**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 #1

Received and published: 6 August 2010

General comments:

Ambient ions are often measured with ion spectrometers. Recent field measurements using these techniques show atmospheric ion concentrations are typically below 1e5 cm-3 in mobility size range of about 0.5-10 nm. However, ion spectrometers measure ions with poor mobility resolution and have very poor mass-resolved capability. In this manuscript, ion compositions were measured with a recently-developed mass spectrometer (the APi-TOF), which has a relatively higher mass resolution for ion composition identification. The authors showed composition and diurnal variation of ambient ions in a boreal forest in Finland. They found the ion spectra were dominated by strong acids and strong bases in negative and positive ion modes respectively. The detection of strong organic acids (e.g., malonic acid) was further confirmed with their lower val-

ues (hence higher acidity) of gas-phase acidities compared to that of the nitric acid in their quantum chemical calculations. Major ions and their relative abundances during new particle formation events were also investigated. Ion clusters containing sulfuric acid and ammonia were observed during some strong events. Although ion-induced nucleation only accounts for about 10% in the boreal forest, high resolution measurements of atmospheric ions have important implication in atmospheric nucleation/new particle formation because these ions are related (might be proportional) to their corresponding neutral clusters. For ion clusters relevant to atmospheric nucleation (e.g. ion clusters containing several sulfuric acid molecules), the formation mechanisms (from neutral vs from ion-induced) are still poorly understood and await future investigation. The paper also reported the first observation of organosulfate in ambient ions.

The manuscript is fitted into the scope of the ACP. However, the following issues need to be addressed before its final publication.

Major issues/comments:

1) The ion concentrations reported in this manuscript use a unit of ion cm-3. Can the authors give an estimated uncertainty for the measurements since the reference Junninen et al. (2010) does not report the uncertainty for the ion measurements?

2) Bisulfate ions and Sulfuric acid ion clusters up to tetramer were observed as major ions in the APi-TOF negative spectra during strong nucleation events (e.g., Fig. 1). Can the authors give plausible formation mechanisms for these ions?

3) The acidities of organic acids are associated with their chemical structures as shown in Fig A1-3 with quantum chemical calculations. The authors stated that malonic acid is stronger than other organic acids (e.g., oxalic and succinic acid) because it bears a six-member ring in its ion form (Page 14906, second paragraph). Please give an explanation or reference why acids with six-member ring are stronger than others with less or more member rings.

4) According to previous quantum chemical calculations, pure neutral sulfuric acid clusters do not exist in significant concentrations in the lower atmosphere. However, these studies didn't consider the effect of water in stabilization of sulfuric acid clusters. Atmospheric nucleation relevant clusters will undoubtedly contain some water molecules. Like ammonia/amines/organic acids, inclusion of water will greatly increase the Gibbs free energy of formation and hence enhance the stability of the nucleating clusters. Unfortunately, water molecules are lost from the negatively-charged clusters inside the vacuum system of any mass spectrometer. As reported in a recent paper, neutral sulfuric acid clusters were measured with a quadrupole mass spectrometer during atmospheric nucleation events (Zhao et al., 2010). A few sentences to describe the role of water in stabilizing the nucleating clusters will be beneficial to the general readers of this journal.

5) Nitrogen-containing compounds are recently speculated to stabilize sulfuric acid clusters. However, no direct observatory evidence has been given to support this speculation. In supplementary material (Table S3), one particular cluster (372.051 Th) corresponding to mass of sulfuric acid trimer ion plus pyridine was observed with a considerable average concentration. Given that pyridine is the most abundant organic ion in the positive ion spectra, observation of this ion has potentially important implication for the role of organic compounds in atmospheric nucleation. Can the authors show more data on how this ion varies between nucleation events and non-event periods and how it is correlated with sulfuric acid and its ion clusters?

Minor comments/typos:

1) Page 14902, line 12. "a sensitivity of 0.1-1%", do the authors mean "transmission efficiency"? What is this related to Page 14904, line 7 "total transmissions of 0.033% and 0.1% for negative and positive ions"?

2) Page 14906, line 3. Delete "very". Line 17. "it" here should be referred to "malonic acid" not its ion. Lines 18-20. Ambiguous statements about the malonic acid with CIMS

detection. Please specify what primary ions are used for the ionization scheme. Line 7 from bottom, "high a certainty", any typos?

3) Page 14915, line 2. "their charges". Line 2. Please give a justification for why use mass 340.05 Th as a surrogate for all the night time molecules observed at the high masses;

4) Page 14918, line 1 and other pages. "neutral molecules and clusters", please put "neutral" before "clusters" as a molecule is always neutral;

5) Figure A1-A3. The bond length of hydrogen bonds are suggested to be given in these figures.

References

Junninen, H., Ehn, M., Pet Âĺ aj Âĺ a, T., LuosujÂĺ arvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech. Discuss., 3, 599–636, doi:10.5194/amtd-3-599-2010, 2010.

Zhao, J., F. L. Eisele, M. Titcombe, C. Kuang, and P. H. McMurry (2010), Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the clusterâĂŘCIMS, J. Geophys. Res., 115, D08205, doi:10.1029/2009JD012606.

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