

Composition and temporal behavior of ambient ions in the boreal forest

M. Ehn¹, H. Junninen¹, T. Petäjä¹, T. Kurtén¹, V.-M. Kerminen^{1,2}, S. Schobesberger¹, H. E. Manninen¹, I. K. Ortega¹, H. Vehkamäki¹, M. Kulmala¹, and D. R. Worsnop^{1,2,3}

[1] {Department of Physics, P.O.Box 64, FI-00014, University of Helsinki, Finland}

[2] {Finnish Meteorological Institute, Research and Development, P.O. Box 503, FI-00101 Helsinki, Finland}

[3] {Aerodyne Research Inc, Billerica, MA 01821, USA}

Supplementary material

1. Identified ambient ions

Below are listed all the ions that we believe to have identified during the measurements, negative ions in Table S1 and positive ions in Table S2. In some cases only the elemental composition is identified, but in most cases also the compound names are given. For the ions containing several alkyl groups, we have only listed the number of C atoms in the alkyl groups, as we cannot distinguish between several shorter alkyl groups and one longer, for instance dimethyl amine and ethyl amine. Grey backgrounds in Table S1 show that the ion is identified as a cluster.

Integer mass [Da]	Elemental formula	Chemical formula	Identified ions		Exact mass [Da]	Conc. [cm ⁻³]	
			Name (adding H+)			Max	Mean
45	CHO2-	CHO2-	Formic acid		44.9982	2.6	0.1
60	CO3-	CO3-			59.9853	2.9	0.1
62	O3N-	NO3-	Nitric acid (NA)		61.9884	2.9	0.3
78	CH2O4-	H2O*CO3-			77.9959	1.9	0.0
80	SO3-	SO3-			79.9574	3.8	0.7
80	H2O4N-	H2O*NO3-	NA + water		79.9989	3.8	0.7
87	C3H3O3-	C3H3O3-	Pyruvic acid		87.0088	2.8	0.5
89	C2HO4-	C2HO4-	Oxalic acid		88.9880	7.3	1.2
89	C3H5O3-	C3H5O3-	Lactic acid		89.0244	7.3	1.2
96	O4S-	SO4-			95.9523	14.0	1.9
97	HO4S-	HSO4-	Sulfuric acid (SA)		96.9601	242.7	49.1
103	C3H3O4-	C3H3O4-	Malonic acid (MA)		103.0037	29.9	12.5
112	O5S-	SO5-			111.9472	51.7	11.9
113	HO5S-	HSO5-	Peroxymonosulfuric acid		112.9550	7.9	2.6
113	C4HO4-	C4HO4-	Squaric acid		112.9880	7.9	2.6
115	C4H3O4-	C4H3O4-	Fumaric/maleic acid (FMA)		115.0037	43.2	4.5
119	C3H3O5-	C3H3O5-	Tartronic acid		118.9986	2.7	0.6
124	CH2O6N-	H2CO3*NO3-	Carbonic acid + NA		123.9888	5.0	1.9
125	HO6N2-	HNO3*NO3-	NA dimer		124.9840	34.4	15.1
129	C5H5O4-	C5H5O4-	Glutaconic acid		129.0193	7.0	1.1
133	C4H5O5-	C4H5O5-	Malic acid		133.0142	4.6	1.2
142	O6NS-	NO3*SO3-			141.9452	19.8	1.6
147	C5H7O5-	C5H7O5-	Hydroxypentanedioic acid		147.0299	3.2	0.7
149	C4H5O6-	C4H5O6-	Tartaric acid		149.0092	4.9	1.1
155	C2H3O6S-	C2H3O2SO4-	Glycolic acid sulfate (GAS)		154.9656	6.7	1.4
158	O7NS-	NO3*SO4-			157.9401	6.0	0.8
160	H2O7NS-	HNO3*HSO4-	NA + SA		159.9557	6.6	1.3
161	C5H5O6-	C5H5O6-			161.0092	5.9	1.4
166	C3H4O7N-	C3H4O4*NO3-	MA + NA		165.9993	26.6	10.3
175	O3I-	IO3-	Iodic acid		174.8954	10.5	2.5
176	C4H2O7N-	C4H2O4*NO3-	SqA + NA		175.9837	5.0	1.0
178	C4H4O7N-	C4H4O4*NO3-	FMA + NA		177.9993	17.3	2.2
192	C5H6O7N-	C5H6O4*NO3-	Glutaconic acid + NA		192.0150	3.6	1.0
195	H3O8S2-	H2SO4*HSO4-	SA dimer		194.9275	142.0	23.0
201	C3H5O8S-	C3H4O4*HSO4-	MA + SA		200.9888	6.9	2.6
207	C6H7O8-	C3H4O4*C3H3O4-	Malonic acid dimer (MA2)		207.0146	5.6	1.2
211	H3S2O9-				210.9224	3.7	0.6
219	C7H7O8-	C4H4O4*C3H3O4-	FMA + MA		219.0146	3.9	0.6
224	C5H6O9N-	C5H6O6*NO3-	? + NA		224.0048	19.4	3.3
231	C8H7O8-	C4H4O4*C4H3O4-	FMA dimer		231.0146	5.3	0.7
238	HO6NI-	HNO3*IO3-	NA + Iodic acid		237.8854	6.7	1.3
253	C2H5O10S2-	H2SO4*C2H3O2SO4-	SA + GAS		252.9330	6.7	1.4
259	C5H7O10S-	C3H4O4*C2H3O2SO4-	MA + GAS		258.9765	5.7	1.1
265	C8H9O10-	C5H6O6*C3H3O4-	? + MA		265.0262	9.7	1.4
293	H5O12S3-	(H2SO4)2*HSO4-	SA trimer		292.8949	100.7	6.0
391	H7O16S4-	(H2SO4)3*HSO4-	SA tetramer		390.8622	3.8	1.1
408	H10O16NS4-	NH3*(H2SO4)3*HSO4-	Ammonia + SA tetramer		407.8888	4.8	1.6

Table S1: List of all identified negative ion molecules (white background) and clusters (grey background). The concentrations are listed as the maximum and mean 30 min averages during April 30 – May 5.

Integer mass [Da]	Elemental formula	Z	Identified compound name without H+	Exact mass [Da]	Conc. [cm ⁻³]	
					integer masses	Max
70	C4H8N+	0N	Pyrroline	70.0651	12.0	4.2
74	C4H12N+	4N	Alkyl amine (4)	74.0964	3.1	1.0
80	C5H6N+	-4N	Pyridine	80.0495	82.1	36.4
84	C5H10N+	0N	Alkyl pyrroline (1)	84.0808	2.9	1.2
88	C5H14N+	4N	Alkyl amine (5)	88.1126	5.8	1.3
91	C7H7+	-7	Tropylium ion	91.0542	12.6	4.3
92	C6H6N+	-6N		92.0495	3.7	1.6
93	C6H7N+	-5N		93.0573	8.3	4.4
94	C6H8N+	-4N	Alkyl pyridine (1)	94.0651	119.1	57.3
100	C5H10ON+	0NO		100.0757	3.4	1.0
102	C6H16N+	4N	Alkyl amine (6)	102.1277	8.8	1.8
106	C7H8N+	-6N		106.0651	6.0	3.1
107	C7H9N+	-5N		107.0730	9.6	5.0
108	C7H10N+	-4N	Alkyl pyridine (2)	108.0808	74.9	33.5
110	C6H8ON+	-4NO		110.0600	13.2	6.1
120	C8H10N+	-6N		120.0808	6.2	3.0
121	C8H11N+	-5N		121.0886	3.0	1.4
122	C8H12N+	-4N	Alkyl pyridine (3)	122.0964	36.7	15.6
124	C7H10ON+	-4NO		124.0757	7.1	3.1
128	C8H18N+	2N		128.1439	15.3	4.3
130	C9H8N+	-10N	Quinoline	130.0651	36.1	18.1
130	C8H20N+	4N	Alkyl amine (8)	130.1590	36.1	18.1
136	C9H14N+	-4N	Alkyl pyridine (4)	136.1121	58.9	18.5
144	C10H10N+	-10N	Alkyl quinoline (1)	144.0808	12.6	5.2
150	C10H16N+	-4N	Alkyl pyridine (5)	150.1277	12.8	5.5
152	C9H14ON+	-4NO		152.1070	3.8	1.7
158	C11H12N+	-10N	Alkyl quinoline (2)	158.0964	7.1	3.5
170	C12H12N+	-12N		170.0964	4.1	1.7

Table S2: List of all identified positive ion molecules. Compound groups are mainly colored according to the Kendrick diagram (Figure 4). The concentrations are listed as the maximum and mean 30 min averages during May 5 – 8. Numbers in parenthesis after the compound names signify the number of C atoms in the added alkyl groups.

2. List of all detected ions

The software package tofTools was used to analyze the data from Hytiälä. Below are two tables summarizing the m/Q and mean concentrations of all the output peaks for both polarities (negative ions in S3 and positive ions in S4). Some of the peaks have been identified above, but some remain unidentified.

Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.
79.957	0.01	192.018	0.02	284.044	0.01	342.067	0.14
88.990	0.02	194.928	0.31	285.024	0.01	343.061	0.04
95.950	0.05	196.927	0.03	292.894	0.04	344.057	0.02
96.958	0.95	197.009	0.01	294.078	0.02	345.036	0.01
97.956	0.01	201.007	0.03	295.064	0.02	355.071	0.05
98.954	0.05	207.019	0.02	296.069	0.02	356.060	0.05
103.003	0.31	212.997	0.01	297.049	0.02	357.066	0.06
111.945	0.25	217.015	0.02	298.048	0.02	358.068	0.08
112.986	0.04	220.040	0.01	299.038	0.02	359.056	0.03
113.943	0.01	224.013	0.04	300.035	0.02	360.058	0.01
115.007	0.13	231.035	0.01	307.084	0.01	361.027	0.01
118.994	0.01	234.047	0.02	308.068	0.16	370.071	0.02
123.988	0.04	236.040	0.01	309.064	0.04	371.071	0.02
124.985	0.36	238.041	0.01	310.072	0.05	372.051	0.11
129.027	0.02	239.028	0.01	311.066	0.03	373.056	0.05
131.002	0.01	240.006	0.03	312.063	0.02	374.060	0.03
133.012	0.02	241.004	0.01	313.050	0.01	375.035	0.02
141.946	0.03	248.057	0.01	314.044	0.02	377.046	0.01
149.012	0.02	250.055	0.02	316.015	0.01	386.070	0.01
154.016	0.02	252.038	0.01	323.066	0.02	387.060	0.06
154.962	0.02	255.019	0.02	324.069	0.02	388.060	0.03
157.955	0.01	264.058	0.01	325.068	0.04	389.049	0.01
157.941	0.02	265.033	0.01	326.063	0.07	390.053	0.01
159.958	0.02	266.044	0.01	327.058	0.02	402.073	0.01
161.024	0.02	267.037	0.01	328.056	0.03	403.059	0.02
166.002	0.19	268.035	0.01	329.038	0.02	404.051	0.01
174.892	0.04	269.034	0.02	330.046	0.01	407.038	0.01
175.991	0.01	281.034	0.02	339.070	0.04	408.094	0.01
178.006	0.05	282.038	0.05	340.060	0.20	478.153	0.01
182.013	0.02	283.042	0.02	341.063	0.05	494.157	0.03
182.998	0.01						

Table S3. Anion m/Q and mean concentration as given by tofTools during 1-5 May, 2009. The concentrations are normalized so that the maximum peak is 1.00. Only peaks above 0.005 are listed.

Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.	Measured mass [Da]	Normalized mean conc.
70.065	0.07	139.091	0.0	213.137	0.01	286.197	0.03
71.013	0.03	141.078	0.0	214.252	0.06	288.197	0.03
74.093	0.01	143.081	0.0	215.120	0.01	290.184	0.02
78.034	0.02	144.081	0.1	215.251	0.01	292.182	0.01
80.049	0.71	144.944	0.0	216.140	0.01	294.186	0.01
81.053	0.05	145.086	0.0	217.143	0.01	295.195	0.01
82.987	0.03	148.100	0.0	218.142	0.01	296.209	0.01
83.055	0.02	150.122	0.1	219.158	0.01	297.186	0.02
84.080	0.02	151.113	0.0	221.154	0.02	298.209	0.02
87.043	0.03	152.103	0.0	222.157	0.01	300.208	0.02
88.109	0.02	153.098	0.0	223.159	0.02	302.196	0.03
91.054	0.08	155.101	0.0	224.179	0.04	304.199	0.02
92.050	0.02	156.087	0.0	225.156	0.02	306.194	0.01
93.058	0.07	157.090	0.0	227.153	0.02	310.216	0.01
94.065	1.00	158.096	0.0	230.158	0.01	312.218	0.04
95.066	0.09	159.101	0.0	232.143	0.01	313.213	0.01
96.045	0.03	163.120	0.0	234.139	0.01	314.218	0.03
98.986	0.02	164.136	0.03	235.164	0.02	316.210	0.02
100.079	0.01	165.115	0.02	237.174	0.03	318.200	0.02
102.127	0.02	166.112	0.01	238.173	0.01	320.203	0.02
105.069	0.01	167.105	0.02	239.167	0.04	322.211	0.01
106.065	0.05	169.115	0.03	240.176	0.01	326.227	0.02
106.947	0.02	170.097	0.02	241.159	0.01	328.225	0.03
107.074	0.06	171.113	0.02	242.161	0.01	330.215	0.03
108.081	0.52	172.112	0.02	244.174	0.02	332.220	0.02
108.925	0.05	178.143	0.01	246.165	0.03	334.207	0.02
109.082	0.06	179.065	0.01	248.153	0.01	336.209	0.01
110.060	0.09	179.133	0.01	249.179	0.01	338.212	0.01
111.062	0.01	180.084	0.01	250.152	0.01	340.231	0.02
114.097	0.01	181.116	0.02	251.171	0.02	342.236	0.02
115.058	0.02	182.134	0.01	252.190	0.01	344.228	0.02
117.063	0.01	183.090	0.04	253.179	0.03	346.224	0.04
119.080	0.01	184.114	0.01	254.193	0.02	347.213	0.01
120.077	0.04	185.114	0.02	255.173	0.01	348.218	0.01
121.087	0.02	186.132	0.01	256.186	0.03	350.218	0.01
122.096	0.23	187.107	0.01	258.174	0.02	356.245	0.02
123.098	0.04	192.146	0.01	260.168	0.02	358.235	0.02
124.080	0.04	193.140	0.02	262.164	0.02	360.230	0.02
125.078	0.01	195.129	0.01	266.189	0.01	362.227	0.02
126.938	0.09	197.127	0.01	268.197	0.02	364.226	0.01
127.074	0.01	199.131	0.02	269.180	0.02	370.246	0.01
128.141	0.1	200.131	0.01	270.196	0.03	372.243	0.01
128.063	0.0	201.123	0.01	271.197	0.01	374.248	0.01
130.066	0.2	202.137	0.01	272.190	0.02	376.239	0.01
131.072	0.0	203.135	0.01	274.177	0.02	378.226	0.01
134.088	0.0	205.140	0.02	276.173	0.02	386.253	0.01
135.100	0.0	207.157	0.05	277.159	0.01	388.262	0.01
136.112	0.3	208.159	0.01	278.172	0.01	390.247	0.01
136.994	0.1	209.146	0.02	279.167	0.01	398.256	0.01
137.111	0.0	210.151	0.02	280.186	0.01	402.258	0.01
138.094	0.0	211.145	0.02	284.198	0.01	404.248	0.01

Table S4. Cation m/Q and mean concentration as given by tofTools during 6-7 May, 2009. The concentrations are normalized so that the maximum peak is 1.00. Only peaks above 0.005 are listed.

3. Additional figures

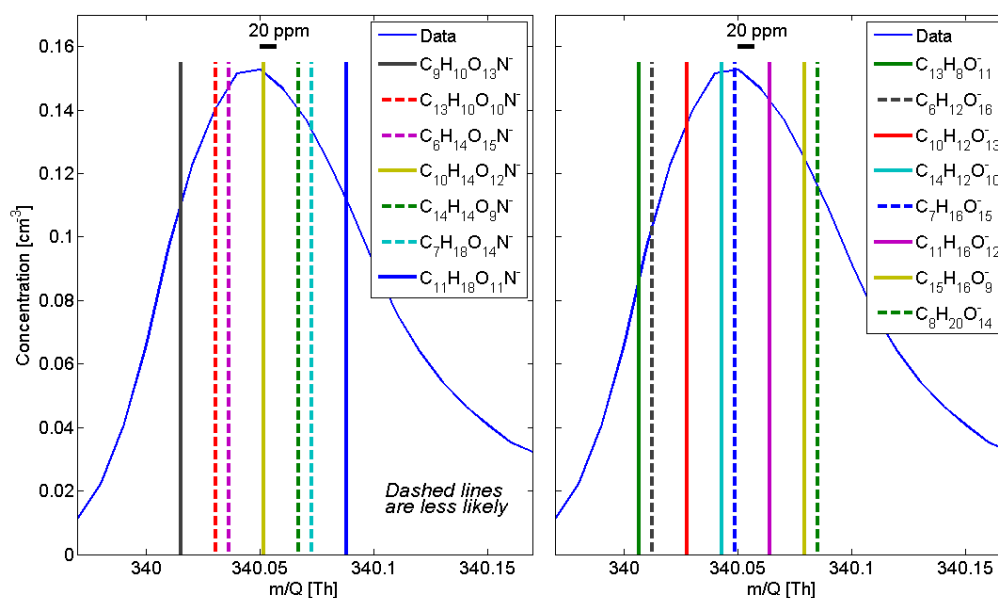


Figure S1. Average mass spectrum around m/Q 340 during 2 May, 2009. In the left panel all $C_cH_hO_oN_n$ compounds with masses between 340.000 and 340.100 are plotted, and in the right panel all $C_cH_hO_o$ in the same m/Q range. This figure illustrates the amount of compounds that are possible at this m/Q . According to the nitrogen rule an even m/Q peak must include an odd number of N, thus the most likely compound at this mass was proposed to be $C_{10}H_{14}O_{12}N$. The best estimate for the exact mass of this peak was determined from many different time periods, including periods when small amount of iodine was mixed with the sample, to get reference peaks at higher masses (mainly I_3 at 380.713 Th). For these plots, 340.058 was used as one of the m/Q calibration peaks. However, considering the 20 ppm accuracy of the instrument, the m/Q calibration would have to be 100 pm off to fit either of the two other reasonable options in the left panel. If, for some reason, the nitrogen rule does not apply for this ion, the amount of possibilities increases. And finally, if the ion contains other compounds than C, H, O and N, the possibilities also increase.

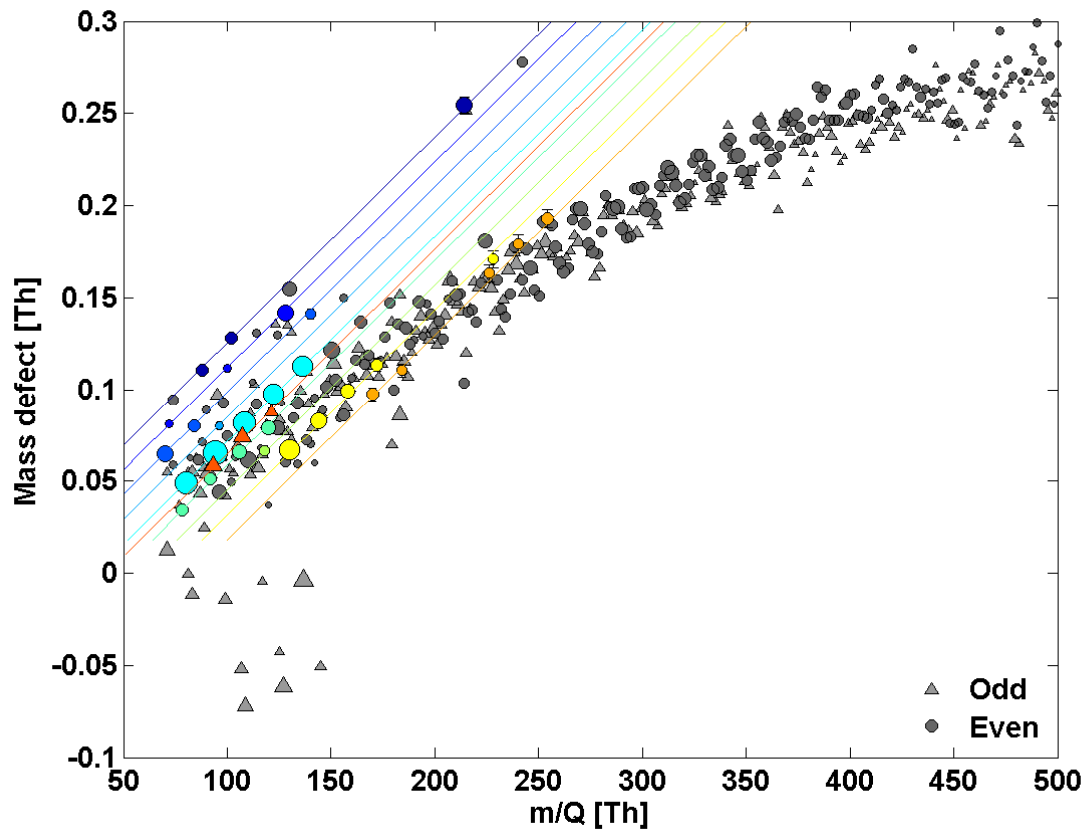


Figure S2. Mass defects as a function of m/Q for the positive ion in Hyytiälä during 6-7 May, 2009. This figure is similar to Fig. 5, but in normal scale and not Kendrick mass scale.