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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Composition and temporal behavior of ambient ions in the boreal forest" *by* M. Ehn et al.

Anonymous Referee #2

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Mass spectrometric techniques have previously been shown to be a powerful tool for the measurement of ambient ions. This paper presents the application of a time of flight mass spectrometer operating in both the positive and negative ion modes to the detection of ambient ions in a boreal forest in southern Finland. In this work, ion composition measurements using the recently developed atmospheric pressure interface time-of-flight mass spectrometer (APi-TOF) were compared to existing data from previous work. In general, the various works show good agreement. The high mass resolution of the APi-TOF allowed for the positive elemental composition of close to 80 ambient ions, including the first observations of organosulfate. Mass identification of ions was validated in many cases by quantum chemical calculations of gas-phase acidities. APi-TOF measured positive ion spectra were dominated by strong bases (such as alkyl pyridines and quinolines), and negative ions spectra dominated by strong acids

(such as nitric, sulfuric). A focus on particle formation events showed a dominance of di-, tri- and tetramer sulfuric acid clusters as well as ammonia/sulfuric acid clustering. The presence of these ions suggests that the corresponding neutral clusters play a significant role in atmospheric nucleation. This work represents a significant step forward in the analysis of ambient ions due to the high degree of speciation achieved with APi-TOF.

This is a well-written work describing the presence of ambient ions as well as demonstration of a new mass spectrometric method for the analysis of ambient ions and is within the scope of ACP. I recommend this manuscript for publication after the following concerns have been addressed.

Specific Comments:

1) How are the authors correcting for instrumental backgrounds during this study. Assuming the small ion transmission efficiencies quoted and such small ion concentrations, particularly for organosulfates, one could imagine that the instrumental backgrounds are on the order of the ambient signals observed. How are the authors addressing the errors associated with this and what are the measurement uncertainties of the data presented in this work?

2) The TOF used in this work operates in both the "V" and "W" modes. The authors give a resolving power of 3000 Th/Th for the TOF. Which mode is the given resolving power for? In this work only "V" mode is used, what is the resolving power and mass accuracy of this mode specifically.

3) The loss of clusters due to expansion into low pressure and ion-gas collisions in the quadrupole has been briefly mentioned in this work. Can the authors comment as to how this was considered when comparing the relative magnitude of ions observed. It is also possible that the clusters observed are not present in the atmosphere and are created through collisions in the system. How are these effects dealt with during the data analysis?

4) The authors consider the presence of SO5- ions in the atmosphere and state HSO5 as an unlikely candidate due to no previous reports of its presence. What concentrations of HSO5 would be necessary to produce the amount of SO5- detected? One would expect inlet transmission of this species to be extremely low even if instrumentation were available to measure this species. To the knowledge of the authors, are there any instrumental techniques available that would be sensitive enough to detect those concentrations? Assuming that this is a negligible formation pathway, can the authors suggest an alternative formation pathway for SO5-?

5) The discussion on ambient ions observed during particle formation events is of considerable interest. However, I think it is lacking in detail particularly in showing evidence that there is in fact a particle formation event occurring. One can assume the particulate data collected suggests this but it may be beneficial to the reader if ambient particle data was shown in a figure for the time frame discussed (i.e. a banana plot). It would be a significant benefit to the argument if one can clearly see, via a figure, that the concentrations of the sulfuric acid tetramer clustered with ammonia and the presence of ammines were larger during the presumed event with the corresponding particle data versus the rest of the data collected during this study. Otherwise this discussion could be considered quite speculative and not necessarily a special focus on ion composition during new particle formation events. Without this type of in-depth discussion the authors can state the technique can measure species which may be important to particle formation events, and should shy from stating "We established the APi-TOF measurements of ambient ions as a powerful tool in studying nucleation in the atmosphere..."

Technical comments:

1) P. 14898, line 20. Suggest rewording "During the strongest events, also the tetramer. . ." to "During the strongest events, the tetramer and a cluster with the tetramer and ammonia were also detected,"

2) P. 14899, line 6. I would suggest describing "a series of collisions towards. . ." as " a series of charge transfer reactions towards. . ." Collisions imply a transfer of energy without a reaction necessarily taking place. In this case, the transfer of a proton must occur for the charge to be transferred from one species to the next, assuming the reaction is favorable considering the relative proton affinities.

3) P. 14899, line 20. "suggestive of a minor contribution of ions" instead of "suggestive of minor contribution of ions"

4) P. 14900, line 22. Although the APi-TOF acronym has been defined in the manuscript, TOF-MS up to this point has not.

5) P. 14904, line 9. In "these values are low, but the calibrations did not include and inlet losses" please specify that these are laboratory calibrations as the sentence begins with Junninen et al. 2010 calibrations, switches to field data i.e. "these values are low" then back to laboratory data?

6) P. 14904, line 25. Suggest rewording something like "with HSO4-, the concentration of SO5- was roughly. . ."

7) P. 14908, line 4. Is "suppl.mat" an abbreviation of something or a typo?

8) P. 14913, line 3. Suggest adding the word colored to read "The colored dots on the horizontal lines. . ."

9) P. 14915, line 5. Is 10 a factor here or should it have units?

10) P. 14917, line 1. The sentence beginning "In the previously described. . ." is Fig. 2 referring to the figure in Eisele et al. 2006, or figure 2 in this manuscript? As worded the word 'also' in line 2 should be removed.

11) P. 14917 line 8. Suggest deleting 'the' from "other and the most of the pyridines."

12) P. 14917, line 12. I believe this should be Fig. 9 and not Fig. 8.

Figure 1. NH3 is shown in yellow which is the label for sulfur isotopes in the bottom panel. This is a bit confusing, suggest changing.

Figure 6. What is the time resolution of the Api-TOF data shown in the Figure?

Figure 7 and 8. Are the diurnal trends the average over the entire measurement period or just an example of one day? This is important information to include in the description. If these are over the duration of the experiment can the authors comment on any specific meteorological differences that occurred which may have influences the observed trends due to the small amount of data sampled?

Figure 9. Again what is the time resolution of the APi-TOF data shown here?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 14897, 2010.