

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 NO_x 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 NO₃ 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.