



1 **Insight into naturally-charged Highly Oxidized Molecules** 2 **(HOMs) in the boreal forest**

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16 **Abstract.** In order to investigate the role of the naturally charged highly oxidised molecules (HOMs) in the boreal
17 forest we have performed measurements to chemically characterize the composition of negatively charged ions.
18 Additionally, we compared this information with the chemical composition of the neutral (HOMs) detected in the
19 ambient air during the same period. The chemical composition of the ions was retrieved using an Atmospheric
20 Pressure interface Time-Of-Flight mass spectrometer (APi-TOF) while the gas phase neutral molecules (mainly
21 sulphuric acid and HOMs) were characterized using the same mass spectrometer coupled to a nitrate-based
22 chemical ionization unit (CI-APi-TOF). Overall, we divided the identified HOMs in two classes, HOMs
23 containing only carbon, hydrogen and oxygen and nitrogen-containing HOMs or organonitrates (ONs). During
24 the day, among the ions, in addition to the well-known sulphuric acid clusters, we found a large number of HOMs
25 clustered with the two most common inorganic acids, nitrate (NO_3^-) or bisulphate (HSO_4^-), the first one being
26 predominant. During the night, the detected ions were very similar to the neutral compounds and were mainly
27 composed of HOMs clustered with NO_3^- .

28 For the first time, we identified several clusters contain up to 40 carbon atoms clustered with NO_3^- . At this regard,
29 we think that these naturally charged clusters are formed by up to 4 oxidized α -pinene units.

30 Finally, diurnal profiles of the negative ions were consistent with the neutral compounds revealing that ONs peak
31 during the day while non-nitrate HOMs are more abundant at night-time. However, during the day, a big fraction
32 of the negative charge is taken up by the sulphuric acid clusters causing differences between detected neutral and
33 ion HOM/ON species. As a result, the total signal of the ionised organic compounds was much lower during day
34 than during the night.

35



36 1 Introduction

37 Ions are present everywhere in the atmosphere. They arise from, for example, galactic cosmic rays (GCR) and/or
38 radioactive decay from the soil (radon and gamma) (Harrison and Carslaw, 2003; Hirsikko et al., 2011). The initial
39 ions have generally a very simple structure. In the upper atmosphere, the primary ions are O^+ , O_2^+ and NO^+ , while
40 in the dense air they are N_2^+ , O_2^+ , O_2^- and O^- (Smith and Spanel, 1995). Collisions of these ions with various trace
41 gases lead to charge transfer to compounds with higher charge affinity and formation of a large variety of cluster
42 ions. Negative charge is preferably transferred to acidic compounds like nitric acid, sulphuric acid and few other
43 strong acid (lowest proton affinity), while positive charge is carried by basic compounds such as ammonia and
44 amines (highest proton affinity) (Smith and Spanel, 1995). The production rate of the ions can vary depending on
45 the altitude, location and the time of the year. In the boreal forest, such as Hyytiälä located at 61N, early spring
46 average production rate calculated based on external radiation and radon measurements is about 4.5 ion pairs
47 $cm^{-3}s^{-1}$ (Laakso et al., 2004).

48 It is well known that natural ions are able to enhance the formation rate of new particles and the mechanism
49 is known as ion-induced nucleation (Raes et al., 1986; Yu and Turco, 2001; Kirkby, 2007; Arnold, 2008; Hirsikko
50 et al., 2011). Recent laboratory experiments performed in the European Centre for Nuclear Research (CERN,
51 CLOUD experiment) have systematically explored the influence of ions on new particle formation (NPF) in
52 several different chemical systems. The presence of ions strongly enhanced pure sulphuric acid nucleation
53 (Kirkby et al., 2011; Duplissy et al., 2016) as well as sulphuric acid – ammonia nucleation (Kirkby et al., 2011;
54 Bianchi et al., 2012; Schobesberger et al., 2015; Kurten et al., 2016), while showed little to no effect on the
55 sulphuric acid – amine nucleation (Almeida et al., 2013; Kuerten et al., 2014; Bianchi et al., 2014). Recently, the
56 results from the same experiment revealed that ions can strongly enhance also pure organic nucleation in absence
57 of sulphuric acid (Kirkby et al., 2016). Although Bianchi and co-workers (2016) have observed that new particle
58 formation in the free troposphere depends on the availability of highly oxidized organic species, they have seen
59 only a weak ion enhancement. Several studies have demonstrated also that the compounds participating in this
60 process, the so-called Highly Oxidised Molecules (HOMs), play often a central role in NPF events (Kulmala et al.,
61 1998; Ehn et al., 2014; Krechmer et al., 2015; Ortega et al., 2016; Kirkby et al., 2016; Bianchi et al., 2016).

62 HOMs can exist in the atmosphere both as ionized (naturally clustered with nitrate ions) and neutral species
63 (Ehn et al., 2012; Ehn et al., 2014; Bianchi et al., 2016). Main source of HOMs to the atmosphere is likely the
64 oxidation of terpenes, which are biogenically-emitted volatile organic compounds (BVOCs). The most abundant
65 HOM precursor in the boreal forest is α -pinene, originating primarily from coniferous trees (Ehn et al., 2014;
66 Jokinen et al., 2015). Ehn et al. (2014) have highlighted the formation of HOMs as first-generation oxidation
67 products from the oxidation of monoterpenes. The HOMs are produced through the formation of peroxy radicals
68 (RO_2) and subsequent intramolecular hydrogen-shifts followed by rapid reactions with oxygen, also called
69 “autoxidation” (Crouse et al., 2013; Rissanen et al., 2014; Jokinen et al., 2015; Berndt et al., 2016). They are
70 expected to contain a wide range of chemical functional groups, including hydroxyl, hydroperoxides, carbonyls
71 and epoxides. Consequently, some of the HOMs have very low vapour pressures allowing them to react and/or
72 condense nearly irreversibly onto aerosol surfaces (Trostl et al., 2016).

73 In oxidation of monoterpenes, such as α -pinene, characteristic HOMs contain similar amount of carbon and
74 hydrogen to the parent molecule (i.e. $C_{10}H_{16}$), while the oxygen amount varies and can be as high as 13 atoms (Ehn
75 et al., 2012; Ehn et al., 2014; Trostl et al., 2016; Kirkby et al., 2016). Beside monomer HOMs (C_{10}), dimer HOMs
76 with an approximate composition of either $C_{19}H_{28}O_x$ or $C_{20}H_{30}O_x$ were also observed in both gas and particulate
77 phases (Ehn et al., 2014; Lopez-Hilfiker et al., 2014). Rissanen et al. (2014) and Ehn et al. (2014) proposed that
78 the bimolecular reactions of two peroxy radicals ($RO_2 + RO_2$) is one of the likely chemical pathways leading to the
79 formation of dimers in the gas phase.



80 Organonitrates (ONs) were also identified in both gas and particulate phases from the oxidation of biogenic
81 compounds in the presence of NO_x ($\text{NO} + \text{NO}_2$) and NO_3 radical (Ehn et al., 2014; Lee et al., 2016; Yan et al.,
82 2016). In addition to carbon, hydrogen and oxygen, these molecules contain at least one nitrogen atom. Different
83 reaction pathways leading to ON formation have been proposed. Due to their low vapour pressures, ONs are also
84 expected to have a potential important role in the formation and growth of secondary organic aerosol (SOA)
85 (Farmer et al., 2010; Kiendler-Scharr et al., 2016; Lee et al., 2016; Ng et al., 2017). In addition, Kulmala et al.
86 (2013) have recently proposed that the organonitrate $\text{C}_{10}\text{H}_{15}\text{O}_5\text{NO}_3$ is important for NPF. On the other hand
87 Jokinen et al. (2017) have shown the clustering and ONs are connected to each other during solar eclipse.

88 Although recently it has been demonstrated that the ions as well as the HOMs are very important during NPF
89 processes, their role in the boreal forest is still somewhat unclear. It has been shown that ion nucleation can
90 contribute up to 10% of the total nucleation, however it is still not known what is the role of the different ion
91 families (Kulmala et al., 2013). While few previous studies have shown the presence of naturally charged HOMs,
92 a careful comparison between naturally charged clusters and neutral organic compounds has not been attempted
93 so far. The aim of this study was to investigate the composition and diurnal changes of ambient ions, focusing on
94 the one composed by HOMs and ONs, and comparing them with the neutral species observed in previous studies.

95 2 Materials and Methods

96 All the measurements presented in this study were performed at the Station for Measuring Ecosystem-Atmosphere
97 Relations (SMEARII) located at Hyytiälä Forestry Field Station in Southern Finland (Hari and Kulmala, 2005)
98 during spring 2013, covering April, May and June. The SMEARII station is located on a flat terrain covered by a
99 homogeneous Scots pine (*Pinus sylvestris*) forest which is representative of the boreal coniferous forest. Two
100 Atmospheric Pressure interface Time-of-Flight (APi-TOF) (Aerodyne Research Inc. & Tofwerk AG; Junninen et
101 al., 2010) mass spectrometers in Hyytiälä were deployed to obtain data on naturally charged negative ions and
102 neutral molecules. An APi-TOF consists of a time-of-flight mass spectrometer (TOF) coupled to an atmospheric
103 pressure interface unit (APi) that allows sampling directly from the ambient air. The instrument that is used for
104 detection of neutral molecules is further equipped with a chemical ionization (CI) inlet (Jokinen et al., 2012).

105 In the APi-TOF, the naturally charged ions are sampled directly from the air (Junninen et al., 2010), while in
106 CI-APi-TOF, the ions are artificially created in the ambient pressure chemical ionisation inlet that is placed in
107 front of APi-TOF. The CI-APi-TOF inlet deployed for this campaign utilized nitrate-ionisation method and was
108 designed initially to measure neutral sulphuric acid, and later on was shown to also detect neutral HOMs and ONs
109 (Jokinen et al., 2012; Ehn et al., 2014). Chemical ionization is achieved by exposing clean air (sheath flow)
110 containing nitric acid (HNO_3) to alpha radiation ($10 \text{ MBq } ^{241}\text{Am}$ source) or X-rays, which produces nitrate (NO_3^-)
111 ions. NO_3^- ions in the sheath flow are directed into the sample flow by an electric field where they ionize the
112 ambient molecules by clustering (e.g. selected organic compounds) or proton transfer (e.g. sulphuric and some
113 dicarboxylic acids). The ionized molecules are then guided through a critical orifice to the TOF mass analyser.
114 NO_3^- clustering ionisation is very selective to highly functionalised organic compounds (the molecule should
115 have at least two hydroxy or hydroperoxy groups), which makes this method ideal for measurement of HOMs
116 (Hytinen et al., 2015). High resolving power of TOF mass analyser makes it possible to identify the chemical
117 composition of the detected molecules. The mass spectrometry data were processed and analysed using the
118 MATLAB-implemented latest version (6.03) of tofTools developed by Junninen et al. (2010).

119 For the purposes of this study, we will refer to non-nitrogen containing organics as “HOM-monomers” (C_{10}
120 molecules) and “HOM-dimers” (C_{20} molecules). We will use “ONs” to refer to the nitrogen-containing HOMs.



121 When discussing ions, we will refer as “HOM/ON-nitrate” and “HOM/ON-bisulphate” to clusters of HOMs/ONs
122 with NO_3^- and HSO_4^- ions, respectively.

123 3 Results and Discussion

124 The focus of this work is to investigate the chemical composition of the naturally charged ions formed in the
125 Boreal forest and compare it with the neutral compounds detected by the CI-API-TOF. Ehn et al. (2010) have
126 previously reported that during the day the main peaks observed are cluster composed by sulphuric acid, whereas
127 during night the major identified ions are HOMs clustered with NO_3^- . Day and night UMR (unit mass resolution)
128 spectra, averaged throughout the campaign, were analysed and detailed high-resolution mass spectra analyses are
129 provided for a typical clear sky day (diurnal and nocturnal spectra).

130 Figure 1 presents the average mass spectra of 10 clear-sky days during April and May 2013 of the negative
131 ions (Panel A and C) and neutral molecules (Panel B and D). The daily spectra (Panel A and B) are an average of
132 all of the mass spectra recorded from 09:00 to 13:00 (local time), while during the night (Panel C and D) the mass
133 spectra cover the time range from 23:00 until 03:00. Peaks with an odd and even mass-to-charge ratio (m/z) are
134 coloured in blue and red, respectively as a first indication of the nitrogen-containing molecules. This is based on
135 the nitrogen rule, where a deprotonated molecule/cluster containing one (odd) nitrogen will have an even mass
136 ($\text{HOM}\cdot\text{NO}_3^-$ and/or $\text{ON}\cdot\text{HSO}_4^-$). While a deprotonated molecule/cluster containing zero or two (even) nitrogen
137 will have an odd mass ($\text{ON}\cdot\text{NO}_3^-$ and/or $\text{HOM}\cdot\text{HSO}_4^-$). The rule is reversed for radical species that can be
138 detected by CI-API-TOF.

139 As previously reported by Yan et al. (2016), the mass spectra for the neutral compounds are dominated by
140 the species with an odd mass number ($\text{ON}\cdot\text{NO}_3^-$) during daytime while during the night-time peaks with an even
141 mass number ($\text{HOM}\cdot\text{NO}_3^-$) are the most abundant. From Figure 1, we can see the same pattern for naturally
142 charged clusters, although with some differences. While for the neutral compounds there is a clear odd/even
143 pattern during the day, the negative ions show only a small predominance of the odd masses. The main reason is
144 that while in the ionization unit of the CI-API-TOF the HOMs and the ONs are ionized almost exclusively by the
145 primary ion (NO_3^-), in the atmosphere, during the day, the HOMs and the ONs can be ionized by either NO_3^- or
146 HSO_4^- ions. As ONs-nitrate will appear at odd mass and ON-bisulphate will appear at even mass, the difference
147 between odd and even m/z is less pronounced.

148 During the night, the organic species are mainly charged by NO_3^- ions since the photochemical production of
149 sulphuric acid, and therefore HSO_4^- ions, is inhibited. As a result, the composition of naturally charged ions are the
150 same as the neutral molecules measured by the CI-API-TOF making the two spectra (Panel C and D) in Figure 1
151 more comparable. In both mass spectra, we can still observe few peaks at high intensity with an odd atomic
152 number. These peaks are not ONs but are radicals formed from the ozonolysis of monoterpenes (m/z 325 -
153 $\text{C}_{10}\text{H}_{15}\text{O}_8\cdot\text{NO}_3^-$ and 357 - $\text{C}_{10}\text{H}_{15}\text{O}_{10}\cdot\text{NO}_3^-$ (Ehn et al., 2014; Yan et al., 2016)) and are highlighted in Panel D.
154 Contrary to a one large group of ions/neutral compounds within m/z 250 to 500 observed during the day, during
155 night two groups of molecules were distinguished. The first one, from m/z 250 to 450, are all identified as HOMs
156 clustered with NO_3^- ions containing 8-10 carbon atoms. The second group (from m/z 450 to 650) are also HOMs
157 clustered with NO_3^- ions but comprised of a larger number of carbon atoms ($\text{C}_{16}\text{-C}_{20}$) and are assigned to
158 HOM-dimers. Several studies have now reported that such dimer compounds are formed from the ozonolysis of
159 α -pinene (Ehn et al., 2014; Trostl et al., 2016; Kirkby et al., 2016). However, in this case, there are still some peaks
160 at odd masses (i.e. m/z 555: $\text{C}_{10}\text{H}_{31}\text{O}_{10}\text{NO}_3$) that have been attributed to night time NO_3 chemistry (Yan et al.,
161 2016).



162 3.1 Detailed chemical composition

163 To get further chemical information and confirmed as well the previous analysis we investigated a specific day by
164 high-resolution peak fitting. Here we show mass defect plots (Schobesberger et al., 2013; Bianchi et al., 2014) of
165 the negative ions and neutral molecules during the night (23:00 – 03:00) and during the day (09:00 – 13:00) on
166 April 20th 2013. In Figure 2, the top two panels report the chemical composition during night-time while the
167 bottom panels present the composition during daytime. In all the four mass defect plots, the coloured filled dots
168 correspond to the identified group of compounds described in the legend and the unfilled dots represent the
169 unidentified species. The size of the dot is proportional to the ion signal intensity of the different compounds.

170 As expected and partially shown in previous studies (Ehn et al., 2012; Yan et al., 2016), the mass defect plots
171 reveal that the chemical composition of the negative ions and the neutral compounds is different between day and
172 night. As shown in the UMR analysis, the neutral molecules as well as the negative ions indicate that, during the
173 day, ONs are formed at higher rate than during the night (light blue dots) while, during the night, non-nitrate
174 HOMs have higher concentrations (green dots). Interestingly, larger concentration of organic compounds such as
175 HOM-dimers could also be observed during the night, which is consistent with a decrease of the NO concentration
176 and subsequent increase of self- and cross-reactions of RO₂ radicals. From figure 2, we can clearly see that during
177 the night negatively charged ions and neutral compounds have similar composition. Several studies have
178 discussed that most of the HOMs detected during the night are formed by the reaction of monoterpene (e.g.
179 α -pinene) with ozone (Schobesberger et al., 2013; Ehn et al., 2014; Trostl et al., 2016; Kirkby et al., 2016). Some
180 of these studies have also shown that via the same reaction (i.e. α -pinene ozonolysis) it is possible to form clusters
181 that contain several C₁₀-monomers (C₂₀, C₃₀ and C₄₀). In addition, Yan et al. (2016) have also observed the
182 formation of the HOM dimers (C₁₉-C₂₀) during the night. Besides these oligomers, other ONs (blue dots) were
183 also observed during night. These ONs are likely formed from the NO₃-initiated oxidation of monoterpene. It is
184 worth noting that such behaviour has been observed previously for the neutral clusters, where the ONs and HOMs
185 are more abundant during the day and night-time, respectively (Yan et al., 2016).

186 The naturally charged ions reveal, however, additional information, which are mainly due to the fact that the
187 API-TOF can also observe HOMs clustered with HSO₄⁻ ions. Since sulphuric acid (and consequently the
188 bisulphate ion) is produced mainly during daytime from the OH-initiated oxidation of SO₂, the differences in
189 composition of ambient ions and neutral species is larger during the day. For example, at noon, all the major
190 naturally charged ions are composed by HSO₄⁻ (m/z 97), sulphuric acid dimer (H₂SO₄HSO₄⁻; m/z 195) and trimer
191 ((H₂SO₄)₂HSO₄⁻; m/z 293), while the neutral sulphuric acid measured by the CI-API-TOF is by far not the
192 dominant peak. This is due to the strong electron affinity of sulphuric acid. The other remarkable feature in the
193 negative ion spectra is the daytime band of peaks (unfilled circles in Figure 2C) that spreads on the mass defect
194 plot wider than night-time dimers (Figure 2A) and day-time neutral species (Figure 2D). As shown in Figure 2,
195 these peaks are still unidentified. We suggest that some of the peaks reported in Figure 2C are HOMs and ONs as
196 seen in the neutral mass spectra, but clustered with HSO₄⁻ ions. This is consistent with the fact that a lot of peaks
197 have a near zero or negative mass defect. To highlight the presence of these different species in the API-TOF
198 during the day, a reference line (violet) was added. This line represents the most oxidised HOMs/ONs detected in
199 the neutral mode (Figure 2B). These compounds are the one with the lowest mass defect. By definition, in the
200 CI-API-TOF, all the peaks appeared above the line. During the night-time, the naturally charged ions are also all
201 above the line, because in this case the ions are mainly formed by HOMs cluster with NO₃⁻ ions, that is the same
202 mechanism inside the CI-API-TOF. However, during daytime, the behaviour is totally different. The band is much
203 broader and many new peaks are situated below this line, suggesting that HOMs and ONs are clustered with
204 HSO₄⁻ ions (orange dots). In addition, formation of naturally charged ions containing sulphuric dimer or trimer as



205 a core ion might be expected and could explain the formation of some ions observed solely during the day,
206 especially the one at really low mass defect. It is worth noting that sulphuric acid – HOM clusters have been
207 demonstrated to participate in NPF (Schobesberger et al., 2013; Riccobono et al., 2014) and similarly might be
208 involved in such processes in the boreal forest. This is the first time that such clusters have been detected in the
209 ambient.

210 In addition to the mass defect plots presented in Figure 2, the chemical composition of the naturally charged
211 negative ions measured during several nights the year before (for this specific case it was recorded the 13th of
212 March 2012) is presented in Figure 3. It is important to mention that during that time the instrument was tuned to
213 detect ions at really high masses and could likely explain why such observation was not possible during the 2013
214 campaign (Figure 2). In addition to two bands of monomers and dimers observed in Figure 2, Figure 3 depicts the
215 existence of larger molecules, likely trimer and tetramer clusters (or oligomers). The first band is mainly
216 composed by HOMs with roughly 9-10 carbon atoms, the second band with HOMs having 19-20 carbons. In
217 general, the four bands show that these clusters can contain up to 40 carbon atoms. These larger molecules were
218 previously detected during pure biogenic NPF in the CLOUD chamber from the ozonolysis of α -pinene (Kirkby et
219 al., 2016). This is also the first time that such compounds are recorded in the ambient atmosphere. Further studies
220 will be designed to investigate the formation of such species and to identify their potential impact in NPF.

221 As mentioned previously, HOMNO_3^- and HOMHSO_4^- adducts were identified using an API-TOF. In Figure
222 4, the most abundant HOMs and ONs detected during the day of the 20th of April 2013 (same as Figure 3 C) are
223 presented. 10 HOMs (left panel) and 9 ONs (right panel) were chosen for comparison. The bottom side of the bars
224 referred to the HOMs/ONs clustered with NO_3^- while the top part represents the signal intensity of the same
225 compounds clustered with HSO_4^- . We found that almost all the HOMs/ONs cluster more with NO_3^- ions and on
226 average 60 % of the total signal ($\text{HOMs/ONsNO}_3^- + \text{HOMs/ONsHSO}_4^-$) of these 19 compounds are clustered
227 with the nitrate.

228 3.2 Diurnal variation of ions

229 It is important to point out that different parameters could significantly impact the abundance of the ions detected
230 in the atmosphere. For instance, the charging of the organic molecules will be strongly affected by their
231 concentration, their proton affinity and their ability of forming clusters with acids like sulphuric acid or nitric acid.
232 Indeed, a competition between the different compounds getting the charge will depend on their physical-chemical
233 properties. For example, as a strong electro-negative compound sulphuric acid produced during the day will take a
234 large fraction of the negative charges available in the atmosphere. Such process will result in a reduction of other
235 naturally charged ions, while the concentration of the corresponding neutral species remains less than the
236 concentrations of other compounds. This phenomenon has to be taken into account while interpreting the diurnal
237 variation of the ions, especially during daytime. A direct comparison of the neutral HOMs with the corresponding
238 naturally charged HOMs will help to distinguished such processes since the CI-API-TOF will measure the diurnal
239 evolution of the compounds independently of the ion availability in the ambient air.

240 While the evolution of the neutral HOMs/ONs have been already carefully described by Yan et al. (2016),
241 the diurnal evolution of the naturally charged HOMs is describe in the present study. Figure 5 shows the diurnal
242 cycle of ions measured over 7 clear-sky days during spring 2013. As expected, the diurnal trend of sulphuric acid
243 cluster-ions in Figure 5 tracks the solar radiation since H_2SO_4 , during the day, is mainly photochemically
244 produced from the OH oxidation of SO_2 . Around noon, three peaks attributed to sulphuric acid monomer, dimer
245 and trimer contribute to 20% of the total signal, which is comprised of several hundreds of species. Therefore,
246 during this time, the charge available for other compounds will be less. The sulphate signal anti-correlates with the
247 negatively charged HOM monomers and HOM dimers (i.e. clustered with NO_3^-) where they peak during the



248 night, while their concentrations in the daytime remain small as discussed previously. This is not only because
249 sulphuric acid is taking up the large fraction of the charge available but also because these HOMs are mainly
250 produced from the pure ozonolysis of α -pinene. However, it is not the case for the ONs from the reaction of RO_2
251 radicals with NO , which are, as sulphuric acid, mainly formed during the daytime. During the day, ONs either
252 cluster with NO_3^- or HSO_4^- ions, and their concentrations increase when the solar radiations rise. However, they
253 peak early morning before noon, then the concentration of sulphuric acid steeply limits the charge availability.
254 When sulphuric acid decreases because of the reduced sunlight, a second peak of the naturally charged ONs
255 clustered with NO_3^- could be observed as shown in Figure 5. The ONs clustered with HSO_4^- ions are less affected
256 by the sulphuric acid evolution since they are actually charged by HSO_4^- ions that are increasing during that time.

257 Overall, such diurnal variation of these atmospheric ions is obviously influenced by the abundance of both
258 various neutral molecules and the charge carriers, as well as the charging efficiency between them. The neutral
259 HOMs are more abundant during the night-time, increasing at around 4pm and decreasing at 4am, owing to the
260 diurnal cycle of NO_x (Yan et al., 2016). During this period, nitrate is the major charge carrier due to the inefficient
261 production of sulphuric acid, as a result, the $\text{HOM}\cdot\text{NO}_3^-$ clusters reveal an almost identical diurnal pattern with the
262 neutral HOMs. In correspondence with the decrease of neutral HOMs, the neutral ONs start to increase at around
263 4am in the morning, when the sulphuric concentration remains low and nitrate ion are still dominating, so a
264 corresponding increase of the $\text{ON}\cdot\text{NO}_3^-$ clusters are observed. These $\text{ON}\cdot\text{NO}_3^-$ clusters reach their maximum at
265 about 6am and started to decrease coincidentally with an increase of $\text{ON}\cdot\text{HSO}_4^-$ clusters. We attribute this change
266 to the shift of charge carrier from nitrate to bisulphate when the concentration of sulphuric acid is high enough to
267 take most of the ions. When the concentration of sulphuric acid become even higher, it become more competitive
268 in taking all the ions, and more importantly, in clustering with HSO_4^- . This leads to the reduction of $\text{ON}\cdot\text{HSO}_4^-$
269 clusters and the increase of $(\text{H}_2\text{SO}_4)_{0.3}\text{HSO}_4^-$ clusters. Two important details should be noted here: 1) the
270 concentration of neutral ONs also increase during the day and is usually more than one order of magnitude higher
271 than that of sulphuric acid, so the shift from $\text{ON}\cdot\text{HSO}_4^-$ to $(\text{H}_2\text{SO}_4)_{0.3}\text{HSO}_4^-$ clusters should be explained by the
272 higher charging efficiency (or clustering probability) between sulphuric acid and HSO_4^- ; 2) such higher charging
273 efficiency could be due to the appearance of the “stabilizer”, such as H_2O , NH_3 , and amines (e.g. Kirkby et al.,
274 2011, Almeida et al., 2013). The reverse change in ion composition from midday to midnight can be explained by
275 the same underlying reasons.

276 Figure 6 shows the comparison of different ion families based on the hourly average during 5 sunny days
277 within the campaign period. Panel A in figure 6 shows the positive correlation between sulphuric acid clusters and
278 organic molecules ($\text{HOM}+\text{ON}$) charged by bisulphate ion. This confirms our identification of $\text{HOM}/\text{ON}\cdot\text{HSO}_4^-$
279 compounds as both signals are connected to photochemical production of sulphuric acid during the day. Both of
280 these ion families peak during the day and are absent during the night, which is consistent with figure 5. On the
281 other hand, sulphuric acid clusters anti-correlate with HOM Dimers (figure 6, panel C). As discussed before, the
282 dimers are ions containing two oxidised monoterpene units that are more abundant during the night as the
283 termination reactions of RO_2 radicals with e.g. NO are less likely. As the dimers are not produced efficiently
284 during the day, they are primarily charged with NO_3^- . Among the ionised species, dimers correlate with HOM
285 monomers that are charged with nitrate (figure 6, panel D); therefore, their diurnal profile will follow the green
286 line in figure 5. In panel D, we can observe two groups of points separated by night (blue) and day (green and
287 yellow) as the processes that control the formation of HOM Dimers and $\text{HOM}\cdot\text{NO}_3^-$ are similar: during the day it is
288 the termination reaction of RO_2 with NO , while during the night it is the abundance of ozone and monoterpenes.
289 Finally, in panel B of figure 6, we can see that HOM and ON charged with nitrate show positive dependence
290 during the day, while there is no correlation during the night. The night scatter results from the different formation
291 pathways: oxidation of monoterpenes with NO_3 radical is responsible for ON production, while ozonolysis is



292 responsible for HOM. During the day, the correlation between ONNO_3^- and HOMNO_3^- is coincidental and is
293 driven by the shift in the charger availability from nitrate to bisulphate, as also seen in figure 5.
294

295 4 Conclusion

296 Negative ions from the Finnish Boreal forest have been studied over a period of two months (March-April 2013).
297 In order to determine the ion chemical composition, we used an API-TOF. The results have also been compared
298 with the chemical composition of the neutral compounds detected by the CI-API-TOF. As expected, we found that
299 during the day the most intense ions are composed by sulphuric acid clusters, but this correspond to only 3 ions out
300 of the several hundred that were identified. We found that all the other peaks are mainly composed by HOMs or by
301 ONs clustered with NO_3^- ions. In addition to that, we also observed clusters potentially important for new particle
302 formation composed by HOMs/ONs and HSO_4^- ions. During the night, sulphuric acid concentration is extremely
303 low, as a result, the sulphuric acid clusters disappear. Therefore, also HOMs clustered with HSO_4^- are not present
304 anymore. This lead to the fact that during the night, almost all the ions are formed by HOMs clustered with NO_3^-
305 ions, also the ONs are less abundant because of the low NO concentration during night, however we still observe
306 few ONs that arise from the NO_3^- -initated oxidation of monoterpene.

307 Comparing the chemical composition and diurnal variation of the ions with the neutral compounds measured
308 by the CI-API-TOF we found that the HOMs detected are practically identical. The night-time spectra from the
309 two instruments are very similar. However, during the day, the spectra are quite different. First, the sulphuric acid
310 clusters are the major peaks. Second, the HOMs and the ONs can be detected in two different way, either cluster
311 with NO_3^- or with HSO_4^- ions. This is the first time that bisulphate-organic clusters have been observed during
312 the day. This behaviour is confirmed during all the sunny days that has been analysed. Future studies will focus
313 more on the clustering of the HOMs with HSO_4^- ions and comparing them with the days where we observe NPF.
314 Finally, it is important to note that for the first time we observed pure organic clusters that contain up to 40 carbon
315 atoms (4 α -pinene unit).

316

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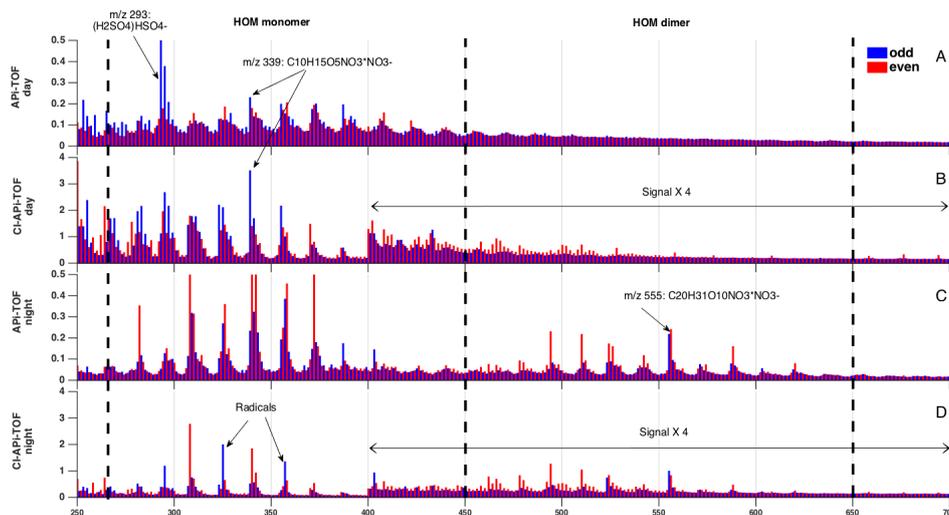
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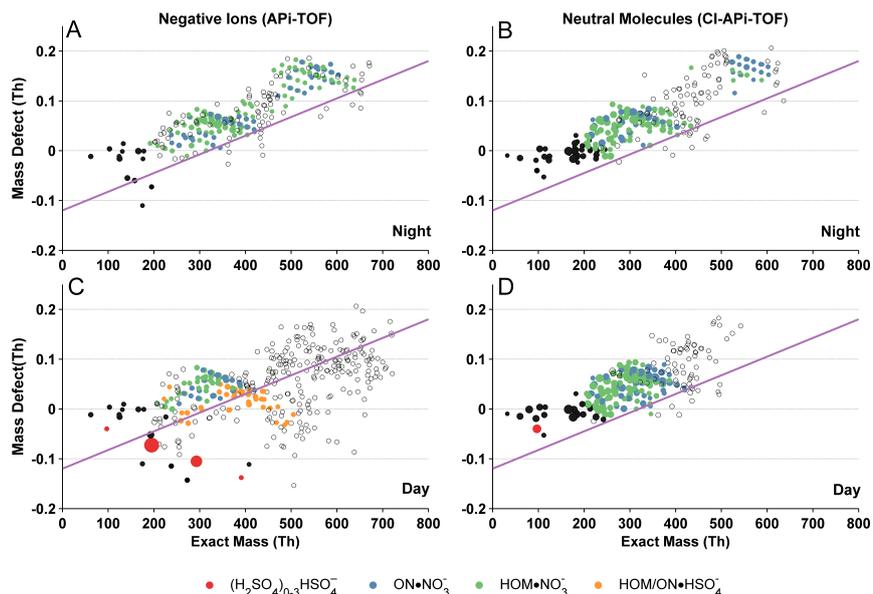
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556 **Figure 1:** Averaged mass spectra of 10 days (clear sky condition) of measurements during April and May 2013.

557 The Y-Axes represent the peak intensity in counts s^{-1} . Panel A and B show, respectively, negative and neutral
558 clusters during the day (09:00-13:00). Panel C and D show, respectively, negative and neutral clusters during the
559 night (23:00-03:00). Odd masses have been colour coded in blue and even masses in red. The two black arrows in
560 panel B and D show the area of the spectrum where the signal have been multiplied by 4 (this was done only for
561 the CI-API-TOF case).

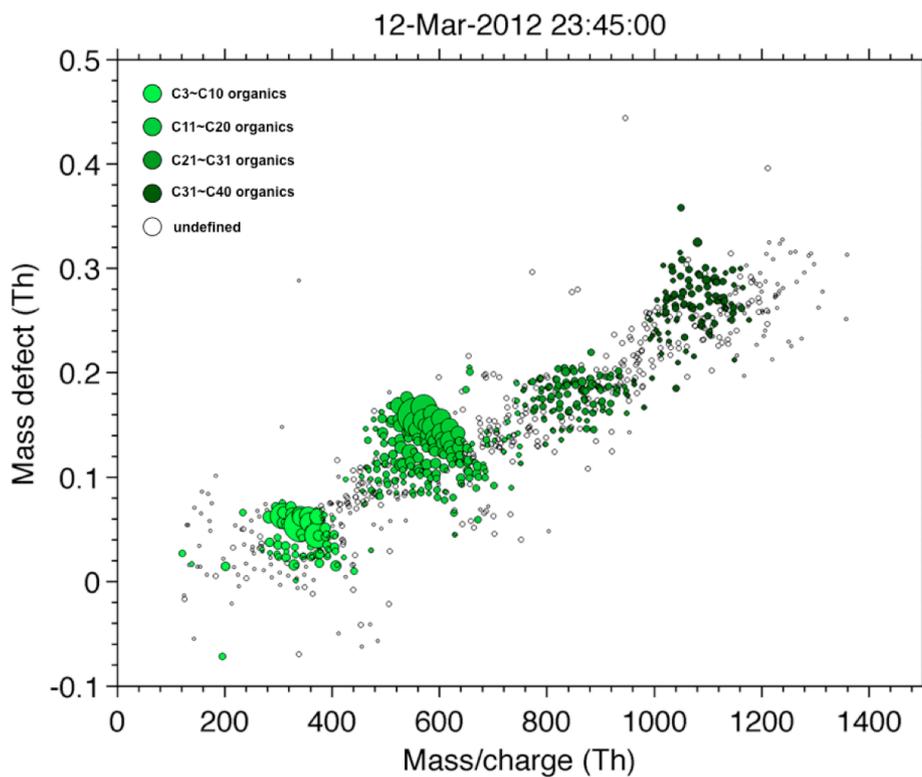


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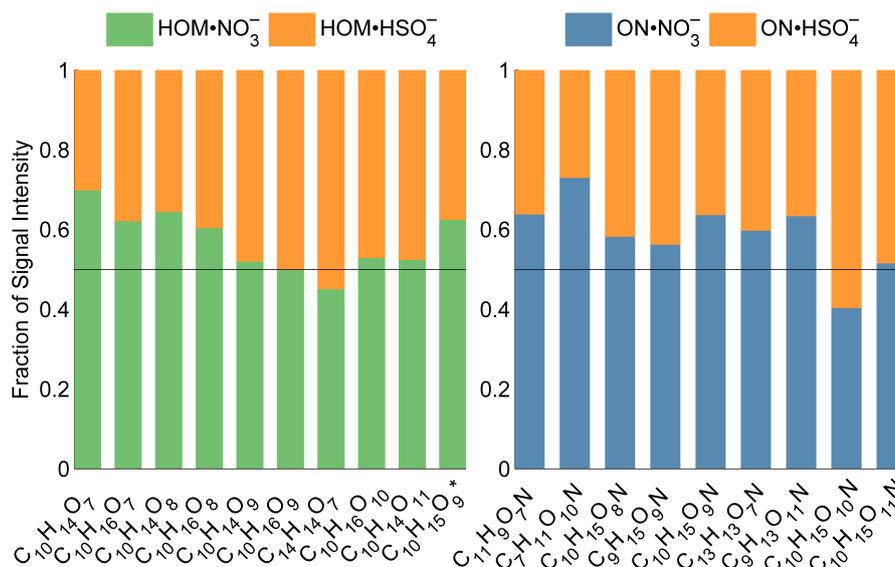
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564 **Figure 2.** Mass defect plots for the neutral clusters and negative ions during the 20th of April 2013. Panel A and B
565 show the night time chemical composition of the negative and neutral clusters, respectively. Panel C and D show
566 the chemical composition during the day of the negative and neutral clusters, respectively. The size of the circle
567 represents the area of the peaks and is proportional to the detected amount. The compounds are coloured in
568 according to their chemical composition. Unfilled dots represent the unidentified compounds, while the black
569 filled dots represent other identified peaks as for example small organic acids. The violet line underlines the most
570 oxidised HOMs detected by CI-API-TOF as clusters with NO₃⁻ ions. Most probably most of the unidentified
571 negative ions that are placed below the line are HOM clusters with HSO₄⁻ ions or H₂SO₄HSO₄⁻ acid clusters.



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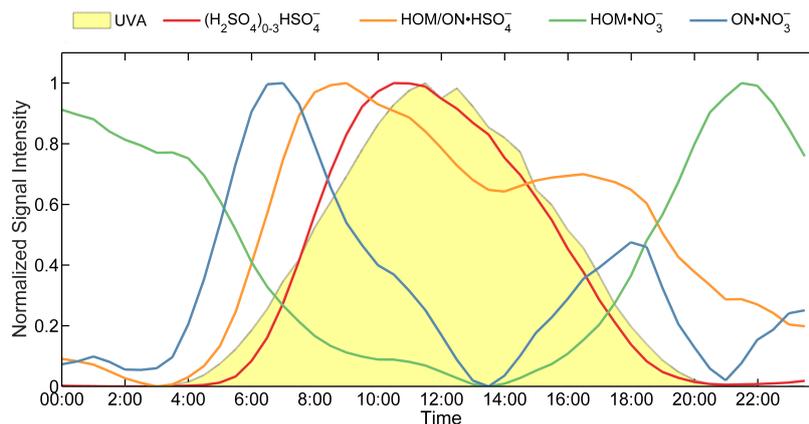
573 **Figure 3.** Mass defect plot of negative naturally charged ions observed during the night-time the 13th of March
574 2012. The four bands represent the HOMs containing approximately 10, 20, 30 and 40 carbon atoms (4 α -pinene
575 units). The majority of the HOMs have NO_3^- as core ion.
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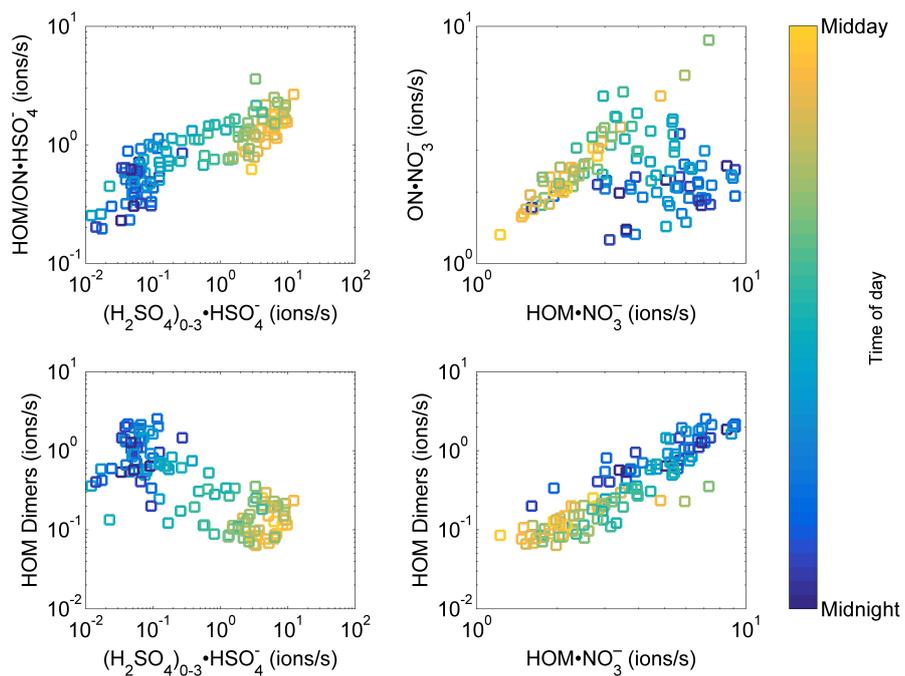
578 **Figure 4.** Naturally charged HOMs detected by the Api-TOF during daytime of April the 20th 2013. On the left
 579 panel, we report the naturally charged HOMs clustered ether with NO_3^- (green) or HSO_4^- (orange), while on the
 580 right panel, we show naturally charged ONs clustered ether with NO_3^- (blue) or HSO_4^- (orange).

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583 **Figure 5.** Averaged diurnal evolution of specific family compounds (ions) during days in clear sky conditions of
584 measurements done in April and May 2013. Colours and their corresponding families are denoted by the legends.
585 Each family is calculated by the sum of signals from the compounds of the family. The daily minimum of each
586 family is subtracted from the time trace, which is then normalized by the daily maximum. The HOM and ON
587 clustered with bisulphate ions (HOM/ON+HSO_4^-) have been grouped together since all these ions are present
588 mainly during the day.
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Figure 6. The diurnal dependency of naturally charged compounds detected by the APi-TOF. The data points are hourly averages for 5 sunny days during April-May 2013. The colour scale is normalised to show the period between midnight and midday, so that the transition between blue to green is around 6:00 and 18:00.

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