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Comment

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

**M. Ehn et al.**

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*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?*

The background noise in the APi-TOF is extremely low, and comes mainly from scattered ions in the TOF, and is therefore spread out fairly evenly over the whole time-of-flight range. The toolbox used for analysis (tofTools) calculates a baseline from the areas between peaks, and this is removed from the peaks themselves before calculating

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Discussion Paper



the concentrations, as mentioned in the recently published AMT technical paper on the APi-TOF (Junninen et al., 2010). It also includes more discussion on the background noise in the instrument than the original AMTD version that the reviewers had access to. It shows that the noise is at all masses below  $5e-4$  cm<sup>-3</sup>, which can be compared to the mean concentration of the organosulfate peak of 1.4 cm<sup>-3</sup>. The measurement uncertainties were already discussed in the response to reviewer 1.

*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.*

Action: It will be specified in the text that all quoted numbers refer to V mode.

*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?*

There is no way of knowing which ions/clusters are merely fragments of larger clusters in ambient air, and thus we could not take this into consideration. A recently submitted comparison between the APi-TOF and ion mobility spectrometers in Hyytiälä showed good agreement between the instrument, leading us to believe that no considerable fragmentation, except for water detachment, occurs in the instrument. The short amount of time the ions spend inside the instrument, and the low pressure they are expanded to makes collisions with trace gases extremely rare. Thus no noticeable formation of the observed clusters happens inside the system.

Action: The reference was updated, and “The fact that the instruments agreed, suggest that no major fragmentation happens inside the APi-TOF” will be added.

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4) *The authors consider the presence of SO<sub>5</sub><sup>-</sup> ions in the atmosphere and state HSO<sub>5</sub> as an unlikely candidate due to no previous reports of its presence. What concentrations of HSO<sub>5</sub> would be necessary to produce the amount of SO<sub>5</sub><sup>-</sup> 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 SO<sub>5</sub><sup>-</sup>?*

Presumably, a ballpark idea of the HSO<sub>5</sub> concentration required to give the observed SO<sub>5</sub><sup>-</sup> signal can be obtained from the SO<sub>5</sub><sup>-</sup>/HSO<sub>4</sub><sup>-</sup> ratio, which is on the order of 20%. If we have 1e6-1e7 H<sub>2</sub>SO<sub>4</sub>, we would have around 2e5-2e6 HSO<sub>5</sub>, which seems quite high, even accounting for the stabilizing effect of hydration w.r.t decomposition into SO<sub>3</sub> + HO<sub>2</sub>. Chemical ionization mass spectrometry should be able to detect concentrations of that level. An alternative pathway for producing SO<sub>5</sub><sup>-</sup> is presented in the paper as SO<sub>3</sub><sup>-</sup> + O<sub>2</sub>. Nevertheless, the origin of SO<sub>5</sub><sup>-</sup> could not be pinpointed with certainty within the frame of this study.

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 amines 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*

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*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...”*

This is an excellent point that will be corrected for.

Action: A trace of sub-5 nm particle concentration will be added to the time-series presented in Fig. 6, which clearly shows the highest amount of new particles during 30 April. Additional text is added to point this out.

*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 HSO<sub>4</sub><sup>-</sup>, the concentration of SO<sub>5</sub><sup>-</sup> was roughly. . .”*

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All the above suggestions will be incorporated.

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

It was an abbreviation, but as it was the only place where it was used, it will be changed to supplementary information.

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

Will be added.

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

Will be changed to “factor of 10”.

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.

“also” will be removed. It should be fairly clear that figure 2 refers to Eisele et al, partly as it says “figure 2 in Eisele et al”, and partly as the figures in the paper itself are always abbreviated “Fig.”.

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.

Will be corrected.

Figure 1. NH<sub>3</sub> is shown in yellow which is the label for sulfur isotopes in the bottom panel. This is a bit confusing, suggest changing.

The sulfur isotope colors will be changed to purple, and Fig. 1 and 3 modified accordingly.

Figure 6. What is the time resolution of the Api-TOF data shown in the Figure? Figure 9. Again what is the time resolution of the APi-TOF data shown here?

It is stated in the beginning of section 3.3 that “When analyzing the time series of the selected ions, we used 30 min averages.”

*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?*

The diurnal trends were averages over the measurement period. A picture of the prevailing met. is seen in Fig. 6 where wind direction and radiation are plotted. These issues will briefly be mentioned in the text.

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

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