Dear Editor,
We would like to thank all referees.
As only referee #5 raised some comments and suggestions (in black), please find enclosed our response (in blue). We hope that the manuscript can now be published in AMT.

With kind regards, Armin Hansel

Anonymous Referee #2

accepted as is

Anonymous Referee #4

accepted as is

Anonymous Referee #5

This review reports on observations of 10 to 30-carbon containing ions formed detected in the new PTR3-TOF instrument from Ionicon during isoprene + O3 experiments conducted at the CERN CLOUD chamber in 2015 and 2016. They conclude that part (2/3) of C10 containing species detected before oxidation arise from secondary ion/molecule reactions of protonated isoprene with additional isoprene within the PTR3 instrument due to the high pressure and long reaction times. The remainder (1/3) of signal is proposed to arise from C10 compounds present in the gas-phase isoprene standard (gas cylinder) formed from diels alder cycloaddition type reactions of isoprene. They show that the C10 compounds can be at least partially removed from the isoprene by passing the gas through a cold trap (-57C), and more importantly, that these impurities constituted a significant fraction of the highly oxygenated material (HOM) formed during the O3 + isoprene experiments.

While the manuscript is not substantially different from the initial submission, I will argue that this type of paper has an important place in the scientific literature. All too often 'negative' type results are not reported due to idea that these are not publishable. While the results published here could easily be placed within another paper alongside more scientifically interesting ideas, there is no reason in today's electronic age that they cannot be also published as standalone technical notes. Not reporting such results leads to others repeating and rediscovering (or worse, not discovering!) the same problems. So, after consideration of the following points, I suggest this manuscript is appropriate for publication in AMT.

Main comments:

Introduction: Own it: I suggest the authors truly commit to writing this type of paper. [Sub-text: Re HOM yield measurements: one needs to be extremely careful regarding purity of precursor, as small impurity high HOM yielding species can have major impact on inferred yield of target species]. Instead of the introduction focusing on how isoprene may suppress HOM formation in the atmosphere – something the rest of the paper really has little to nothing to do with – limit introduction to discussion of what HOM are, why they are important, how they are formed, and why/how very tiny (<1%) impurities in precursor can significantly impact results. What about impurities in other compounds, like say terpenes?

The introduction was rewritten according to the reviewer suggestions to put the focus on HOMs.

Add a figure showing the diels alder dimerization with identified products… with your detection methods and you conclusively identify products? Or do you only get molecular formula?

PTR-TOF technology only allows the measurement of molecular formulas.

Offline GC/MS analysis confirmed the presence of nine monoterpene isomers inside the gas bottle which could not be specified due to lack in standards.

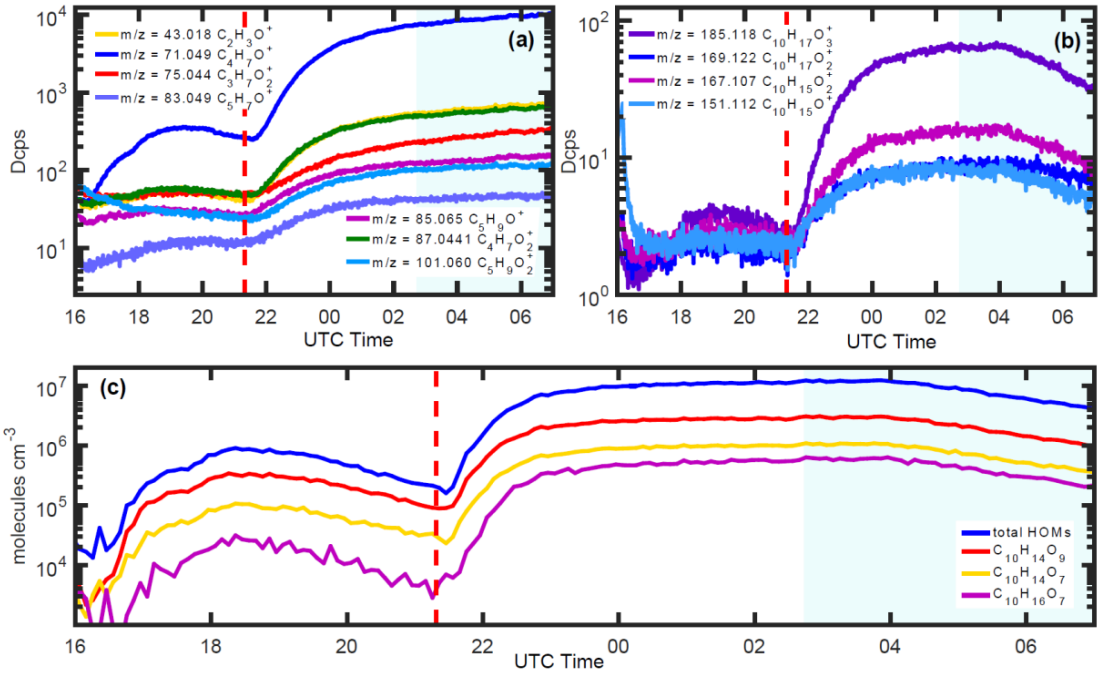
We have discussed these results and cite the relevant literature concerning diel alder dimerization.

Quantification: Manuscript discusses C10 impurities relative to isoprene as a fraction (molar?), while figures show normalized ion counts. The calibration procedure, how one moves from one to the other, needs to be discussed.

This was done, the calibration procedure was described and sensitivities are now included in the 2.1.1 PTR-TOF part.

Add figure, or perhaps a panel to Figure 4 of HOM timeline for experiment shown in figure 4. Show total HOM, and major HOM components.

Figure 4c (panel) was added. (see below)



Specific comments:

P2 L6: define HOM. – done

P2 L20-21: Suggest removal of this sentence. This issue is seemingly unresolved and mounting evidence to the contrary.

The Introduction was rewritten as suggested.

P3 L1: typo ‘20016’ – done

P6 LN20: Maybe… but this statement is somewhat speculative, as is. I.E. Some C10 species could have been introduced into the bottle when standard was made. Or some dimer could be made in regulator on way to instrument? Perhaps expand this discussion to include more possibilities and your lines of reasoning for excluding certain pathways.

The isoprene standard was made by an external supplier (see below) and came with a certificate of analysis, stating the isoprene purity. Section 3.2

We have included GC/MS results from the isoprene bottle showing that 9 monoterpene isomers were present in our bottle.

The total monoterpene impurities increased within one year in the same bottle from 2015 to 2016. We speculate that this is caused by dimerization reactions within the gas bottle. Dimerization was observed by other groups through diel alder reactions, which is referenced.

P7 LN9-10: This statement as written is somewhat confusing: Are you saying that you made the gas standard from liquid isoprene containing 139 ppm TBC? If so, why not include a complete description of the standard; when it was made, how it was made. How it was certified, etc. Note, that some people when working with isoprene use only the vapor over the liquid to use in experiments (presumably this contains much less impurities, than complete evaporations). What type of bottle was this standard stored in? How was standard certified as a function of time? Did you measure the stabilizer with the PTR? – All useful details to include.

This was done.

In detail:

The gas standard was prepared by an external supplier, Carbagas, using purest nitrogen and liquid isoprene (≥99 % purity) from Sigma Aldrich. According to the Isoprene certificate of analysis it contained 139 ppm of TBC and had a purity of 99.8 % according to GC analysis. It is the same kind of liquid isoprene (https://www.sigmaaldrich.com/catalog/product/aldrich/464953?lang=de&region=DE) that other studies use as gas (head space from that liquid). The standard was not certified as a function over time as it's use was still well within the guaranteed timeframe for stability as confirmed by the supplier. However an offline GC analysis of the gas bottle was carried out after CLOUD 10, confirming the presence of TBC as well as the presence of nine different monoterpene isomers. A more conclusive identification of the monoterpene isomers was not done due to lack of standards.

The sentence was changed to: "*This known dimerization is the reason for the addition of p-tert-butyl catechol (TBC) as a stabiliser to the liquid isoprene (Sigma Aldrich, ≥99 % purity, with addition of 139 ppm TBC) which was used for creation of the gas standard provided by the supplier. The stabiliser itself could not be identified by PTR3-TOF due to an interference with major monoterpene oxidation products (C10H14O-H+).*"

P8 L9: insert space between 'that' and 'despite' – done

P8 L29: add 's' to mechanism – done

P8 LN27-30: C10 produces HOM in described experiments appears well established here; however, the second part, is not established well. Does the C10 species impact the HOM production from real isoprene in these experiments significantly? Without further data/quantification included, I'm not sure this can be concluded.

We added the following sentence: *The impact of the C10 contaminant is most prominently visible in the significant decrease of C10 compounds and the disappearance of C15 and C20 compounds upon activation of the cryotrap as shown in fig. 5b where the mentioned formation pathway via said accretion reactions is no longer feasible and less HOMs are formed.*

P9 LN4-5: Is there a better place for this sentence? Seems out of place. Remove 'intensive'. – done

P9 LN14-18: Something amiss with numbers here: higher HOM concentration yields lower J? Also, J1/J2 doesn't give 23? – done.

P9 LN30: add 's' to 'user' – done

P10 L1: word 'identical' is used here but throughout the paper 'monoterpene-like' is used. These seem inconsistent with each other. Either they C10 species are monoterpenes or they aren't

It reads now "monoterpenes" throughout the paper.