Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-481-RC2, 2017

Atmospheric Chemistry and Physics
Discussions
Open Access
EGU

Interactive comment on "Insight into naturally-charged Highly Oxidized Molecules (HOMs) in the boreal forest" *by* Federico Bianch et al.

Anonymous Referee #2

Received and published: 5 July 2017

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.

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.

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.

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!

3. predominant aka most influential but here you specifically mean that nitrate has the highest abundance?
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.)
5. In the context of the preceding comment, the wording 'non-nitrate HOMs' is problematic (l 31).
6. Do these "several clusters..up to 40 C" comprise 4 separate 10 C molecular ligands ?
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 ?

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'?

9. Paragraphs from line 124 to 161 reveal that much of what they observe has already been reported. Can any of these 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. l 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 ?

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 higer 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.

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.

13. Fig. 4 needs a relative intensity indicator. Perhaps replacing the 50 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.

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?

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-481, 2017.