

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-421

Anonymous Referee #2

Referee comment on "Ammonium adduct chemical ionization to investigate anthropogenic oxygenated gas-phase organic compounds in urban air" by Peeyush Khare et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-421-RC2>, 2022

The authors present measurements from New York City, USA, to evaluate the emission strength of oxygenated volatile organic compounds (OVOCs) that originate from volatile chemical products (VCPs). They use the VOCUS in NH_4^+ mode to detect and quantify for the first time OVOCs related to VCP emissions including glycols, glycol ethers, acetates, alcohols, and others. They evaluate the instrument performance for these compound classes based on laboratory calibrations and provide field enhancement ratios with typical tracers including benzene, CO, and acetone. Furthermore, they perform a comparison of the observations to two VCP emission inventories to find good agreement for many compounds but also differences that are further discussed. This paper is great and fits well within the scope of ACP after the following minor comments are answered.

Main comment:

Throughout the paper, the authors have no comments on the influence of other pollution sources. There is still traffic, cooking, biomass burning, and industrial activities that could influence the observed concentrations in NYC. To my knowledge, how much these sources contribute to OVOC emissions is currently unknown; therefore, more discussion is essential here. I understand that performing detailed statistical analysis to apportion the different pollution sources (e.g., PMF) is not the scope of this paper, however, discussing the limitations of the approach followed here will be important especially given that OVOC emissions from the above sources (e.g., cooking and biomass burning) are also not well constrained. Furthermore, OVOCs can be a product of secondary chemistry and although the measurements are during the winter, increased concentration of these OVOCs due to atmospheric chemistry cannot be excluded and should be at least discussed.

I appreciate Figure 2 where the authors highlight the performance of the NH_4^+ VOCUS. It would be great if the authors could comment further on the influence of protonation, charge transfer, and fragmentation on the calibrated target VCP as well as other compounds they calibrated. I think that a table in the supplement showing the percent per compound that was ionized by NH_4^+ , vs. other ionizations at different RH would be

valuable given that these are the first measurements and detailed calibrations of these OVOCs. For example, are there specific compound classes that may be influenced more than others by different ionizations when operating the VOCUS in NH_4^+ that the community should be aware of? I consider that highlighting the limitations of this technique is as valuable.

Minor comments:

Line 137-138: I would delete this line given that this campaign has not happened yet.

Line 225-230: The authors discuss how they exclude the influence of biomass burning. However, this is not the most precise approach to guaranteeing the full separation of this influence. Furthermore, there are more urban sources emitted in NYC than VCPs. Traffic, cooking, and industrial emissions from the outer regions could affect the measurements and therefore also the inventories. Oxygenated compounds that have high background due to long-range transport could also influence the concentration of the OVOCs studied here.

Line 328: I would suggest deleting "slight".

Line 412-438: The authors nicely discuss the influence of chemistry on the chemical degradation of VCP emissions. Given that these are oxygenated compounds I would also expect the influence of secondary production of these pollutants in this region even during the winter. This would be an important point especially when the observations exceed the expected emissions based on the inventories.

Line 487-489: I think it will be important to discuss what the influence of other sources is. For example, although it is winter, chemistry can contribute to these signals but also other sources such as cooking emissions could influence the observed concentrations.

Figure 4-5: It would be interesting to discuss the diurnal variability of these compounds and whether this could tell us something regarding their emission source.

Line 520-524: Acetone also originates from other primary emissions such as traffic, cooking, etc. that the authors should discuss here.

Line 766: It would be good if the authors defend that acetone is predominantly from VCPs vs. other primary or secondary sources with references.

Line 774: Prior work? Reference?

Line 933-934: I would recommend changing "deviated" to a more detailed statement and expanding on the results of this study further here.