Anonymous Referee #1

This manuscript presents measurements of naturally charged highly oxidized molecules (HOMs) by the APi-TOF and their neutral counterparts by the CI-TOF. HOMs were recently found to play important roles in new particle formation (NPF) and their exact formation mechanisms are still poorly understood. Ions on the other hand also play a role in particle formation especially in the free and upper troposphere. It is hence important to evaluate the roles of the charged and neutral HOMs in the process of forming nuclei. Since HOMs are primarily from oxidation of organic species in the atmosphere, considering the significant amount of organic species emitted to the boreal forest and the low abundance of sulfur species in the region, it is reasonable to relate particle formation with those HOMs. In addition, recent studies also pointed out the potential dominant roles of HOMs in NPF in forested area such as Hyytiälä. The paper present interesting results and will potentially improve our understanding of NPF in forest where biogenic hydrocarbons are dominant VOCs in the air. The following issues need to be resolved before it goes to final publication.

We would like to thank the referee for taking the time to read and comment on this manuscript and for the referee's helpful and constructive comments. In green, we report our answer to the reviewer and in blue, the changes applied to the manuscript.

1. The concentrations of naturally charged highly oxidized molecules (HOMs) are much lower (several orders, depending on the charging efficiency) than their corresponding neutral counterparts. Compared to the neutral HOMs, charged HOMs might exert little effects on NPF or if indeed they play important roles, the mechanisms will be likely very different from those of the neutral parts. Figure 1 shows the measured signals in cps which do not reflect the real concentrations. Did the authors convert those signals to concentrations i.e. number concentrations in cm-3? It is difficult to calibrate the instruments to give accurate concentrations but at least estimated concentrations can be obtained provided that a few assumptions were made.

Since both reviewers have mentioned the concentration argument, we have decided to make a new figure 5 where we directly compare the concentrations of the ambient ions with the neutral compounds. As the reviewer mentioned, it is difficult to calibrate the mass spectrometer at all the masses since the transmission curve inside the time-of-flight is not constant. However, it is definitely possible to estimate the concentrations of the ions, at least the order of magnitude.
Instead of just adding an axe in figure one we made an entirely new figure (the new figure 5), where we report the concentrations of the ions for the different families.

We produced two new figures reporting the ion concentration (Figure 5a and Figure 6). We also now discuss in the text these values and compared them with the concentration of the neutral ions.

2. The daytime and nighttime formation of organonitrates (ONs) was different, resulting probably in distinct chemical composition of the ONs between the two formation mechanisms. Can the authors provide further evidences of differences between the daytime and nighttime chemical compositions of the ONs?

The reviewer is right. It is indeed true that the NOx chemistry is very different between daytime and nighttime. During the day, the chemistry is mainly related to NO while during the night the main nitrogen containing oxidant is NO_3 radical. This different chemistry has already been extensively discussed in Yan et al., ACP (2016).

Although, the study of Yan et al., describes that already quite well we decided to add some sentences/comments in this manuscript as well. Here we report just few of them.

… In Figure 1, the neutral molecules as well as the negative ions indicate that, during the day, ONs, formed by the reaction between monoterpene, ozone and NO, have higher concentration than during the night (light blue dots) while …

…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…

…These ONs are quite different from the one observed during the day because they are formed by a different reaction, where the oxidation of monoterpene is initiated by the NO3 radical…

3. According to the paper, there are at least four categories of HOMs: HOMs that contain only C, O, H or ONs that contain N in addition to C, O, H, and their corresponding NO3- or HSO4- clusters. The relationship between the naturally charged and neutral HOMs however has not been explored in details. Are there any correlations between them? i.g. the equilibrium or dynamic partitioning between them.

Actually, only two HOMs categories are discussed in this manuscript, the HOMs that contain only C, O, H or ONs that contain N in addition to C, O, H. These HOMs can easily cluster with NO3- or HSO4-. However, it is not by clustering with these deprotonated acids that the HOMs are different. We made sure that this point is now clear in the manuscript. Moreover, as mentioned in point 1, now we have added a new figure where we directly compare the concentrations of the ambient ions with the neutral species. Additionally, we have also added a figure (New figure 6) where we directly compare the ambient ions composed purely by pure sulphuric acid with the neutral sulphuric acid measured by the CI-APi-TOF.

Regarding the HOMs categories, in the abstract we state that:" Overall, we divided the identified HOMs into two classes: HOMs containing only carbon, hydrogen and oxygen and nitrogen-containing HOMs or organonitrates (ONs)."

As already mentioned it, we added two new figures (Figure 5A and Figure 6) where we directly compare ambient ions with neutral compounds.

Anonymous Referee #2

Review of Bianchi et al. "Insight into naturally-charged [HOMs]..." This paper summarizes atmospheric observations of ambient ions from a forest site in Finland. This reviewer finds it to be of potential interest. Yet, while much of the observations have been attributed by the authors to have been presented before, poor presentation of the present results make discerning the new information difficult. This paper needs a 'sharp edge': a well-defined hypothesis and perhaps some sort of quantification of the reported species.

We would like to thank the referee for taking the time to read and comment on this manuscript and for the referee's helpful and constructive comments. In green, we report our answer to the reviewer and in blue, the changes applied to the manuscript.

0. The authors may be puzzled by seemingly intentional misreadings but misnomers and poor phrasing have seriously hindered this reviewer's understanding of the authors' intent.

We actually agree with the referee and in this revised version we tried to simplify the terminology and we modified the manuscript in order to reach a wider audience. We also agreed that our terminology is not entirely correct from a chemist point of view (eg. Naturally-charged HOMs).

In the new version, we also tried homogenise this problem as well. In the current version, we adopted the referee's terminology (e.g. ambient ions instead of naturally charged clusters).

1. Title " naturally-charged [HOMs]..." This wording suggests the core of the ions are HOM molecules, minus a proton. Or possibly they have large electron affinities, low ionization energies, or act as proton acceptors. The authors use of this terminology needs definition.

Although we can detect some HOM that have been ionised by deprotonation, this is definitely not the main ionization mechanism as pointed out by the referee in their review. We have now defined the terminology in the new manuscript where by naturally-charged HOM we mean an adduct/ligand formed by an HOM with a core ion that is usually a deprotonated strong acid as NO3- and HSO4-. The title has been changed in order to avoid any confusion.

pts 2-7 in the abstract:

2. NO3- is not an inorganic acid. Furthermore, while HSO4- has a proton to donate, it is a very weak acid. These two ions are acting rather like bases in the atmosphere!

The referee is right. NO3- and HSO4- are the conjugated bases of the respective acids (HNO3 and H2SO4). We have now referred to them as deprotonated inorganic acids.

3. predominant aka most influential but here you specifically mean that nitrate has the highest abundance?

We corrected our statement using the referee's suggestion.

4. ’ions were very similar to the detected neutrals’ (the following phrase suggests the neutrals are actually ions, as does line 30.) You apparently mean that the masses of the HOM ligands on ambient NO3- ions are very similar to the masses of the HOM ligands on the NO3- produced in the CI machine? Or should we anticipate plots comparing abundancies (relative or, best case scenario, absolute)? See other loose terminology on this point (e.g. lines 172, 177.)

Here as well the referee is right with this sentence. We meant that the masses of the HOM ligands clustered to ambient NO3- ions are very similar to the masses of the HOM ligands clustered to the NO3- ions produced in the CI machine.
We changed the terminology here and in the manuscript especially in the suggested places. The whole manuscript has been corrected to avoid this confusion.

5. In the context of the preceding comment, the wording ’non-nitrate HOMs’ is problematic (l 31).

We homogenise the terminology and we also correct this particular wording.

6. Do these "several clusters..up to 40 C" comprise 4 separate 10 C molecular ligands ?

Unfortunately, this is not known and our data set doesn’t allow us to understand it any further. As the referee said, these compounds can either be formed by covalent bonds or ligands. In the new manuscript, we added a sentence to specify this point.

… However, while we know that the dimer is probably formed by a covalent bond between two α-pinene oxidized units, it is still not clear what is the bonding that formed these big clusters…

7. Line 34 suggests an important finding (or has it already been reported?) that HOMs and ONs do not cluster well with HSO4-. If the authors could provide semi-quantitative information on their relative ability to serve as molecular ligands to these two ions, that would provide a means to evaluate their (HOMs and ONs) roles in ion-induced NPF.
Exploring this last point further:
l195-197 shows that HOMS and ONs do cluster with HSO4- but presumably weaker than they do with NO3-. Begs the question: How much weaker? Also, and this goes to the choice of time periods (why is the sunlit data mostly before noon?) what is the mechanism for the evolution of the ions? Is it a quick evaporation of the HOMs/ONs (and an HNO3 ligand) once an HSO4- ion replaces the NO3- ion? Do the HOMs and ONs ligands get sequentially replaced by H2SO4 ligands?

We agree with referee that, how it is written now, Line 34 vaguely implies that HOMs and ONs do not cluster well with HSO4-. However, that was not the goal of our statement. Although this might be possible, this dataset can’t provide the required semi-quantitative information. What we know is that $(H_2SO_4)_xHSO_4^-$ clusters are (generally) stronger than HOM*HSO4- from the fact that there are more HOM than SA around.

However, currently there are no (even semi-quantitative) information on the relative efficiency of Org*NO3- vs Org*HSO4- clustering. This makes it impossible to infer about the likelihood of the different clusters - not to mention the dynamics of the clustering process, i.e. "the mechanism for the evolution of the ions". However, since the ions have a relative short lifetime, we can speculate that the main mechanism is just a formation of an adduct between the deprotonated inorganic acid with a neutral HOM/ON without any displacement. But, so far, we have no proof of that.

In the new version of the manuscript we have rephrased that in order to avoid any confusion.

8. (also pts. 1 and 4) Using the word ionize in line 111 to describe what happens to HOM when it attaches to an ion is misleading. Please delineate whether you think HOM acquires a full e- of charge (we probably agree this is unlikely) and then put in your meaning of ’ionize’?

We have rephrased that sentence specifying the mechanism that lead to the detection inside the mass spectrometers of neutral gas phase molecules, whether they are HOMs or strong acid like sulphuric acid.

The new sentence is:
… NO3− ions in the sheath flow are directed into the sample flow by an electric field where by forming an adduct (e.g. with HOM) or by proton transfer reaction (e.g. sulphuric and some dicarboxylic acids) neutral ambient molecules are charged and detected…

In addition to that, and as mentioned already, the whole manuscript has been changed accordingly.

9. Paragraphs from line 124 to 161 reveal that much of what they observe has already been reported. Can any of this qualitative comparison be made quantitative in terms of abundances? Or perhaps there is an advance in this work over the previous ones where quantitative abundances of HOMs and ONs can be estimated? Otherwise, there is a danger that nothing in this part is new...

9b. line 128/129 is confusing. Mentioned without much explanation are Unit mass resolution and high-resolution analyses: what are the and what are presented in the different figures ?

10. lines 144-147 states, rather pedantically, the fact that HSO4- hinders HOM and ON ’detection’. Strange to find it worded like that and also acknowledged so late, especially when this seems to be important for NPF. There seems to be a subtlety in the wording (146,147) that suggests ONs stick better to HSO4- than do HOMS?

There are several new findings that we report in this paper that were probably not highlighted adequately. In this manuscript, we report for the first time the different clusters formed by HOMs and sulfuric acid during the day when nucleation is more important. In addition, we also report clusters containing ONs and sulphuric acid. Moreover, for the first time, we have drawn a detailed comparison between ambient ions and neutral species.

We have now rephrased the paragraph highlighting the new findings and tried to avoid all the confusion that the referee mentioned. For example, we did not intend to say that the ONs stick better to HSO4- than the HOMS. We believe that the higher concentrations of some of the specific ions are just due to the higher concentration of the respective neutral species. The reviewer has suggested a more quantitative comparison in a few of their comments. In response, we have prepared a new figure 5 where we directly report the concentrations of the ambient ions and neutral molecules. We believe that, by adding this extra figure, and by rephrasing the paragraph where we also address comments 9b and 10, this section is now more clear. The changes are highlighted in the manuscript.

11. Figure 1 has large portions of the spectra that appear to be uninteresting. Could the information be better presented by focusing on certain sections of the mass spectra, say only 250-450 for this figure? Then a separate figure for the higher masses with a times 4 vertical axis for all four data sets... This reviewer is also interested in what ions are present below 250 amu. Can these be presented in an SI? The diurnal evolution of the bare NO3- ions (or are they clustered to HNO3/H2O) would be interesting to see. In this vein, what fraction of ions have at their core, NO3- versus the total or vs. HSO4-? That information will provide for more points of discussion.

Although we understand why the reviewer would like us to divide the figure into two, we still prefer to have the HOMs region of the mass spectra all together. However, we have improved the figure, which now focuses on the region that the reviewer asked (250-650 m/z).

Regarding the ions below 250 amu, instead of adding additional SI material, we refer to the previous study made by Ehn et al., 2010. Figure 1 (taken from the mentioned study) shows the negative ion mass spectra for a typical daytime spectrum and a typical nighttime spectrum. It is possible to see from the figure that all the interesting ions below 250 amu have already been explained in detail in the previous work.

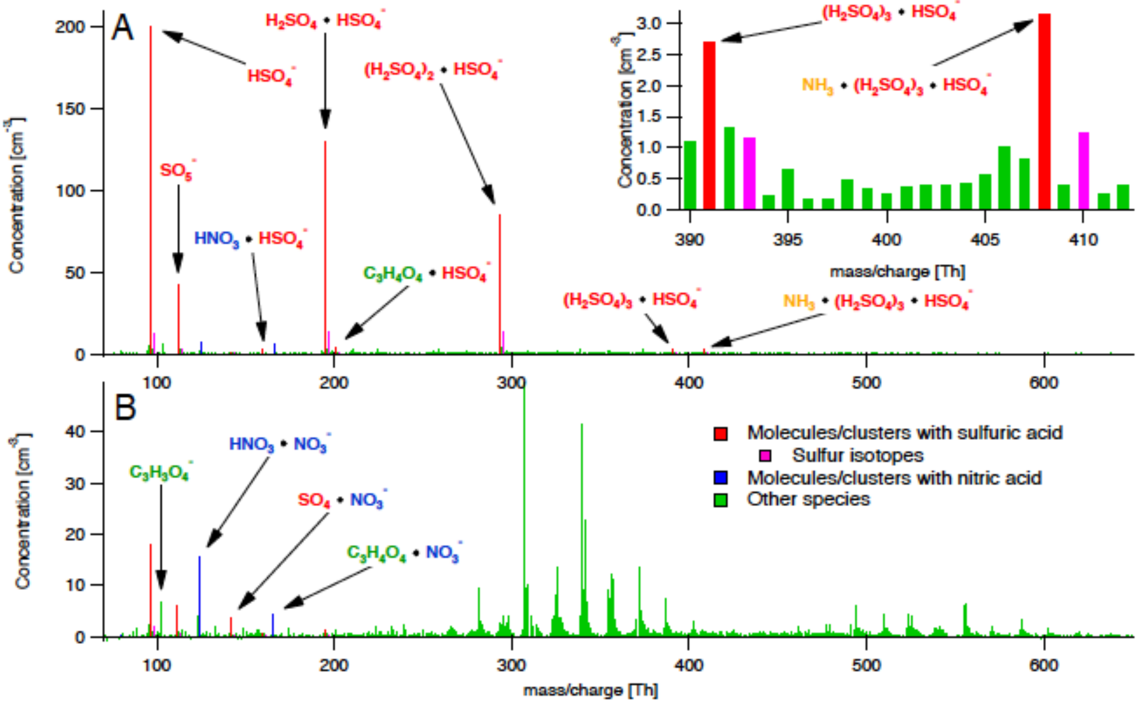

Figure 1. Negative ion mass spectra during the measurements in Hyytiälä, averaged over 3 h. (A) shows a typical daytime spectrum and (B) a typical nighttime spectrum. The ions are colored based on the identified composition. Figure taken from Ehn et al., 2010.

Figure 1 has been modified and in addition to that we have added the diurnal evolution of the bare NO3- ions in figure 5A. As already mentioned, the new figure 5A is now very useful to compare the different quantities.

12. One side of Figure 2 is labeled ’neutral molecule’ does this mean that the ionization process has been identified (proton-transfer or the core ion and ligand, etc.) such that the parent mass of the neutral species can be ascertained and then plotted?

12b. To the untrained eye, these plots are massively defective in communicating quantitative information. It would help to have a legend showing circle size vs. ion intensity. It seems that most of the points are the same size, so only limited hope there. Would be extremely helpful for the uninitiated to have one or two of the most intense ions identified and their composition explained in detail, perhaps with a blowup of a select 'area' of data. Also, please identify the bare nitrate ions, which are apparently very low. The data in Fig. 4 is stated to be from Fig. 3c but this is probably Fig. 2C. These ions could be identified in some way (scoring/arrows?) in Fig. 2C. It is difficult

to follow the discussion of the violet lines in these figures (lines 196-201). Finally, a succint description and definition of 'mass defect' would be appreciated.

By neutral molecules, we refer to those compounds that were not charged prior to entering the ionisation region of our instrument (CI-APi-TOF). Therefore, it is true that what we show here is the adduct formed by the neutral molecule and the primary ion of our CIMS instrument (NO3-). We undoubtedly know the chemical compositions of the detected molecules, but we chose to still plot them in this way as it makes it easier to compare them with the ambient ions, where the same molecule goes through a similar mechanism but on a totally different time scale. To make this clear, our definition of neutral molecules has been elaborated in the text and in the caption.

A mass defect plot is a revealing way to present and compare mass spectra. In those plots, the abscissa represents the measured m/z of the compounds and the ordinate their mass defect, which is the difference between the accurate mass and the nominal mass (e.g., the exact mass of oxygen ^{16}O is 15.9949 Th and its mass defect is thus − 0.0051 Th). In the new version, as suggested by the reviewer, the description of the plot has been improved. We also mention the fact that these plots are very powerful but are mainly useful for qualitative comparisons of mass spectra that include several hundreds of compounds. It is easier to see the difference in signal in Figure 1 or in the new figure 5a, where, following the referee's suggestion (points 15&16), we replotted the figure showing the neutral compounds as well. In addition, we don't use any normalisation anymore, but plot the concentration directly on a log scale so that all the time evolutions are visible.
We have also corrected the typo that referee mentioned (it is figure 2C and not figure 3C, as previously wrongly reported).

13. Fig. 4 needs a relative intensity indicator. Perhaps replacing the 50 % black line with white line and then use a black line as a 'bar' indicator for each ion, all normalized to the most intense ion signal. Now the horizontal axis is identified by the ligand molecule. But again, they are not to be considered charged, either naturally or un-naturally, so as to be detected as HOM- or HOM+ from an ion that is stripped of ligands. This comment harkens all the way back to pts 1, 4, 8, etc. Do you want to identify the descriptor 'naturally-charged' to mean those ligands detected by API-TOF and the 'neutrals' to mean those detected by the un-natural NO3- ions produced in the CI machine? Perhaps it would be better to switch terminology: use ambient ions for naturally-charged ions.

Regarding the suggested change for Figure 4 we don't think it is a good idea to add this extra line. Our scope it is just to compare how the different HOMs are clustering with the two different conjugated bases and not to show how intensive it is the signal of each HOMs. We think that keeping the figure simple will help the reader.

As previously mentioned, we agree with the reviewer regarding the terminology. As already mentioned we now have explained and simplified our terminology. The changes have been made consistently throughout the manuscript.

14. Lines 221-227. Information on the ability to cluster to HSO4- vs. NO3- should be discussed here by presenting also the fraction: NO3- to the sum of NO3- and HSO4- core ion signals.

We did not originally add that discussion because we thought it was too speculative. However, thanks to the reviewer's suggestion, we have now added a few lines about the core ion signal.
We detected a NO_3^- signal of 0.065 cps (counts per second) and a HSO_4^- signal of 0.034 cps. This means that NO_3^- has a concentration that is almost factor of two higher than the bisulphate ion. This could explain why we see more clusters with NO_3^- than with HSO_4^-. However, if we consider all the pure nitric acid clusters (NO_3^- + $HNO_3NO_3^-$) the signal is around (0.065+0.192) = 0.257 cps, while for all the pure sulphuric acid clusters (HSO_4^- + $H_2SO_4HSO_4^-$ + $(H2SO_4)_2HSO_4^-$) the signal is around (0.035+6.7+3.4) = 10.135 cps. This means that sulphuric acid clusters have a concentration that is 40 times higher than that of the nitric acid clusters.

As requested by the reviewer this discussion has been added at the suggested place.

…However, we should mention that we detected a NO_3^- signal of 0.065 cps (counts per second) and a HSO_4^- signal of 0.034 cps. This means that NO_3^- has a concentration that is almost factor of two higher than the bisulphate ion. This could explain why we see more clusters with NO_3^- than with HSO_4^-. However, if we consider all the pure nitric acid clusters (NO_3^- + $HNO_3NO_3^-$) the signal is around (0.065+0.192) = 0.257 cps, while for all the pure sulphuric acid clusters (HSO_4^- + $H_2SO_4HSO_4^-$ + $(H_2SO_4)_2HSO_4^-$) the signal is around (0.035+6.7+3.4) = 10.135 cps. This means that sulphuric acid clusters have a concentration that is 40 times higher than that of the nitric acid clusters, showing once more that the sulphuric acid ions are the dominant peaks and that they cluster together very effectively…

15. Fig. 5: Please provide a reasoning for subtracting the daily minimums in Figure 5. This seem to over-exaggerate tendencies in the measurements. COuld you provide an alternate plot, perhaps in a supplement, of log(signal/TotalSignal) vs. time, that is each ion signal family normalized by the same total ion signal? This plot has the potential to be more informative in an overall sense. The ratio of nitrate to bisulfate core ion signals (see pt. 14) would be a nice plot to see here also.
16. Presumably you have H2SO4 concentrations from CI. Please provide diurnal plot. Something to ponder: The point of CI is to provide a definite ion-molecule reaction (IMR) time so that neutral abundancies can be ascertained. If relative intensities of ions are not much different in API-TOF mass spectra and the CI-mass spectra, then it is reasonable to postulate that the HOMs and ONs in a particular family have the same ion-molecule rate coefficient (one could furthermore speculate that it is near the collisional rate!) Looking at 2a and 2b, stipulating that this reader understands these plots, it seems that the both sets of ONs (250-300 and 500-600) have about the same signal intensities whether allowed a long time to cluster with NO3- (ambient) or just a fraction of a second (CI). Thus the heavier ions with larger ONs do not seem to grow in time more than do the lighter ON ions. But the HOMS behave a little differently, where the higher mass set is more intense in the ambient ion spectra than in the short IMR. Is this an indication of sequential addition to ions of HOM monomer units and something different for ONs?

We combined point 15 and point 16 because they are strictly related.

Regarding the old figure 5, we agree with the reviewer that it over-exaggerates the tendencies in our measurements. Instead of providing a reason of our previous figure we decide to follow completely the reviewer suggestions and we therefore provided a new figure where we show the concentrations of the ions family. In the new figure, we also added the nitrate signal so that make it easier to compare the sulphate ions with the nitrate one. Additionally, we have also added a plot which includes the respective family in the neutral mode, that include sulphuric acid as well as requested.

As already discussed in a previous reviewer comment, we agree that the mass defect plot is not the best way to compare quantities. Figure 5 now shows concentrations instead of normalized signals. Comparing the two plots in figure 5, the difference in signals between the different modalities is clearly visible. Figure 2 has been kept as is as we still think that the mass defect plot is quite useful for a qualitative comparison.

These information are now presented in the new figure 5 (Panel A & B) where we report the variation of the neutral species during the day. As requested by the reviewer, we don’t normalize the signal anymore and only report the concentration on a log scale. Obviously, the variation is less pronounced but it is still very visible. In addition, we have also added an extra figure where we compare the ambient ions purely formed by sulfuric acid and their clusters with the sulfuric acid concentration.

The role of Highly Oxygenated Molecules (HOMs) and ambient ions characterized in the boreal forest.

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Abstract. In order to investigate the role of the ambient ions in the boreal forest we have performed measurements to chemically characterize the composition of negatively charged clusters containing highly oxygenated molecules (HOMs). Additionally, we compared this information with the chemical composition of the neutral gas phase molecules 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 pure sulphuric acid clusters, we found a large number of HOMs clustered with the two most common deprotonated inorganic acids, nitrate (NO_3^-) or bisulphate (HSO_4^-), with the first one being more abundant. During the night, the distribution of ions, mainly composed by HOM clustered with NO_3^-, was very similar to the neutral compounds that are detected in the CI-APi-TOF as adducts with the primary ion (NO_3^-).

For the first time, we identified several clusters containing up to 40 carbon atoms clustered with NO_3^-. At this regard, we think that these ~~naturally charged clusters~~ ions are formed by up to 4 oxidized α-pinene units. However, while we know that the dimer is probably formed by a covalent bond between two α-pinene oxidised units, it is still not clear what is the bonding that formed these big clusters.

Finally, diurnal profiles of the negative ions were consistent with the neutral compounds revealing that ONs peak during the day while HOMs are more abundant at night-time. However, during the day, a ~~big~~ fraction of the negative charge is taken up by the pure sulphuric acid clusters causing differences between ambient ions and neutral compounds (i.e. less available charge for HOM and ON). ~~As a result, the total signal of the ionised organic compounds was much lower during day than during the night.~~

1 Introduction

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; Hirsikko 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_2^- and O^- (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 61N, 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 ambient 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; Hirsikko 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; Duplissy et al., 2016) as well as sulphuric acid – ammonia 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 Oxygenated 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 part of an ion (ligand with a core ion) or neutral species in the gas phase (Ehn et al., 2012; Ehn et al., 2014; Bianchi et al., 2016). Main source of HOM 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 monoterpenes. 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 "autoxidation" (Crounse 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, carbonyls and epoxides. Consequently, some of the HOMs have very low vapour pressures allowing them to react and/or condense nearly irreversibly onto aerosol surfaces (Tröstl et al., 2016).

In oxidation of monoterpenes, 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 $C_{19}H_{28}O_x$ or $C_{20}H_{30}O_x$ 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 organonitrate $C_{10}H_{15}O_5NO_3$ is important for NPF. On the other hand Jokinen 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 in the ambient ions, a careful comparison between those 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~~ ambient 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~~ ambient ions are sampled directly from the air (Junninen et al., 2010), while in the 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).~~ NO_3^- ions in the sheath flow are directed into the sample flow by an electric field where by forming an adduct (e.g. with HOM) or by proton transfer reaction (e.g. sulphuric and some dicarboxylic acids) neutral ambient molecules are charged and detected. The ionized molecules/adducts 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 ambient ions that contain HOM 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 formed by HOMs clustered with NO_3^-. However, no information was retrieved regarding the chemical composition of the ambient ions containing HOM and ON present during the day. Day and night ambient ions spectra, averaged throughout the campaign, were analysed and detailed chemical composition analyses are provided for a typical clear sky day (diurnal and nocturnal spectra). Finally, we compared the negative ions with the neutral compounds detected by the CI-APi-TOF.

Figure 1 presents the average mass spectra with a mass resolution of one amu, focusing on the HOM region (mass-to-charge ratio, *m/z,* between 250 and 650), the least studied so far, 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 simple 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 ($HOM{\cdot}NO_3^-$ and/or $ON{\cdot}HSO_4^-$). While a deprotonated molecule/cluster containing zero or two (even) nitrogen will have an odd mass ($ON{\cdot}NO_3^-$ and/or $HOM{\cdot}HSO_4^-$). The rule is reversed for radical species that can be detected by CI-APi-TOF. It is important to note that the raw signal (counts per second) of the ambient ions is about an order of magnitude lower than the one measured for the neutral compounds. This, after considering the instrument calibration, reflects in several orders of magnitude difference in concentrations (Figure 5A and 5B). However, although present in low concentrations, ambient ions can have a direct impact on atmospheric processes, such as new particle formation (Kirkby et al., 2011; Kirkby et al., 2016).

As previously reported by Yan et al. (2016), during daytime, the mass spectra for the neutral compounds are dominated by the species with an odd mass number ($ON{\cdot}NO_3^-$), while during the night-time peaks with an even mass number ($HOM{\cdot}NO_3^-$) are the most abundant. From Figure 1, we can see a similar pattern for the ambient ions, 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 form almost exclusively an adduct with the primary ion (NO_3^-), in the atmosphere, during the day, the HOMs and the ONs are forming clusters with 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. This was the first daily detection of this type of ion clusters in the ambient, especially the adducts formed by the organonitrates.

During the night, these organic species are mainly forming a cluster with the NO_3^- ions since the photochemical production of sulphuric acid, and therefore HSO_4^- ions, is inhibited. As a result, the composition of ambient ions is very similar to the neutral molecules once they are ionized by the CI-APi-TOF making the final two spectra (Panel C and D) in Figure 1 comparable. However, there are still some differences; in both mass spectra, in the monomer region, 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 monoterpenes (*m/z* 325 - $C_{10}H_{15}O_8{\cdot}NO_3^-$ and 357 - $C_{10}H_{15}O_{10}{\cdot}NO_3^-$ (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 (HOMs monomer). 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_{16}-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; Trostl et al., 2016; Kirkby et al., 2016). However, in this case, there are still some peaks at odd masses (i.e. *m/z* 555: $C_{10}H_{31}O_{10}NO_3$) 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. A revealing way to present and compare qualitatively mass spectra is the mass defect plot (Schobesberger et al., 2013; Bianchi et al., 2014). In those plots, the abscissa represents the measured m/z of the compounds and the ordinate their mass defect, which is the difference between the exact mass and the nominal mass (e.g., the exact mass of oxygen ^{16}O is 15.9949 Th and its mass defect is thus − 0.0051 Th). In these plots, the symbol size is proportional to the peak intensity. However, these peaks can have an intensity that differ by orders of magnitude and we use logarithmic scale to present the concentration. As a result, it is difficult to see the differences in quantitates looking at the size of the dots. The difference in intensities is more clear in Figure 5.

In Figure 2, we show mass defect plots of the negative ambient ions and gas phase molecules (in the plot the neutral molecules are attached to the ligand that in this case is NO_3^-) during the night (23:00 – 03:00; top panels) and during the day (09:00 – 13:00; bottom panels) on April 20th 2013. 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 chemical composition of the negative ions and the neutral compounds is different between day and night. In Figure 1, the neutral molecules as well as the negative ions indicate that, during the day, ONs, formed by the reaction between monoterpene, ozone and NO, have higher concentration than during the night (light blue dots) while, the HOMs (mainly formed by α-pinene ozonolysis) peak during night (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 RO_2 radicals. From figure 2, we can clearly see that during the night ambient ions and neutral compounds (after being ionized in the ionization unit) 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; Tröstl 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 C_{10}-monomers (C_{20}, C_{30} and C_{40}). In addition, Yan et al. (2016) have also observed the formation of the HOM dimers (C_{19}-C_{20}) during the night. Besides these oligomers, other ONs (blue dots) were also observed during night. These ONs are quite different from the one observed during the day because they are formed by a different reaction, where the oxidation of monoterpene is initiated by the NO_3 radical, highlighting once more the different NO_x chemistry during day and night. It is worth noting that such behaviour has been observed previously for the neutral ~~clusters~~ molecules, where the ONs and HOMs are more abundant during the day and night-time, respectively (Yan et al., 2016).

The ambient ions reveal, however, additional information, which are mainly due to the fact that the APi-TOF can also observe HOMs clustered with HSO_4^- ions. Since sulphuric acid (and consequently the bisulphate ion) is produced mainly during daytime from the OH-initiated oxidation of SO_2, the differences in composition of ambient ions and neutral species is larger during the day. For example, at noon, all the major ambient ions are composed by HSO_4^- (*m/z* 97), sulphuric acid dimer ($H_2SO_4HSO_4^-$; *m/z* 195) and trimer ($(H_2SO_4)_2HSO_4^-$; *m/z* 293), while the neutral sulphuric acid measured by the CI-APi-TOF is by far not the dominant peak. See also Figure 5. 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 HSO_4^- 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 adducts with the lowest mass defect, therefore the most oxidised HOMs or ONs clustered with NO_3^- (Figure 2B). By definition, in the CI-APi-TOF, all the peaks appeared above the line because of the chemical ionisation mechanism that is used in this instrument. During the night-time, the ambient ions are also all above the line, because in this case the ions are mainly formed by HOMs or ONs cluster with NO_3^- 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 HSO_4^- ions (orange dots). In addition, formation of ambient 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 (Schobesberger 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 during the day.

In addition to the mass defect plots presented in Figure 2, the chemical composition of the ambient 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 ambient 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, $HOM{\cdot}NO_3^-$ and $HOM{\cdot}HSO_4^-$ 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 2 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 NO_3^- while the top part represents the signal intensity of the same compounds clustered with HSO_4^-. We found that almost all the HOMs/ONs cluster more with NO_3^- ions and on average 60 % of the total signal ($HOMs/ONs{\cdot}NO_3^-$ + $HOMs/ONs{\cdot}HSO_4^-$) of these 19 compounds are clustered with the nitrate. However, we should mention that we detected a NO_3^- signal of 0.065 cps (counts per second) and a HSO_4^- signal of 0.034 cps. This means that NO_3^- has a concentration that is almost factor of two higher than the bisulphate ion. This could explain why we see more clusters with NO_3^- than with HSO_4^-. However, if we consider all the pure nitric acid clusters (NO_3^- + $HNO_3NO_3^-$) the signal is around (0.065+0.192) = 0.257 cps, while for all the pure sulphuric acid clusters (HSO_4^- + $H_2SO_4HSO_4^-$ + $(H_2SO_4)_2HSO_4^-$) the signal is around (0.035+6.7+3.4) = 10.135 cps. This means that sulphuric acid clusters have a concentration that is 40 times higher than that of the nitric acid clusters, showing once more that the sulphuric acid ions are the dominant peaks and that they cluster together very effectively.

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 ambient 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 ambient ions containing HOMs is describe in the present study. Figure 5 shows the diurnal cycle of ions measured over 28 days, most of them in sunny conditions, during spring 2013. In addition to that, to facilitate the comparison, we added the time evolution of the neutral compounds in figure 5B. As expected, the diurnal evolution of sulphuric acid (neutral) and the pure sulfuric cluster-ions peak in the morning, since H_2SO_4, during the day, is mainly photochemically produced from the OH oxidation of SO_2. Around nine, three peaks attributed to sulphuric acid monomer (HSO_4^-), dimer ($H_2SO_4HSO_4^-$) and trimer (H_2SO_4 $H_2SO_4HSO_4^-$) contribute to 20% of the total ion signal, which is comprised of several hundreds of species. Therefore, during this time, the charge available for other compounds will be less. In figure 6 we report a comparison of the sum of these three ion clusters with the measured neutral sulfuric acid concentration. Obviously, as soon sulphuric acid is produced, also these ion clusters are formed, having their maximum around Midday. Although, from Panel B is clear that sulphuric acid is far from being the most abundant compounds, in the ambient ions, these are, beside being only three peaks, the second most intense family. Note that in figure 5A and Figure 6 the signal has not been corrected by the transmission inside the APi-TOF that is usually around 0.5-2% depending on the mass range (Junninen et al., 2010).

From figure 5A and figure 7 is also possible to see that the signal of these sulfuric acid clusters anti-correlates with the negatively charged HOM (CHO) monomers and HOM (CHON) dimers (i.e. clustered with NO_3^-) 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. This information is confirmed by the panel B where it is possible to see that the respective neutrals have a very similar behave. However, this is not the case for the ONs (CHON), that are formed by the reaction of RO_2 radicals with NO, which are, as sulphuric acid, mainly formed during the daytime. During the day, in the ambient, ONs either cluster with NO_3^- or HSO_4^- ions, and their concentrations increase when the solar radiations rise. However, they peak early morning before that 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 NO_3^- could be observed as shown in Figure 5.~~ The ONs clustered with HSO_4^- ions are less affected by the sulphuric acid evolution since they are actually charged by HSO_4^- 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 NO_x (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 $HOM{\cdot}NO_3^-$ 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 $ON{\cdot}NO_3^-$ clusters are observed. These $ON{\cdot}NO_3^-$ clusters reach their maximum at about 6am and started to decrease coincidentally with an increase of $ON{\cdot}HSO_4^-$ 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 HSO_4^-. This leads to the reduction of $ON{\cdot}HSO_4^-$ clusters and the increase of $(H_2SO_4)_{0\text{-}3}HSO_4^-$ 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 $ON{\cdot}HSO_4^-$ to $(H_2SO_4)_{0\text{-}3}HSO_4^-$ clusters should be explained by the higher charging efficiency (or clustering probability) between sulphuric acid and HSO_4^- ; 2) such higher charging efficiency could be due to the appearance of the “stabilizer”, such as H_2O, NH_3, 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 7 shows the comparison of different ion families based on the hourly average during 5 sunny days within the campaign period. Panel A in figure 7 shows the positive correlation between sulphuric acid clusters and organic molecules (HOM+ON) charged by bisulphate ion. This confirms our identification of $HOM/ON{\cdot}HSO_4^-$ 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 5A. On the other hand, sulphuric acid clusters anti-correlate with HOM Dimers (figure 7, 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 RO_2 radicals with e.g. NO are less likely. As the dimers are not produced efficiently during the day, they are primarily charged with NO_3^-. Among the ionised species, dimers correlate with HOM monomers that are charged with nitrate (figure 7, panel D); therefore, their diurnal profile will follow the green line in figure 5A. 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 $HOM{\cdot}NO_3^-$ are similar: during the day it is the termination reaction of RO_2 with NO, while during the night it is the abundance of ozone and monoterpenes. Finally, in panel B of figure 7, 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 NO_3 radical is responsible for ON production, while ozonolysis is responsible for HOM. During the day, the correlation between $ON{\cdot}NO_3^-$ and $HOM{\cdot}NO_3^-$ is coincidental and is driven by the shift in the charger availability from nitrate to bisulphate, as also seen in figure 5A.

4 Conclusion

Negative ambient 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 the concentration of HOMs clustered with HSO_4^- is very low ~~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-initated 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 $HSO4^-$ 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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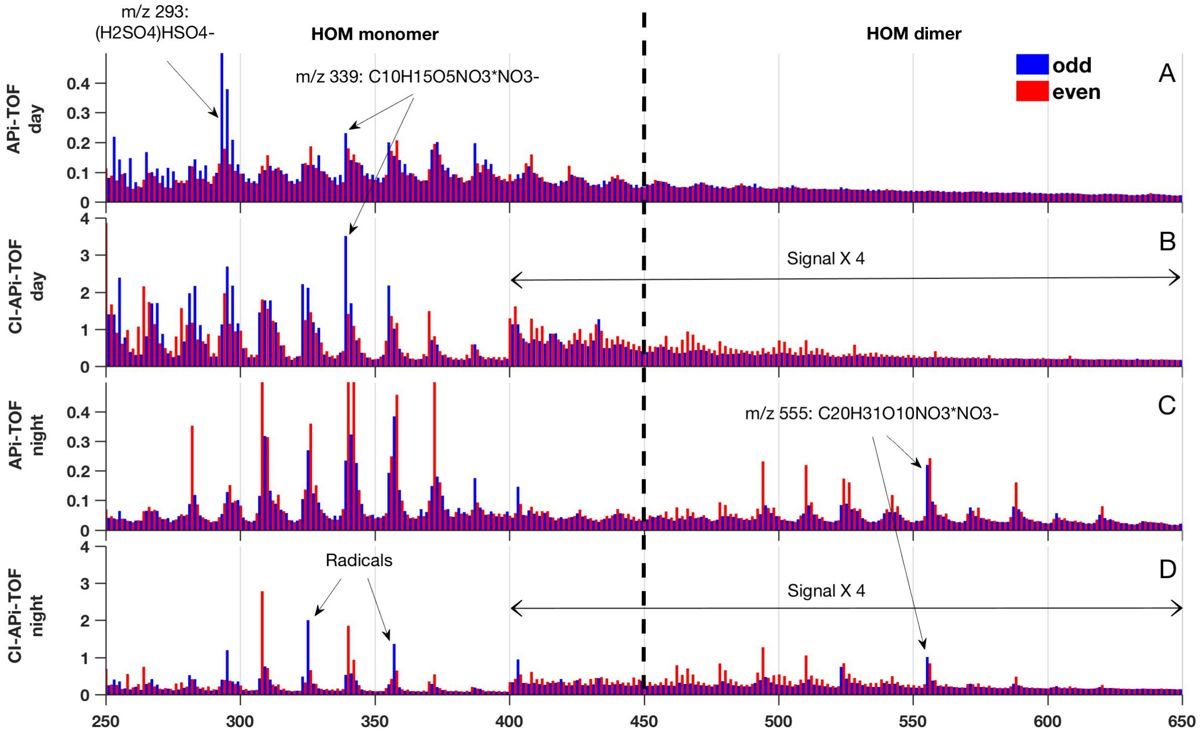

Figure 1: Averaged mass spectra of 10 days (clear sky condition) of measurements during April and May 2013. The Y-Axes represent the peak intensity in counts s^{-1}. Note that the intensities of the measured ions (APi-TOF) is an order of magnitude lower than the one detected after being ionized in the CI unit. Panel A and B show, respectively, negative ions (APi-TOF) and neutral clusters (CI-APi-TOF) 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 (done only for the CI-APi-TOF).

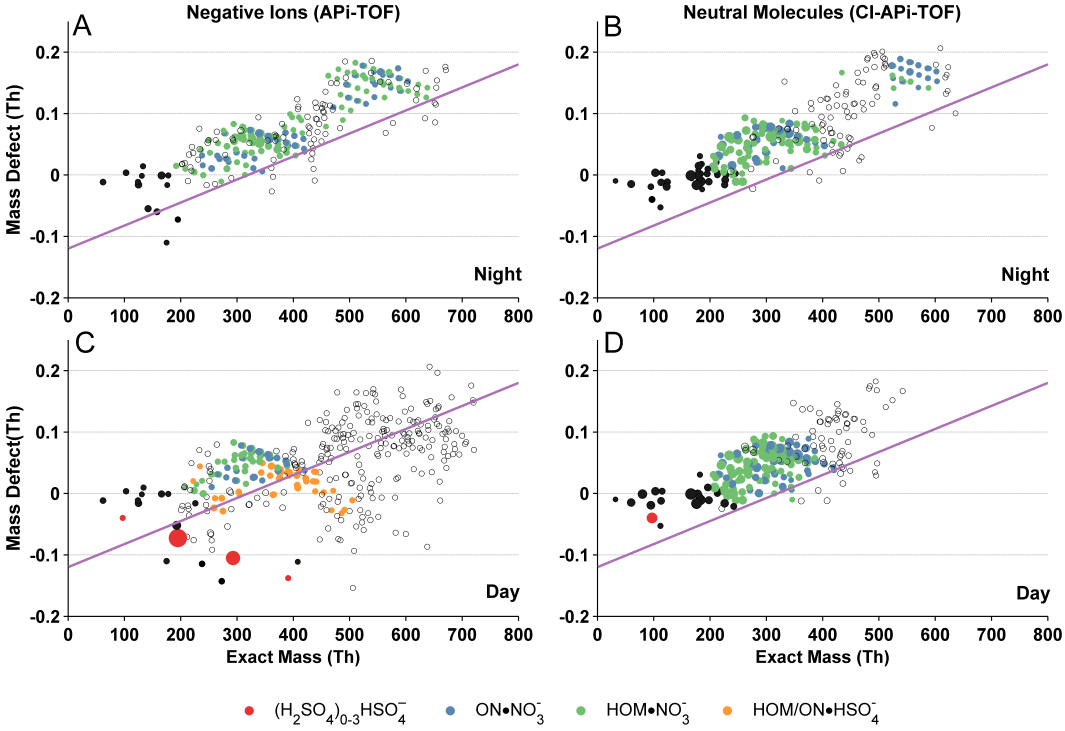

Figure 2. Mass defect plots for the neutral clusters and negative ions during the 20th of April 2013. Panel A and B show the night time chemical composition of the negative and neutral clusters, respectively. Panel C and D show the chemical composition during the day of the negative and neutral clusters, respectively. The size of the circle represents the area of the peaks and is proportional to the detected amount. All the four plots show the clusters/ligands as seen by the detector, therefore including the ligand (NO_3^-) in case of the neutral molecules. 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 $H_2SO_4HSO_4^-$ acid clusters.

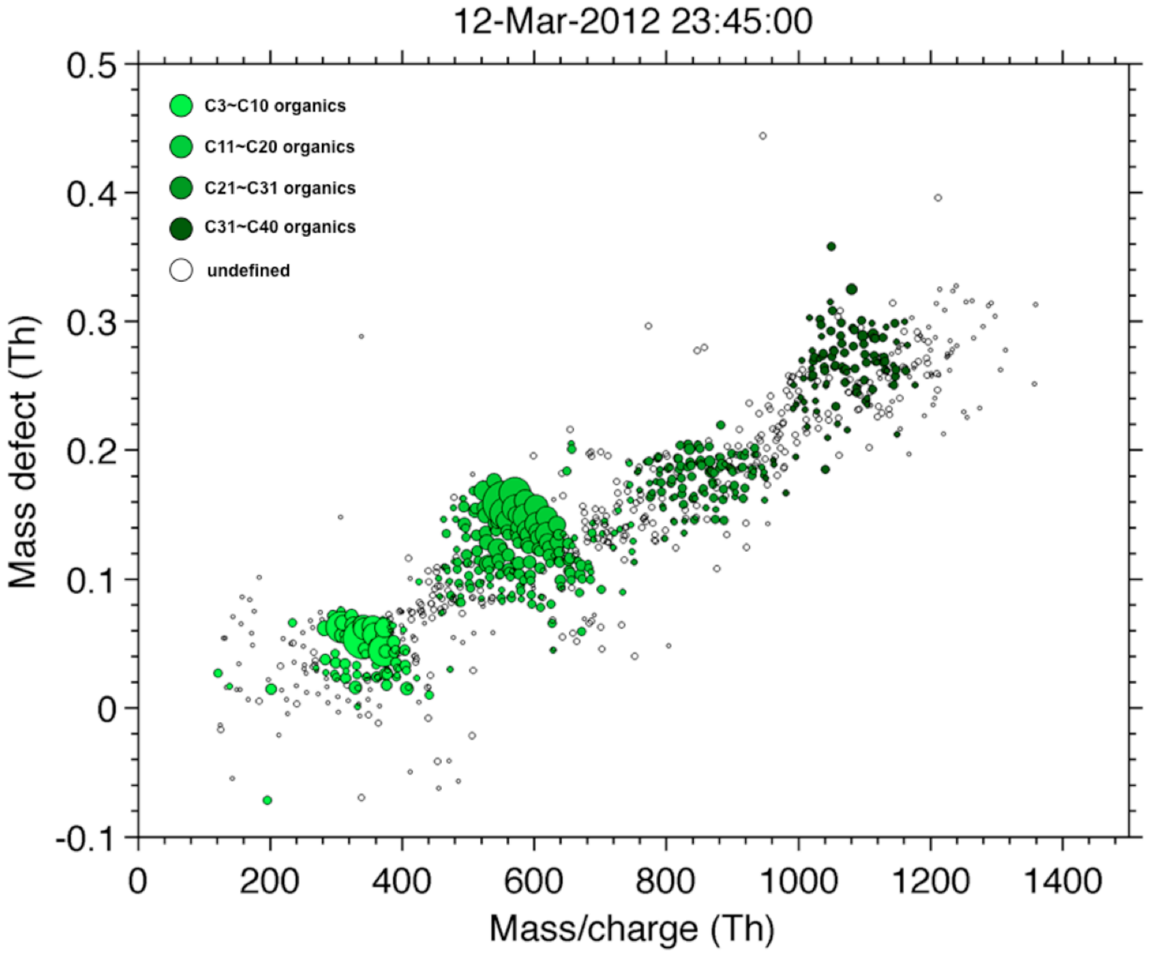

Figure 3. Mass defect plot of negative ambient ions observed during the night-time the 13th of March 2012. The four bands represent the HOMs containing approximately 10, 20, 30 and 40 carbon atoms (4 α-pinene units). The majority of the HOMs have NO_3^- as core ion.

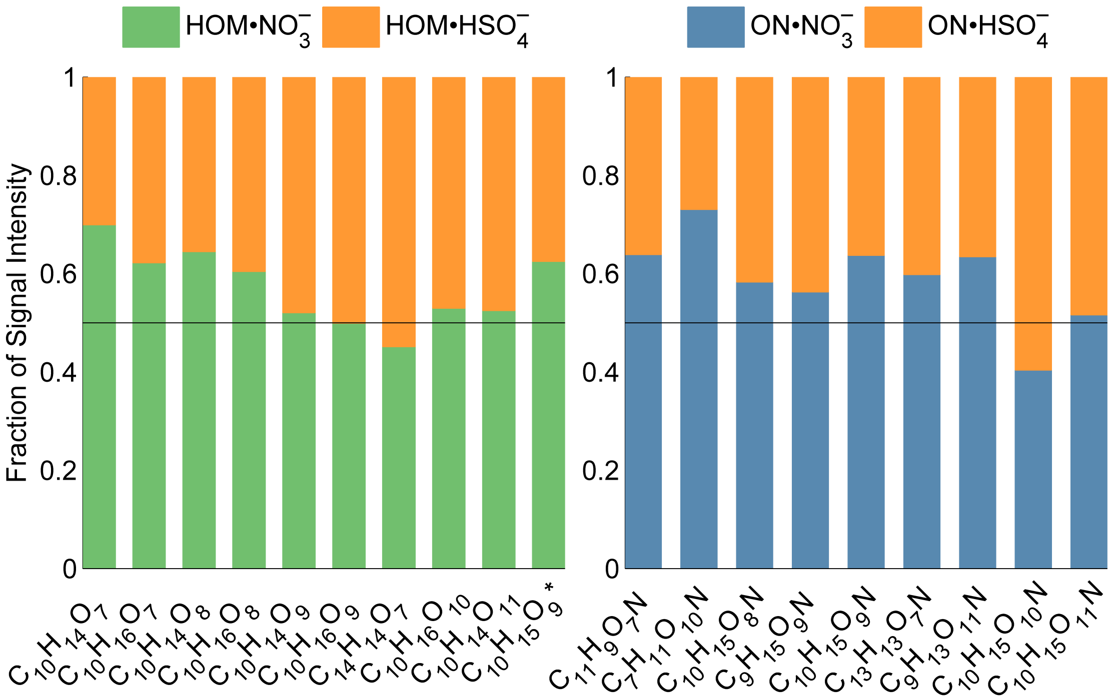

Figure 4. Naturally charged HOMs detected by the APi-TOF during daytime of April the 20th2013. On the left panel, we report the ambient ions that contain HOMs clustered ether with NO_3^- (green) or HSO_4^- (orange), while on the right panel, we show ambient ions that contain ONs clustered ether with NO_3^- (blue) or HSO_4^- (orange).

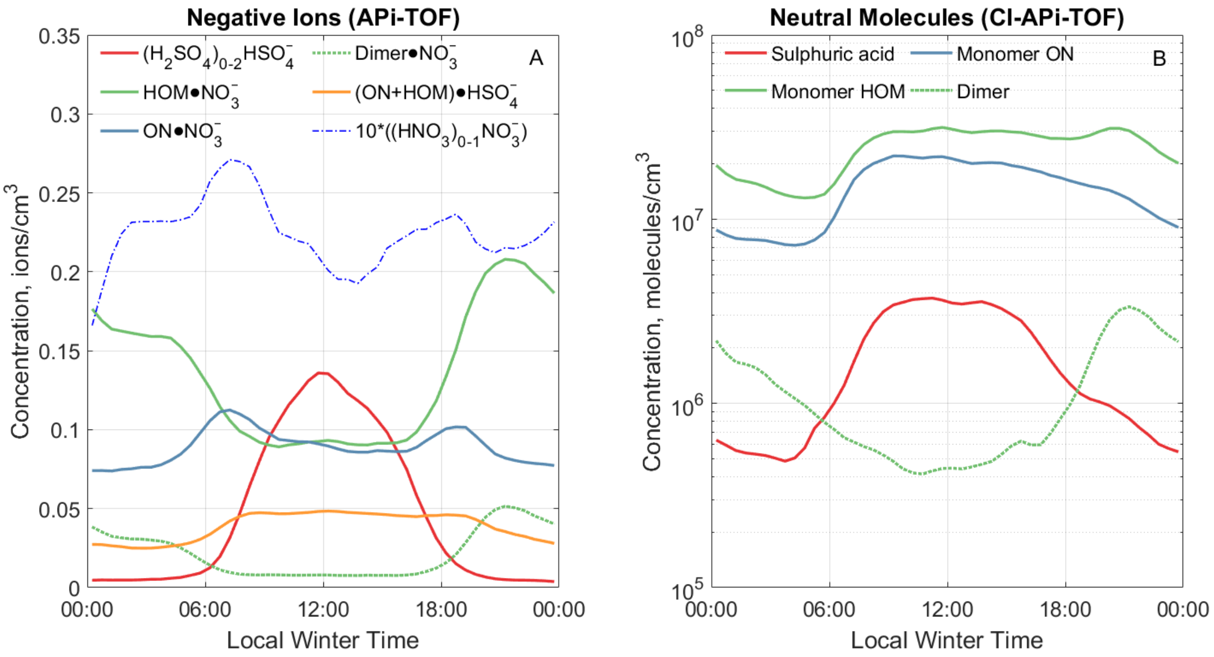

Figure 5. ~~Averaged diurnal evolution of specific family compounds (ions) during days in clear sky conditions of measurements done in April and May 2013. Colours and their corresponding families are denoted by the legends. Each family is calculated by the sum of signals from the compounds of the family. 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·HSO_4^-) have been grouped together since all these ions are present mainly during the day.~~

Averaged diurnal evolution of specific ion families (Panel A) and neutral compounds (Panel B) during days in clear sky conditions of measurements done in Spring 2013. Colours and their corresponding families are denoted by the legends. Note that, in panel A, the signal of the Nitric acid clusters (blue dotted line) have been multiple by 10.

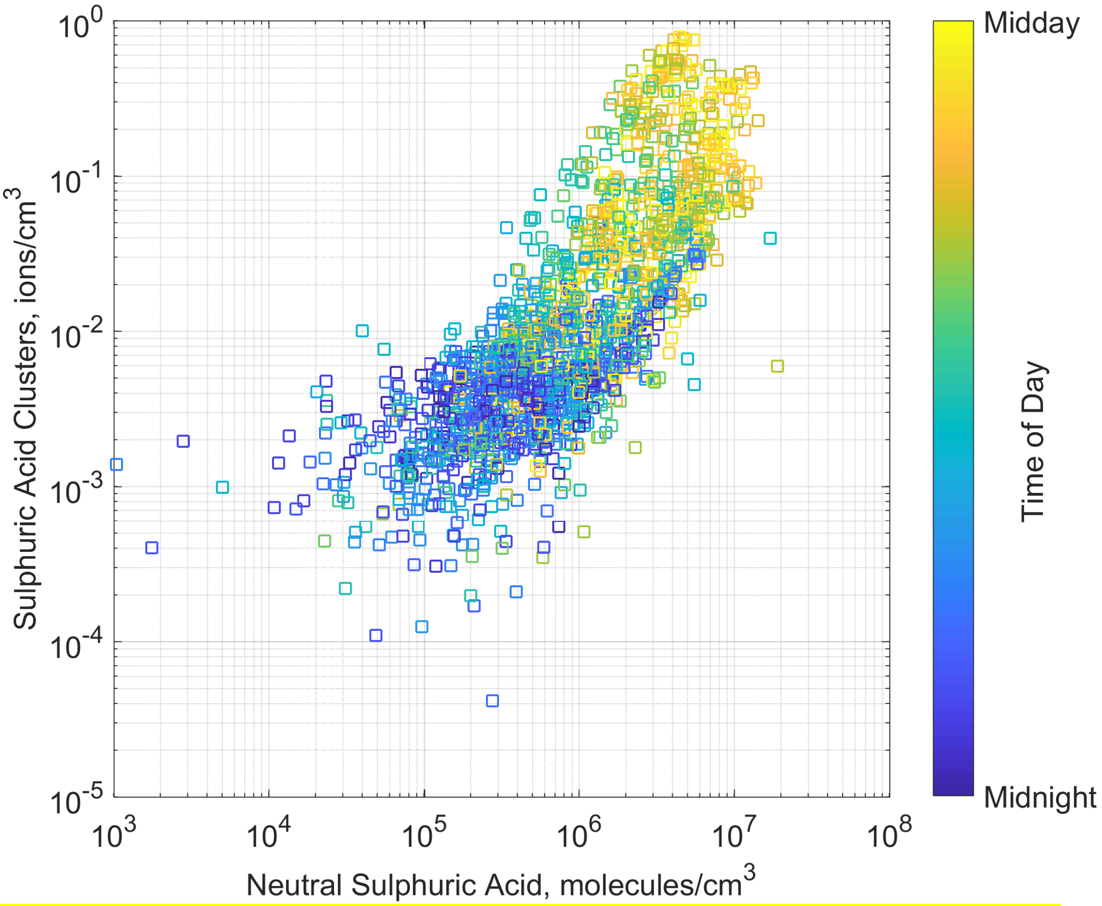

Figure 6. Correlation of negative sulphuric acid ion clusters ($(H_2SO_4)_{0\text{-}2}HSO_4^-$) and the concentration of sulphuric acid, colour coded by the time of the day.

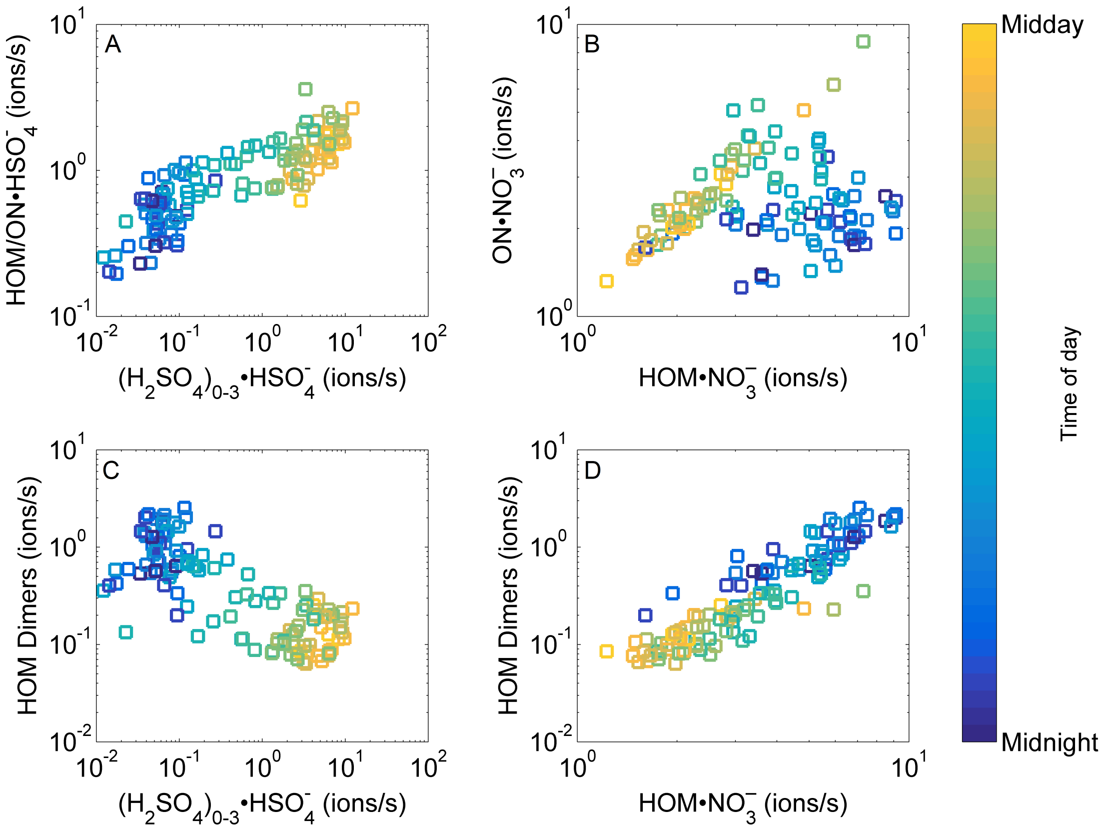

Figure 7. The diurnal dependency of ~~naturally charged compounds~~ ambient ions detected by the APi-TOF. The data points are hourly averages for 5 sunny days during April-May 2013. The colour scale is normalised to show the period between midnight and midday, so that the transition between blue to green is around 6:00 and 18:00.