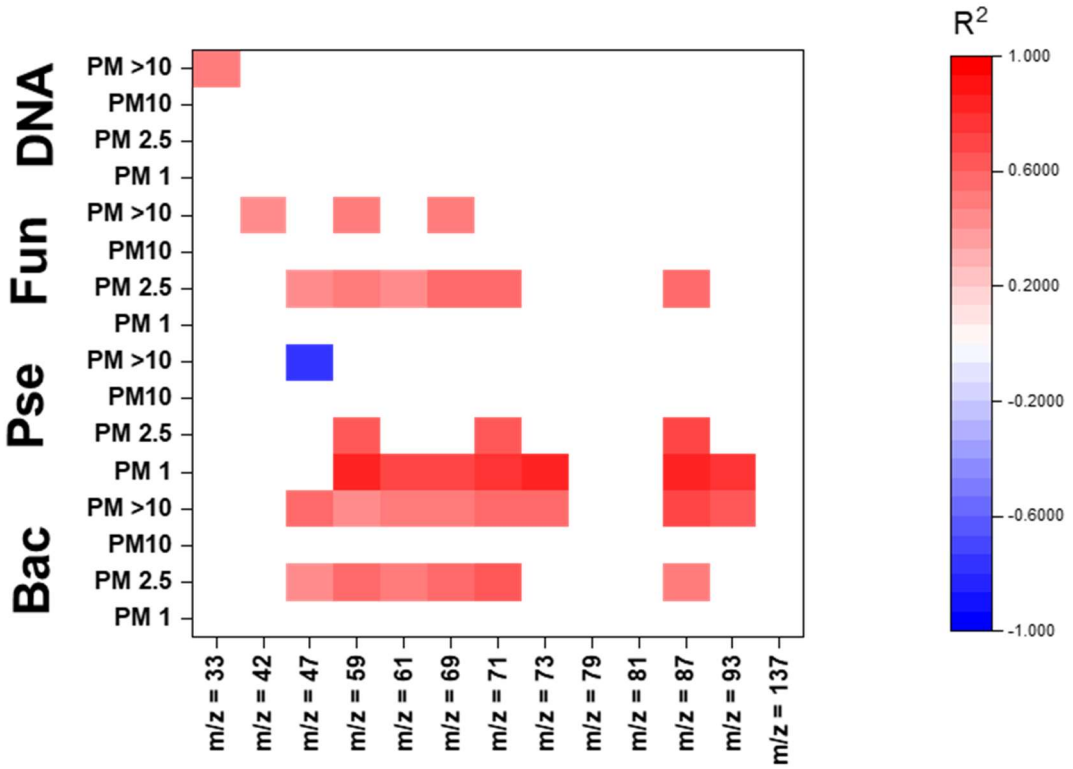


Figure S7. Pearson correlation results for the comparison between the gas phase VOCs and the microbiological composition of PBAPs. Correlations with P-values > 0.05 are not shown in this figure. Negative R2 values are used in the figure to show negative correlations between the microbial groups and the VOCs.

References

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, J. Geophys. Res., 108, D21, 4682 https://doi.org/10.1029/2003JD003863, 2003.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26, 223–257. https://doi.org/10.1002/mas.20119, 2007.

Rantala, P., Aalto, J., Taipale, R., Ruuskanen, M. T., and Rinne, J.: Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere. Biogeosciences 12, 5753–5770. https://doi.org/10.5194/bg-12-5753-2015, 2015

Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods, Atmos. Chem. Phys., 8, 6681–6698, https://doi.org/10.5194/acp-8-6681-2008, 2008.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K. and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117 (21), 13187–13229, https://doi.org/10.1021/acs.chemrev.7b00325, 2017.