

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-994

Anonymous Referee #2

Referee comment on "Diurnal evolution of negative atmospheric ions above the boreal forest: from ground level to the free troposphere" by Lisa J. Beck et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-994-RC2>, 2022

Summary and general comment:

This study by Beck et al. characterizes the atmospheric negative ion composition of various tropospheric layers (from 100m to 3200m) above the SMEAR II research station in the Finnish boreal forest. By deploying an API-TOF mass spectrometer in a Cessna 172 aircraft, the authors resolved the vertical distribution and diurnal variation of naturally charged molecular ions and ion-clusters from the stable boundary layer up to the free troposphere. While the ion composition of the stable boundary layer coincides with the simultaneous measurements placed at the field station on top of a 35m tower above the forest canopy, the other layers showed a clearly distinguishable ion composition. In the residual and mixing layers, the ion composition is strongly dependent on the origin of air masses, the turbulent mixing, and the photochemistry throughout the day. Most of the detected ions during daytime are comprised of sulfur-containing compounds, while the nocturnal ion compositions are more diverse. The detection of various halogens and carboxylic acids as well as the absence of HOMs in the free troposphere indicates that this layer is mainly influenced by long-term transported air mass.

I agree with the general comment by reviewer 1. The authors realized a difficult technical measurement and showed through comprehensive investigations the composition and chemical processes of negative ions in various tropospheric layers and their diurnal evolution. The methods are extensively illustrated and clearly written, enabling a good evaluation of the results by the scientific community, and promoting a continuation of the study in this field of research. However, the manuscript lacks a detailed discussion and developed conclusion of the atmospheric implication to obtain a comprehensive understanding of ion chemistry and its role for NPF in the various tropospheric layers. I would recommend the manuscript for publication in ACP as a measurement report after the following minor comments have been addressed.

Minor comments:

Line 35ff.: Please also consider the earlier work of Yu, F., and R. P. Turco (2001), From

molecular clusters to nanoparticles: Role of ambient ionization in tropospheric aerosol formation, *J. Geophys. Res.*, 106, 4797–4814, 10.1029/2000JD900539.

Line 49: Please also consider the earlier work of Lovejoy, E. R., Curtius, J., Froyd, K. D. (2004), 'Atmospheric ion-induced nucleation of sulphuric acid and water', *J. Geophys. Res.* 109, 10.1029/2003JD004460.

Line 153: I wonder if the active ionization by the x-ray source during the flights might provide some helpful information (even of its short period) to support some conclusions.

Line 155: Did you observe a significant variation of the total ion count (TIC or ions per second, including transmission correction) during the flights in the different tropospheric layers or times of the day?

Line 163ff.: You may add the TIC to Figure S2 if there is a variation.

Line 164ff.: Can you estimate qualitatively how strong the measurements can be influenced by the pressure changes (e.g., transmission and ion-cluster stability).

Figure 5: Please mention the black dotted line and its meaning in the figure caption.

Line 371ff: Similar to reviewer 1; you showed that during daytime MSA is present in the FT, while iodic acid and halogenated compounds are almost absent. On the basis that the measured air mass had a marine origin (as shown in Fig. S15), can you elaborate a bit more on your conclusion? Typically, you would expect all species from marine sources. Can MSA also be formed by a different source, e.g., degassing of MSA from dehydrated aerosol (Zhang et al. (2014); doi: 10.1002/2014GL060934).

Figure 7: What element composition corresponds to the strong iodine peak in between the sulfur-containing molecules close to 200Th? Please mark/add this one also in table A1.

Line 409ff.: Are any ammonia-containing clusters measured at the ground station during this time to support your conclusion for this case study?

Line 436ff.: The concentration of HOM dimers and iodic acid could also be reduced due to NPF or atmospheric chemical processes. In my opinion, the statement "their charges being

transferred to SA" is not fully valid here. Please elaborate a bit more on this conclusion.

Figure 6 + 10: You may want to add the estimated sulfuric acid concentration also in these figures as shown in Figure 7b.

Figure 11+12+13+14+16+18: Why are the detected HOMs (shown in the figures before and table A1) now combined with all (unidentified ion compounds)?

Technical comments:

Line 254: better use "sources of uncertainty" instead of "source of error".

Line 276: better use "upward trend" instead of "buoyancy".

Line 385: The estimated sulfuric acid concentration [...] varied from 0.3 to $1 \cdot 10^6 \text{ cm}^{-3}$ and [...].

Line 402: reference should be Fig. S15, not S6.

Line 505: You may focus the reader on the trajectory you referring to (e.g., Fig. S14 blue trace).

Reference to Fig. S17 is missing.