

***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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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?

To be able to transform APi-TOF counts into ambient concentrations, some transmission function needs to be taken into account. The exact shape of the transmission curve is hard to measure in the field, and specifically for the negative ions, mobility standards are lacking. Thus, as we wrote on page 14902, line 27 onward: “The final total detection efficiency of the instrument during this campaign was determined by comparing the total ion counts measured by the APi-TOF and a BSMA (see Sect.

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2.2.2). No size dependence was taken into account, as this could not be done reliably enough.” In other words, the absolute error is based on the uncertainty of the BSMA, which is reported to be below 20%.

Action: The line “The uncertainty of the BSMA is reported to be <20%, and this uncertainty will translate to the reported API-TOF concentrations.” will be added to the manuscript after the above-mentioned lines.

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?

We are not completely sure what the reviewer is referring to here, but the complete process goes roughly as follows: Sulfuric acid is formed via the standard mechanism ($\text{SO}_2 + \text{OH} \Rightarrow \text{HSO}_3$, $\text{HSO}_3 + \text{O}_2 \Rightarrow \text{HSO}_5 \Rightarrow \text{SO}_3 + \text{HO}_2$, $\text{SO}_3 + 2 \text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$), bisulfate ions are formed by proton transfer from H_2SO_4 to practically any other negative ion it collides with. Clusters are formed either by neutral H_2SO_4 and HSO_4^- colliding and sticking together, or by neutral clusters becoming charged. Water and base molecules are likely involved as well, but bases tend to evaporate from the negatively charged clusters and water is lost in the instrument.

In summary, the production of H_2SO_4 is discussed elsewhere, the cluster formation is only based on specific molecules colliding, and the evaporation is already discussed in the paper.

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.

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This is a good point, as we should rephrase that paragraph to say that the formed ions are more stable if they have six-membered rings due to the bond angles being more optimized than in the five or seven membered rings. In other words, the rings themselves do not directly influence the strength of the acid, but the stability of the ions is enhanced by ring formation, making deprotonation more energetically favorable.

Action: Reformulation.

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.

Previous studies have addressed the effect of water, please see e.g. Kurtén et al (2007) and Nadykto et al (2007a, 2007b). We agree with the referee that water will tend to stabilize the neutral clusters somewhat, and that real atmospheric clusters will very likely contain some water molecules, at least in the absence of e.g. amines (recent modeling indicates that amine-acid clusters might remain dry; see Loukonen et al., 2010). However, the stabilizing effect of water is much smaller than that of base molecules, and very likely it is not (on its own) strong enough to keep pure acid-water clusters together. In terms of the Gibbs free energy of sulfuric acid dimer formation, the presence of water aids the process by 1-4 kcal/mol, while ammonia aids it by more than 7 kcal/mol and dimethylamine by more than 12 kcal/mol, based on the best available

quantum chemical data (Nadykto et al 2007a, Kurtén et al 2008). Also, the effects of water and base molecules do not (based on calculations) seem to be additive - rather, they compete for the available acids.

Theo Kurtén, Leena Torpo, Chang-Geng Ding, Hanna Vehkamäki, Markku R. Sundberg, Kari Laasonen and Markku Kulmala: *Å* density functional study on water-sulfuric acid-ammonia clusters and implications for atmospheric cluster formation. *Journal Geophysical Research - Atmospheres*, Vol. 112 D04210, 2007

Loukonen, V., Kurtén, T., Ortega, I. K., Vehkamäki, H., Pádua, A., Sellegri, K., and M., K.: Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study, *Atmos. Chem. Phys. Disc.*, 10, 2321-2356, 2010.

Nadykto, A. B., and F. Yu, Strong hydrogen bonding between atmospheric nucleation precursors and organic acids, *Chem. Phys. Lett*, 435, 14-18, 2007a

Nadykto, A.B. and F. Yu: Thermochemistry of $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{NH}_4)_k$: a DFT Study. In "Nucleation and Atmospheric Aerosols", edited by Colin O'Dowd and Paul Wagner, pp 297-301, Springer 2007b.

Action: "At ambient pressure and RH, most neutral sulfuric acid molecules and clusters will have water molecules attached to them. Although to a much lesser extent than ammonia or amines, water can also stabilize pure sulfuric acid clusters." will be added to section 3.4.

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 au-

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thors 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?

The mass of a cluster of the sulfuric acid trimer with pyridine would have a mass of 371.937 Da, and as the measured mass was 372.051, the difference is more than 1000 ppm (the instrument accuracy was 20 ppm). In other words, this ion cannot be the cluster suggested by the reviewer. This ion is one of the larger peaks visible in the typical night-time spectrum, i.e. it will anti-correlate with sulfuric acid.

Minor comments/typos: 1) Page 14902, line 12. “a sensitivity of 0.1-1 efficiency”? What is this related to Page 14904, line 7 “total transmissions of 0.033 and 0.1% for negative and positive ions”?

The reviewer is correct, “sensitivity” was a poorly chosen word, and should say transmission. They all refer to the same numbers, and the latter ones are lower due to inlet losses as explained later on page 14904.

Action: “sensitivity” changed to “transmission efficiency”.

2) Page 14906, line 3. Delete “very”. Line 17. “it” here should be referred to “malonic acid” not its ion. Lines 18-20.

Action: “very” deleted, “it” changed to “malonic acid”.

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?

The negative ion referred to the ions measured by the APi-TOF. These will be made clear.

Action: “measured by the APi-TOF” will be added, “a” deleted.

3) Page 14915, line 2. “their charges”. Line 2.

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Action: "s" added.

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;

Action: "as the time behavior of all of these were similar." will be added.

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

This will be changed.

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

The values will be added to the figure caption of Fig. A1, as here the values function as comparable measures for the stability of the ions. For Fig. A2 and A3, we do not feel that the addition of hydrogen bond lengths adds enough relevant information, but instead, especially in Fig. A2 with 7 H bonds, may make the figures/captions harder to read.

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

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