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

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Abstract. In order to investigate the role of the naturally charged highly oxidised molecules (HOMs) in the boreal forest we have performed measurements to chemically characterize the composition of negatively charged ions. Additionally, we compared this information with the chemical composition of the neutral (HOMs) detected in the ambient air during the same period. The chemical composition of the ions was retrieved using an Atmospheric Pressure interface Time-Of-Flight mass spectrometer (API-TOF) while the gas phase neutral molecules (mainly sulphuric acid and HOMs) were characterized using the same mass spectrometer coupled to a nitrate-based chemical ionization unit (CI-API-TOF). Overall, we divided the identified HOMs in two classes, HOMs containing only carbon, hydrogen and oxygen and nitrogen-containing HOMs or organonitrates (ONs). During the day, among the ions, in addition to the well-known sulphuric acid clusters, we found a large number of HOMs clustered with the two most common inorganic acids, nitrate (NO$_3^-$) or bisulphate (HSO$_4^-$), the first one being predominant. During the night, the detected ions were very similar to the neutral compounds and were mainly composed of HOMs clustered with NO$_3^-$.

For the first time, we identified several clusters contain up to 40 carbon atoms clustered with NO$_3^-$. At this regard, we think that these naturally charged clusters are formed by up to 4 oxidized $\alpha$-pinene units.

Finally, diurnal profiles of the negative ions were consistent with the neutral compounds revealing that ONs peak during the day while non-nitrate HOMs are more abundant at night-time. However, during the day, a big fraction of the negative charge is taken up by the sulphuric acid clusters causing differences between detected neutral and ion HOM/ON species. As a result, the total signal of the ionised organic compounds was much lower during day than during the night.
Ions are present everywhere in the atmosphere. They arise from, for example, galactic cosmic rays (GCR) and/or radioactive decay from the soil (radon and gamma) (Harrison and Carslaw, 2003; Hirskikko et al., 2011). The initial ions have generally a very simple structure. In the upper atmosphere, the primary ions are O\(^+\), O\(^{2+}\) and NO\(^{+}\), while in the dense air they are N\(_2\)\(^+\), O\(_2\)\(^+\), O\(^{3+}\) and O\(^{5+}\) (Smith and Spanel, 1995). Collisions of these ions with various trace gases lead to charge transfer to compounds with higher charge affinity and formation of a large variety of cluster ions. Negative charge is preferably transferred to acidic compounds like nitric acid, sulphuric acid and few other strong acid (lowest proton affinity), while positive charge is carried by basic compounds such as ammonia and amines (highest proton affinity) (Smith and Spanel, 1995). The production rate of the ions can vary depending on the altitude, location and the time of the year. In the boreal forest, such as Hyytiälä located at 61°N, early spring average production rate calculated based on external radiation and radon measurements is about 4.5 ion pairs cm\(^{-3}\) s\(^{-1}\) (Laakso et al., 2004).

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

HOMs can exist in the atmosphere both as ionized (naturally clustered with nitrate ions) and neutral species (Ehn et al., 2012; Ehn et al., 2014; Bianchi et al., 2016). Main source of HOMs to the atmosphere is likely the oxidation of terpenes, which are biogenically-emitted volatile organic compounds (BVOCs). The most abundant HOM precursor in the boreal forest is α-pinene, originating primarily from coniferous trees (Ehn et al., 2014; Jokinen et al., 2015). Ehn et al. (2014) have highlighted the formation of HOMs as first-generation oxidation products from the oxidation of monoterpens. The HOMs are produced through the formation of peroxy radicals (RO\(_2\)) and subsequent intramolecular hydrogen-shifts followed by rapid reactions with oxygen, also called “autooxidation” (Crouse et al., 2013; Rissanen et al., 2014; Jokinen et al., 2015; Berndt et al., 2016). They are expected to contain a wide range of chemical functional groups, including hydroxyl, hydroperoxides, carboxyls and epoxides. Consequently, some of the HOMs have very low vapour pressures allowing them to react and/or condense nearly irreversibly onto aerosol surfaces (Trostl et al., 2016).

In oxidation of monoterpens, such as α-pinene, characteristic HOMs contain similar amount of carbon and 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 et al., 2012; Ehn et al., 2014; Trostl et al., 2016; Kirkby et al., 2016). Beside monomer HOMs (C\(_{10}\)) dimer HOMs with an approximate composition of either C\(_{16}\)H\(_{26}\)O\(_2\) or C\(_{20}\)H\(_{30}\)O\(_4\) were also observed in both gas and particulate phases (Ehn et al., 2014; Lopez-Hilfiker et al., 2014). Rissanen et al. (2014) and Ehn et al. (2014) proposed that the bimolecular reactions of two peroxy radicals (RO\(_2\) + RO\(_2\)) is one of the likely chemical pathways leading to the formation of dimers in the gas phase.
Organonitrates (ONs) were also identified in both gas and particulate phases from the oxidation of biogenic compounds in the presence of NO\(_x\) (NO + NO\(_2\)) and NO\(_3\) radical (Ehn et al., 2014; Lee et al., 2016; Yan et al., 2016). In addition to carbon, hydrogen and oxygen, these molecules contain at least one nitrogen atom. Different reaction pathways leading to ON formation have been proposed. Due to their low vapour pressures, ONs are also expected to have a potential important role in the formation and growth of secondary organic aerosol (SOA) (Farmer et al., 2010; Kiendler-Scharr et al., 2016; Lee et al., 2016; Ng et al., 2017). In addition, Kulmala et al. (2013) have recently proposed that the organonitrates C\(_{10}\)H\(_2\)O\(_3\)NO\(_3\) is important for NPF. On the other hand, Joikinen et al. (2017) have shown the clustering and ONs are connected to each other during solar eclipse.

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

2 Materials and Methods

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

In the APi-TOF, the naturally charged ions are sampled directly from the air (Junninen et al., 2010), while in CI-API-TOF, the ions are artificially created in the ambient pressure chemical ionisation inlet that is placed in front of APi-TOF. The CI-API-TOF inlet deployed for this campaign utilized nitrate-ionisation method and was designed initially to measure neutral sulphuric acid, and later on was shown to also detect neutral HOMs and ONs (Jokinen et al., 2012; Ehn et al., 2014). Chemical ionization is achieved by exposing clean air (sheath flow) containing nitric acid (HNO\(_3\)) to alpha radiation (10 MBq\(^{241}\)Am source) or X-rays, which produces nitrate (NO\(_3^−\)) ions. NO\(_3^−\) ions in the sheath flow are directed into the sample flow by an electric field where they ionize the ambient molecules by clustering (e.g. selected organic compounds) or proton transfer (e.g. sulphuric and some dicarboxylic acids). The ionized molecules are then guided through a critical orifice to the TOF mass analyser.

NO\(_3^−\) clustering ionisation is very selective to highly functionalised organic compounds (the molecule should have at least two hydroxy or hydroperoxy groups), which makes this method ideal for measurement of HOMs (Hyttinen et al., 2015). High resolving power of TOF mass analyser makes it possible to identify the chemical composition of the detected molecules. The mass spectrometry data were processed and analysed using the MATLAB-implemented latest version (6.03) of tofTools developed by Junninen et al. (2010).

For the purposes of this study, we will refer to non-nitrogen containing organics as “HOM-monomers” (C\(_{10}\) molecules) and “HOM-dimers” (C\(_{20}\) molecules). We will use “ONs” to refer to the nitrogen-containing HOMs.
When discussing ions, we will refer as “HOM/ON-nitrate” and “HOM/ON-bisulphate” to clusters of HOMs/ONs with NO$_3^-$ and HSO$_4^-$ ions, respectively.

3 Results and Discussion

The focus of this work is to investigate the chemical composition of the naturally charged ions formed in the Boreal forest and compare it with the neutral compounds detected by the CI-API-TOF. Ehn et al. (2010) have previously reported that during the day the main peaks observed are cluster composed by sulphuric acid, whereas during night the major identified ions are HOMs clustered with NO$_3^-$. Day and night UMR (unit mass resolution) spectra, averaged throughout the campaign, were analysed and detailed high-resolution mass spectra analyses are provided for a typical clear sky day (diurnal and nocturnal spectra).

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

As previously reported by Yan et al. (2016), the mass spectra for the neutral compounds are dominated by the species with an odd mass number (ON: NO$_3^-$) during daytime while during the night-time peaks with an even mass number (HOM-NO$_3^-$) are the most abundant. From Figure 1, we can see the same pattern for naturally charged clusters, although with some differences. While for the neutral compounds there is a clear odd/even pattern during the day, the negative ions show only a small predominance of the odd masses. The main reason is that while in the ionization unit of the CI-API-TOF the HOMs and the ONs are ionized almost exclusively by the primary ion (NO$_3^-$), in the atmosphere, during the day, the HOMs and the ONs can be ionized by either NO$_3^-$ or HSO$_4^-$ ions. As ONs-nitrate will appear at odd mass and ON-bisulphate will appear at even mass, the difference between odd and even m/z is less pronounced.

During the night, the organic species are mainly charged by NO$_3^-$ ions since the photochemical production of sulphuric acid, and therefore HSO$_4^-$ ions, is inhibited. As a result, the composition of naturally charged ions are the same as the neutral molecules measured by the CI-API-TOF making the two spectra (Panel C and D) in Figure 1 more comparable. In both mass spectra, we can still observe few peaks at high intensity with an odd atomic number. These peaks are not ONs but are radicals formed from the ozonolysis of monoterpene (m/z 325 - C$_{10}$H$_{16}$O$_{10}$NO$_3^-$ and 357 - C$_{10}$H$_{16}$O$_{10}$NO$_3^-$ (Ehn et al., 2014; Yan et al., 2016)) and are highlighted in Panel D. Contrary to a one large group of ions/neutral compounds within m/z 250 to 500 observed during the day, during night two groups of molecules were distinguished. The first one, from m/z 250 to 450, are all identified as HOMs clustered with NO$_3^-$ ions containing 8-10 carbon atoms. The second group (from m/z 450 to 650) are also HOMs clustered with NO$_3^-$ ions but comprised of a larger number of carbon atoms (C$_{10}$-C$_{20}$) and are assigned to HOM-dimers. Several studies have now reported that such dimer compounds are formed from the ozonolysis of α-pinene (Ehn et al., 2014; Trosnt et al., 2016; Kirkby et al., 2016). However, in this case, there are still some peaks at odd masses (i.e. m/z 555: C$_{10}$H$_{16}$O$_{10}$NO$_3^-$) that have been attributed to night time NO$_3$ chemistry (Yan et al., 2016).
3.1 Detailed chemical composition

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

As expected and partially shown in previous studies (Ehn et al., 2012; Yan et al., 2016), the mass defect plots reveal that the chemical composition of the negative ions and the neutral compounds is different between day and night. As shown in the UMR analysis, the neutral molecules as well as the negative ions indicate that, during the day, ONs are formed at higher rate than during the night (light blue dots) while, during the night, non-nitrate HOMs have higher concentrations (green dots). Interestingly, larger concentration of organic compounds such as HOM-dimers could also be observed during the night, which is consistent with a decrease of the NO concentration and subsequent increase of self- and cross-reactions of RO2 radicals. From figure 2, we can clearly see that during the night negatively charged ions and neutral compounds have similar composition. Several studies have discussed that most of the HOMs detected during the night are formed by the reaction of monoterpene (e.g. α-pinene) with ozone (Schobesberger et al., 2013; Ehn et al., 2014; Trostl et al., 2016; Kirkby et al., 2016). Some of these studies have also shown that via the same reaction (i.e. α-pinene ozonolysis) it is possible to form clusters that contain several C18-meromers (C20, C30 and C40). In addition, Yan et al. (2016) have also observed the formation of the HOM dimers (C17-C30) during the night. Besides these oligomers, other ONs (blue dots) were also observed during night. These ONs are likely formed from the NO3-initiated oxidation of monoterpene. It is worth noting that such behaviour has been observed previously for the neutral clusters, where the ONs and HOMs are more abundant during the day and night-time, respectively (Yan et al., 2016).

The naturally charged ions reveal, however, additional information, which are mainly due to the fact that the API-TOF can also observe HOMs clustered with HSO4− ions. Since sulphuric acid (and consequently the bisulphate ion) is produced mainly during daytime from the OH-initiated oxidation of SO2, the differences in composition of ambient ions and neutral species is larger during the day. For example, at noon, all the major naturally charged ions are composed by HSO4− (m/z 97), sulphuric acid dimer (H2SO4/HSO4− ; m/z 195) and trimer ((H2SO4)2/HSO4− ; m/z 293), while the neutral sulphuric acid measured by the CI-API-TOF is by far not the dominant peak. This is due to the strong electron affinity of sulphuric acid. The other remarkable feature in the negative ion spectra is the daytime band of peaks (unfilled circles in Figure 2C) that spreads on the mass defect plot wider than night-time dimers (Figure 2A) and day-time neutral species (Figure 2D). As shown in Figure 2, these peaks are still unidentified. We suggest that some of the peaks reported in Figure 2C are HOMs and ONs as seen in the neutral mass spectra, but clustered with HSO4− ions. This is consistent with the fact that a lot of peaks have a near zero or negative mass defect. To highlight the presence of these different species in the API-TOF during the day, a reference line (violet) was added. This line represents the most oxidised HOMs/ONs detected in the neutral mode (Figure 2B). These compounds are the one with the lowest mass defect. By definition, in the CI-API-TOF, all the peaks appeared above the line. During the night-time, the naturally charged ions are also all above the line, because in this case the ions are mainly formed by HOMs cluster with NO3− ions, that is the same mechanism inside the CI-API-TOF. However, during daytime, the behaviour is totally different. The band is much broader and many new peaks are situated below this line, suggesting that HOMs and ONs are clustered with HSO4− ions (orange dots). In addition, formation of naturally charged ions containing sulphuric dimer or trimer as
a core ion might be expected and could explain the formation of some ions observed solely during the day, especially the one at really low mass defect. It is worth noting that sulphuric acid – HOM clusters have been demonstrated to participate in NPF (Schoebesberger et al., 2013; Riccobono et al., 2014) and similarly might be involved in such processes in the boreal forest. This is the first time that such clusters have been detected in the ambient.

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

As mentioned previously, HOM NO₃⁻ and HOM HSO₄⁻ adducts were identified using an API-TOF. In Figure 4, the most abundant HOMs and ONs detected during the day of the 20th of April 2013 (same as Figure 3 C) are presented. 10 HOMs (left panel) and 9 ONs (right panel) were chosen for comparison. The bottom side of the bars referred to the HOMs/ONs clustered with NO₃⁻ while the top part represents the signal intensity of the same compounds clustered with HSO₄⁻. We found that almost all the HOMs/ONs cluster more with NO₃⁻ ions and on average 60 % of the total signal (HOMs/ONs NO₃⁻ + HOMs/ONs HSO₄⁻) of these 19 compounds are clustered with the nitrate.

3.2 Diurnal variation of ions

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

While the evolution of the neutral HOMs/ONs have been already carefully described by Yan et al. (2016), the diurnal evolution of the naturally charged HOMs is describe in the present study. Figure 5 shows the diurnal cycle of ions measured over 7 clear-sky days during spring 2013. As expected, the diurnal trend of sulphuric acid cluster-ions in Figure 5 tracks the solar radiation since H₂SO₄ during the day, is mainly photochemically produced from the OH oxidation of SO₂. Around noon, three peaks attributed to sulphuric acid monomer, dimer and trimer contribute to 20% of the total signal, which is comprised of several hundreds of species. Therefore, during this time, the charge available for other compounds will be less. The sulphate signal anti-correlates with the negatively charged HOM monomers and HOM dimers (i.e. clustered with NO₃⁻) where they peak during the
night, while their concentrations in the daytime remain small as discussed previously. This is not only because sulphuric acid is taking up the large fraction of the charge available but also because these HOMs are mainly produced from the pure ozonolysis of α-pinene. However, it is not the case for the ONs from the reaction of RO₂ radicals with NO, which are, as sulphuric acid, mainly formed during the daytime. During the day, ONs either cluster with NO₃⁻ or HSO₄⁻ ions, and their concentrations increase when the solar radiations rise. However, they peak early morning before noon, then the concentration of sulphuric acid steeply limits the charge availability. When sulphuric acid decreases because of the reduced sunlight, a second peak of the naturally charged ONs clustered with NO₃⁻ could be observed as shown in Figure 5. The ONs clustered with HSO₄⁻ ions are less affected by the sulphuric acid evolution since they are actually charged by HSO₄⁻ ions that are increasing during that time.

Overall, such diurnal variation of these atmospheric ions is obviously influenced by the abundance of both various neutral molecules and the charge carriers, as well as the charging efficiency between them. The neutral HOMs are more abundant during the night-time, increasing at around 4pm and decreasing at 4am, owing to the diurnal cycle of NO₃ (Yan et al., 2016). During this period, nitrate is the major charge carrier due to the inefficient production of sulphuric acid, as a result, the HOM NO₃⁻ clusters reveal an almost identical diurnal pattern with the neutral HOMs. In correspondence with the decrease of neutral HOMs, the neutral ONs start to increase at around 4am in the morning, when the sulphuric concentration remains low and nitrate ion are still dominating, so a corresponding increase of the ON NO₃⁻ clusters are observed. These ON NO₃⁻ clusters reach their maximum at about 6am and started to decrease coincidently with an increase of ON HSO₄⁻ clusters. We attribute this change to the shift of charge carrier from nitrate to bisulphate when the concentration of sulphuric acid is high enough to take most of the ions. When the concentration of sulphuric acid become even higher, it become more competitive in taking all the ions, and more importantly, in clustering with HSO₄⁻. This leads to the reduction of ON HSO₄⁻ clusters and the increase of (H₂SO₄)ₙ,HSO₄⁻ clusters. Two important details should be noted here: 1) the concentration of neutral ONs also increase during the day and is usually more than one order of magnitude higher than that of sulphuric acid, so the shift from ON HSO₄⁻ to (H₂SO₄)ₙ,HSO₄⁻ clusters should be explained by the higher charging efficiency (or clustering probability) between sulphuric acid and HSO₄⁻ ; 2) such higher charging efficiency could be due to the appearance of the “stabilizer”, such as H₂O, NH₃, and amines (e.g. Kirkby et al., 2011, Almeida et al., 2013). The reverse change in ion composition from midday to midnight can be explained by the same underlying reasons.

Figure 6 shows the comparison of different ion families based on the hourly average during 5 sunny days within the campaign period. Panel A in figure 6 shows the positive correlation between sulphuric acid clusters and organic molecules (HOM+ON) charged by bisulphate ion. This confirms our identification of HOM/ON HSO₄⁻ compounds as both signals are connected to photochemical production of sulphuric acid during the day. Both of these ion families peak during the day and are absent during the night, which is consistent with figure 5. On the other hand, sulphuric acid clusters anti-correlate with HOM Dimers (figure 6, panel C). As discussed before, the dimers are ions containing two oxidised monoterpene units that are more abundant during the night as the termination reactions of RO₂ radicals with e.g. NO are less likely. As the dimers are not produced efficiently during the day, they are primarily charged with NO₃⁻. Among the ionised species, dimers correlate with HOM monomers that are charged with nitrate (figure 6, panel D), therefore, their diurnal profile will follow the green line in figure 5. In panel D, we can observe two groups of points separated by night (blue) and day (green and yellow) as the processes that control the formation of HOM Dimers and HOM NO₃⁻ are similar: during the day it is the termination reaction of RO₂ with NO, while during the night it is the abundance of ozone and monoterpenes.

Finally, in panel B of figure 6, we can see that HOM and ON charged with nitrate show positive dependence during the day, while there is no correlation during the night. The night scatter results from the different formation pathways: oxidation of monoterpenes with NO₃ radical is responsible for ON production, while ozonolysis is
responsible for HOM. During the day, the correlation between ON-NO$_3^-$ and HOM-NO$_3^-$ is coincidental and is
driven by the shift in the charge availability from nitrate to bisulphate, as also seen in figure 5.

4 Conclusion

Negative ions from the Finnish Boreal forest have been studied over a period of two months (March-April 2013).
In order to determine the ion chemical composition, we used an API-TOF. The results have also been compared
with the chemical composition of the neutral compounds detected by the CI-API-TOF. As expected, we found that
during the day the most intense ions are composed by sulphuric acid clusters, but this correspond to only 3 ions out
of the several hundred that were identified. We found that all the other peaks are mainly composed by HOMs or by
ONs clustered with NO$_3^-$ ions. In addition to that, we also observed clusters potentially important for new particle
formation composed by HOMs/ONs and HSO$_4^-$ ions. During the night, sulphuric acid concentration is extremely
low, as a result, the sulphuric acid clusters disappear. Therefore, also HOMs clustered with HSO$_4^-$ are not present
anymore. This lead to the fact that during the night, almost all the ions are formed by HOMs clustered with NO$_3^-$
ions, also the ONs are less abundant because of the low NO concentration during night, however we still observe
few ONs that arise from the NO$_3^-$ initiated oxidation of monoterpene.

Comparing the chemical composition and diurnal variation of the ions with the neutral compounds measured
by the CI-API-TOF we found that the HOMs detected are practically identical. The night-time spectra from the
two instruments are very similar. However, during the day, the spectra are quite different. First, the sulphuric acid
clusters are the major peaks. Second, the HOMs and the ONs can be detected in two different way, either cluster
with NO$_3^-$ or with HSO$_4^-$ ions. This is the first time that bisulphate-organic clusters have been observed during
the day. This behaviour is confirmed during all the sunny days that has been analysed. Future studies will focus
more on the clustering of the HOMs with HSO$_4^-$ ions and comparing them with the days where we observe NPF.
Finally, it is important to note that for the first time we observed pure organic clusters that contain up to 40 carbon
atoms (4 α-pinene unit).

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References


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Figure 1: Averaged mass spectra of 10 days (clear sky condition) of measurements during April and May 2013. The Y-Axes represent the peak intensity in counts s⁻¹. Panel A and B show, respectively, negative and neutral clusters during the day (09:00-13:00). Panel C and D show, respectively, negative and neutral clusters during the night (23:00-03:00). Odd masses have been colour coded in blue and even masses in red. The two black arrows in panel B and D show the area of the spectrum where the signal have been multiplied by 4 (this was done only for the CI-APi-TOF case).
Figure 2. Mass defect plots for the neutral clusters and negative ions during the 20th of April 2013. Panel A and B show the night time chemical composition of the negative and neutral clusters, respectively. Panel C and D show the chemical composition during the day of the negative and neutral clusters, respectively. The size of the circle represents the area of the peaks and is proportional to the detected amount. The compounds are coloured in according to their chemical composition. Unfilled dots represent the unidentified compounds, while the black filled dots represent other identified peaks as for example small organic acids. The violet line underlines the most oxidised HOMs detected by CI-API-TOF as clusters with NO$_3^-$ ions. Most probably most of the unidentified negative ions that are placed below the line are HOM clusters with HSO$_4^-$ ions or H$_2$SO$_4$HSO$_4^-$ acid clusters.
Figure 3. Mass defect plot of negative naturally charged ions observed during the night-time the 13th of March 2012. The four bands represent the HOMs containing approximately 10, 20, 30 and 40 carbon atoms (4 α-pinene units). The majority of the HOMs have NO$_3^-$ as core ion.
Figure 4. Naturally charged HOMs detected by the APi-TOF during daytime of April the 20th, 2013. On the left panel, we report the naturally charged HOMs clustered either with NO$_3^-$ (green) or HSO$_4^-$ (orange), while on the right panel, we show naturally charged ONs clustered either with NO$_3^-$ (blue) or HSO$_4^-$ (orange).
Figure 5. Averaged diurnal evolution of specific family compounds (ions) during days in clear sky conditions of measurements done in April and May 2013. Colours and their corresponding families are denoted by the legends. Each family is calculated by the sum of signals from the compounds of the family. The daily minimum of each family is subtracted from the time trace, which is then normalized by the daily maximum. The HOM and ON clustered with bisulphate ions (HOM/ON\(\text{HSO}_4^-\)) have been grouped together since all these ions are present mainly during the day.
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.