



EGUsphere, referee comment RC1
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Comment on egusphere-2022-1318

Anonymous Referee #1

Referee comment on "Chemical identification of new particle formation and growth precursors through positive matrix factorization of ambient ion measurements" by Daniel John Katz et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-1318-RC1>, 2022

In this work, the authors present measurements of atmospheric cations and anions using an APi-TOF at the SGP site. They further deploy the binPMF to aid the identification of ions and find distinct chemical characteristics and temporal behaviors. The neutral species in the atmosphere that can be inferred from ion measurements have meaningful implications on the atmospheric new particle formation and growth, although quantitative studies require further measurement using active chemical ionization schemes. One main difficulty in understanding ion behaviors is that the abundance of ions is a result of both the concentration of respective neutral species and the charging potential (i.e., proton affinity, molecular polarity, etc.). The authors are fully aware of this complexity and the interpretation in this study is careful and reasonable, which I do appreciate. In general, I think this paper has certainly new insights into the understanding of atmospheric ions at this site and presents an excellent example of what we can learn from ion measurements. Therefore, I recommend the acceptance of this manuscript for publication in ACP, after a few minor concerns are addressed.

Line 21-22. HOMs are spelled as "highly oxidized molecules", while in Line 44, it is spelled as "highly oxygenated molecules". I suggest following the definition by Bianchi et al., i.e., "highly oxygenated organic molecules".

Line 104-105. The authors mentioned that the pinhole of APiTOF was clogged partway through the campaign. I wonder whether there is any influence by the clog, for example on the total ion counts? Please add a sentence about this.

Line 190. For NPF identification, the cut-off size of SMPS is important. The authors mentioned in Line 214 that the low abundance of higher-order sulfuric acid clusters is consistent with the lack of nanoparticles. According to my experience, the sulfuric acid trimer to dimer ratio is always very low (a few %) even in amine-rich environments, so the ratio of 2% here probably can't be simply taken as indicative of negligible NPF. Could it be possible that SMPS is not able to detect particles down to a few nanometers?

Line 237. The chemical species with m/z located at 288 could also be $C_5H_{10}N_2O_8$, a widely-observed peak in isoprene-rich environments. The double-bond-equivalent of $C_{10}H_{10}O_6$, as suggested by the authors, seems too high in my opinion. Please double-check the formula assignment on this nominal mass.

Line 292-293. "The increased intensity at odd m/z suggests that neutral organonitrate species clusters with NO_3^- are more abundant than clusters of HOMs with NO_3^- ". This statement isn't right. By definition, organonitrates (with enough oxygen atoms) are a subset of HOMs. Maybe rephrase it as "... than clusters of non-nitrate HOMs with NO_3^- ".

Line 295-300. I buy that the nighttime $NO_3 + SQT$ reaction could be strong, but what about the daytime. SQT reacts with O_3 fairly effectively, and if the subsequent RO_2 reacts with NO , C15 ONs will also be formed. So, I am a bit surprised that no C15 ONs observed during the day. One possibility could be that C15-ONs do not bind with HSO_4^- as efficiently as it does with NO_3^- ; in this regard, are there any SQT-originated ONs appear in the daytime high-mass factor in the positive ion mode? Another possibility is that the O_3 concentration at SGP site is quite low during the day. It would be very helpful if the concentrations of NO , O_3 , and NO_2 are provided. Anyway, please consider rephrasing this part.

Line 301-302. Related to my former comment about NO concentration at SGP site. I'd like to see a short discussion on the reason for the suppressed RO₂ cross-reactions. If NO₃ is present in a considerable amount, NO concentration has to be very low, which shouldn't suppress dimer (C₃₀) formation. Maybe this is due to the RO₂+NO₃ → RO + NO₂ + O₂?

I find the discussion on the positive HOM ions a bit unclear. How many HOM-related ions are identified, what are they, and how different are they from the daytime SQT ones and why? I hope to see some discussion on these points.