

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2022-421

Anonymous Referee #3

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-RC3>, 2022

General comments

Khare and coauthors show the utility of ammonium-adduct chemical ionization in measuring a range of species from VCPs in the NYC metro area. They give a detailed explanation of the method, identify compound classes measured in the area with a generalized estimate in sourcing, and compare these measurements to VCP inventories. The measurements provide constraints on the inventories of many VCPs and shows that these inventories need to be modified for some species in the region. This analysis gives a preliminary survey of the region in the wintertime and sets the stage for future, more detailed measurements in this area to come in a different season.

My main comment is that there were collocated PTRMS and GCMS measurements that should be leveraged more to help with conclusions made on magnitudes in concentration and for isomer identification. This should be addressed to some degree since it could be used in the evaluation of inventories. This does not have to be done for every species listed but should be for the few species that overlap in each spectrum and considerably deviate from inventory estimates (e.g. acetone, ethanol, ethylene glycol). These species and suggestions for comparisons are listed in the specific comments below. The limitations of the GCMS are not clear so if isomer identification cannot be performed it should be explained why.

I also believe there should be more discussion of figures of merit and uncertainties in both the ammonium-adduct CIMS measurement and inventories. For some species the concentrations are listed at <10 ppt and there should be some statement of limits of detection as well as signal to noise filtering. After these two main comments and other minor comments are addressed, I believe this manuscript is suitable for publication.

Specific comments

Introduction: this is a small comment but there is a little confusion as to how VCP is defined. Are VCPs the actual material (ink, paint, etc.) from which emissions come from or are they the emitted chemical species? Your definition on line 59-60 make it sound like the former but the rest of the introduction sounds like the latter. I think there should be consistency or more definition for the reader since this is propagated throughout.

Line 120: a lot of the species you list that have previous "measurement challenges" can be measured with an iodide adduct CIMS. It seems like one of the largest advantages is the low water dependence on signal but it is not clear which species your method can measure that the ICIMS cannot or the differences in signal and sensitivity. Can you list either in the introduction or methods these advantages for someone who might be considering this method? Since this manuscript is a balance of a technical discussion of the utility of this novel method as well as measurements focused it would be good to highlight how the method stands out.

Line 138: you should either explain what AEROMMA is (and define the acronym) to show why it is important that there would be preliminary VCP measurements here or remove this line. I would suggest removing the line since you reference AEROMMA and GOTHAAM later (which should also be explained with a line if still referencing).

Line 146-147: state in general what factor higher this sensitivity is for relevant molecules to support this.

Line 261-267: there are many species listed in this manuscript with concentrations that cannot be predicted with VCPy which is fine because it's an inventory. I am wondering if the uncertainty in product-specific indoor emission fractions is large enough to account for these discrepancies. Either listing uncertainties for those fractions here or giving an example of why it would or wouldn't change results (e.g., the difference in acetone and ethylene glycol) would reduce some reader assumptions.

Line 283-284: what was your criteria for high signal to noise?

Line 287-290: you should put a y axis on figure 2a even if it is just a relative amount just to show that it is linear and support your statement that there is a low parent ion to fragment ratio. I am assuming it's not a log plot like 2b but I can't make an assumption on no axis. Also if you are going to state that the PTRMS has high parent ion to fragment ratio for similar classes of molecules you should either show a comparative spectrum like in 2b or list some species ratios across the two instruments.

Figure 2: are the high peaks $\geq m/z$ 300 internal standards? If so list that in the figure

caption.

Line 327-331: Since you refer to over and under estimations due to the ensemble of isomers detected in ambient air, can you reduce this uncertainty when using the isomers detected onsite with the GC?

Line 349-350: Can you get closure in the differences in C₃H₆O signal using the contributions of the GC? It looks like from table 1 you were monitoring C₃H₆O.

Line 355-357: without any calibration time series your statement as written does not convince me that this was not ethanol. The PTRMS also has a low response to ethanol but should still provide a measurement to compare this against. The PTRMS also shouldn't measure dimethyl ether well so it would be more ethanol signal for that instrument. I suggest including this comparison.

Line 366-368: this statement of low collisional energy for higher masses seems to be supported from your figure 1 temperature dependence of alpha pinene relative to the other smaller compounds, although this is a hydrocarbon. In fact, the sensitivity goes up for alpha pinene. Would you say that it is the thermal stability of the adduct that drives this temperature dependence or the increased frequency of lower energy collisions of larger compounds? Or is it the relative amount of NH₄H₂O⁺ to NH₄⁺? You should try adding another higher MW compound to figure 1 to support or disprove this or add a line about ion adduct strengths near figure 1.

Figure 4: list where these uncertainties come from. Is it just the standard deviation used in table S2?

Figure S8: is there a reason alpha cedrene and alpha pinene are chosen for OH oxidation? Is that what is prominent in an inventory or was it chosen based on the GC?

Line 552-555: this underestimation in ethylene glycol is interesting. Does this molecule correlate with any other in the spectrum in a meaningful way or is there just a general enhancement in many molecules pre-01/25? This molecule should also be detected by a PTRMS. Was there a strong corresponding signal in the PTRMS? It would be helpful to have a calibrated comparison for this since it's such a large unpredicted concentration and currently there is no explanation other than there must be a higher emission (which is fine).

Line 568: 10 ppt of C₄H₁₀O₂ and 5 ppt of C₆H₁₂O₃ is great. Are these concentrations listed averaged over 1 Hz or higher? It would be helpful to list some general limits of

detection for this method and if they're already presented in another paper you should refer to that paper with some numbers. It would support how useful this method could be for the reader.

Line 708-711: can you show that this was from a biomass burning source from a backward trajectory analysis or a CO measurement? If these species tracked with others that you would assume were from VCPs this could be a helpful way to distinguish them and reduce uncertainty in your model.

Figure 7: is there any product-specific uncertainty you can place on these models that would modify the emissions ratios or is the uncertainty just general that applies to all species? I think including some model uncertainty in either the model descriptions or here would be helpful.

Line 863-865: some of these species could be measured with a PTRMS. Can you provide a comparison to show that there is a strong deviation from the model for this ratio for the PTRMS too?

Technical corrections

Line 152: use consistency in ammonium or NH_4^+ .

Figure S9: the species need to be legible.

Line 428: define "k value"

Figure 5: the x axis ticks need to be consistent for each figure.

Figure S9: the axes and error bars are illegible even if zoomed all the way in. This needs to be corrected.

Figure S10: a suggestion: making the colorbar linear (e.g., viridis in python) would make this a lot easier to interpret. This could be a really neat plot if it was easier to track the inventory emissions.

Figure S13: same comment as Fig S9. The axes and error bars are illegible even if zoomed all the way in. There are a lot of species but they can't be read.