A Vocus CI-ToF with a NH$_4^+$ reagent ion source was applied to sample the roof air in Upper Manhattan in wintertime. A range of VOCs to I/SVOCs including acetates, glycols, glycol ethers, alcohols, etc., which have uses in personal care products, fragrances, solvents, and/or other volatile consumer products, have been measured. Concentrations, dependences of meteorology conditions, and the relative enhancement ratios with typical tracers of the targeted compounds were discussed. The application of ammonium as the positive-ion reagent gas provides another angle of understanding of the compounds with a diverse range of chemical functionalities, showing the advantage of NH$_4^+$ ionization, which would enhance the knowledge of VCPs-related emissions in the megacity region. The concentration ratios of the targeted compounds to several common tracers, such as acetone, CO, and benzene, would be helpful to understand the emission structure. Overall, I believe this paper is worth publication after some minor revision.

As said in Line 151-152, the measured concentration of functionalized compounds could be emitted from diverse, distributed sources around New York City. And the additional contribution from other sources (e.g., biomass burning) would bias calculations of urban emission ratios in this study, as described in Line 225-226. Both local and regional sources can contribute to the concentration of functionalized compounds measured in the roof, but the authors seemed to attribute all the emissions to local VCP sources without any discussion about long-range transport contribution or local non-VCP sources. I am confused that the emission from vehicles, for example, was completely missed in any of the discussions in this paper. Authors should add words evaluating the impact of regional and local non-VCP sources on the targeted compounds.
Below are several additional comments

- Line 33: It is not accurate to say “online measurements of oxygenated VCPs in a...” because the 10 days measurement was not the direct and exclusive measurement of the VCPs sources. The ambient concentration of these compounds may come from other sources. Using oxygenated organic compounds might be appropriate.
- Line 86-87: “These health impacts will be modulated by the air change rates at which indoor emissions of ROC are transferred outdoors.”
- It might be better to put Line 98-114 before Line 83-96 for a smooth transition of background introduction.
- There is a lack of summary of the advantage and current research state of using NH₄⁺ as the chemical reagent ion in CI-TOF instruments in the Introduction part. Maybe several sentences right after Line 120 describing the ability to measure I/SVOCs and other chemical functionalities, as the follow-up of Line 83-96.
- Line 138: The citation of Warneke et al. needs to be corrected.
- Line 185-186 and Line 335-338: I agree that the buffering effect of water clusters in the reactor can remove the humidity dependence but several more compounds should be added in figure 1 to reinforce your statement. Especially the ones that were discussed in the later sections. Could you also add some discussion on why the sensitivity of MEK increased by 10% with humid calibration?
- Line 221-228: It is fine to filter the data but there was a lack of reference to support the application of benzene-to-toluene ratio>2 as the threshold for identifying biomass burning events. I recommend using the enhancement ratio of acetonitrile to CO as a more exclusive tracer for labeling biomass burning.
- Line 327-331: Examples are needed to show the bound of “slight over-or under-estimation”. Especially the ones that showed deviated results when compared with the VCP inventory. If the calculated concentrations could have a factor of 0.5 to 8 differences depending on the relative abundance of isomers (described in Line 323-325 and figure S5), this impact should be evaluated.
- Line 357-359: Please provide more evidence to support the statement or I am not convinced that C₂H₅OH signal was more like dimethyl ether instead of ethanol.
- Line 590-592: Maybe I missed something, but this statement was not clear. How to translate the emission inventory to concentration? Or where did the factor of 2 come from?
- Line 595-597: I don’t agree with this statement. If D5 has large indoor sinks, either chemically or physically, the reduced ventilation would have less impact on its contribution to ambient levels than a compound that has small indoor sinks.
- Line 600-603: “…, benzyl alcohol showed its potential as an additional VCP compound...”
- Line 644: Authors should be more serious about the determination of background concentrations. More evidence is needed to support using 5th percentile of the data as the regional background. The background can be vital in the discussion in section 3.5. Please add more references as well in Line 774.
- Line 709-711: Since the acetonitrile and CO data were available, the authors might check the enhancement ratio. According to Line 221-228, the data that was influenced by biomass burning had been removed based on benzene-to-toluene ratio, but if the peak of C₂H₇NO was caused by biomass burning, authors should reconsider how to filter the biomass burning event.