Comments prepared by Lindsay Yee, Gabriel Isaacman-VanWertz, and Allen Goldstein

In light of the uncertainty surrounding the molecular structure(s) that actually lead to observations of C5-alkene triols in chromatography based techniques and C5H10O3 measurements in CIMS, we think that there are areas of your manuscript that should be adjusted per below.

I. Citation of literature:

A. Line 87: Reference to Isaacman-VanWertz et al., ES&T 2016 would be appropriate here
B. Section starting line 289: Why not also compare results to field measurements of volatility as in Hu et al, ACP, 2016, DOI: 10.5194/acp-16-11563-2016?
C. Consider providing additional chemical understanding of proposed compounds in Figure 7 and their expected behavior under programmed thermal desorption and hydrolysis affecting oligomer/accretion products recovery as in Claflin and Ziemann et al., AS&T, 2019, DOI: 10.1080/02786826.2019.1576853. Are your isothermal evaporation results with humidified air providing opportunity for hydrolysis? While lines 52-56 state that your methods confirm that these products are artifacts of thermal decomposition/hydrolysis, hydrolysis is not discussed explicitly elsewhere in the manuscript as it applies to your measurements.
D. Lines 224-227: Reword to be more accurate. Lopez-Hilfiker et al., 2016, pg. 2204 states that a sum of tracers in CIMS measurement that are highly correlated with C5H12O4 and C5H10O3 explain 50% of IEPOX-SOA factor mass, not just C5H12O4 and C5H10O3.
E. Line 455: Do you mean Lin et al., ES&T 2014, DOI: 10.1021/es503142b, instead of Lin et al., ES&T 2012, or in addition?

II. Be more precise in language throughout the manuscript relating instrument's observation of a chemical formula (which even stated in line 47 that C5H12O4 is "presumably" 2-methyltetrols) yet in other areas claim unwarranted certainty in the chemical structure of C5H12O4 and C5H10O3. This also needs to be adjusted regarding relation to findings under chamber conditions and then related to atmosphere. Language should be adjusted throughout; some examples specifically listed below:

A. Lines 52-56: "We thus confirm, using controlled laboratory studies, recent analyses of ambient SOA measurements showing that IEPOX SOA is of very low volatility and commonly measured IEPOX SOA tracers, such as methyltetrols and C5-alkene triols, result predominantly from artifacts of measurement techniques associated with thermal decomposition and/or hydrolysis." As it is not verified if the C5-alkene triol structure is what gives C5H10O3 in CIMS (standards don't exist yet, though semi-reasonable to assume from a chamber experiment), this statement is not supported enough. Further, Surratt's HILIC method (Cui et al., Environ. Sci. Process. Impacts, 2018) which does measure some higher order organosulfates and oligomers still does not account for all C5-alkene triols as stemming from decompositon (<50%), so is it fair to say predominant? Maybe just predominant for chamber conditions tested here?
B. Lines 220-224: The chemical formulae observed by FIGAERO CIMS are consistent with those from actual chemical species observed by other techniques. Line 221 should be adjusted to something more like, "These chemical formulae are consistent with those of chemical species (i.e. 2-methyltetrols and C5-alkene triols, respectively) that have been repeatedly shown to be major components of IEPOX SOA…"
C. While lines 270-278 are precisely worded to state that the interpretation of C5H10O3 as observed in chamber SOA derives primarily from thermal degradation, this does not warrant broad generalization to the atmosphere as in lines 52-56, lines 494-497. Considering there are other potential chemical conditions under which C5-alkene triols may be observed, but not tested here there should be room left for these possibilities, even if less abundant in the atmosphere including:
    i. IEPOX uptake on non-acidified seed/dry particles:
        1. Nguyen et al., ACP, 2014, DOI: 10.5194/acp-14-3497-2014
        2. Riva et al., ES&T 2016, DOI: 10.1021/acs.est.5b06050 (Fig. 2 shows C5-alkene triols observed under dry conditions and wet conditions)
        3. Lin et al., ES&T 2014, DOI: 10.1021/es503142b (Fig. S2 shows C5-alkene triols observations under wet_netural and dry_acidic conditions)
        4. D'Ambro et al., ACP, 2017, DOI: 10.5194/acp-17-159-2017 (Fig. 4 shows C5H10O3 observation)
    ii. Non-IEPOX pathways:
        1. Liu et al., ES&T 2016, DOI: 10.1021/acs.est.6b01872, as C5H10O3 is also observed here reported in Figure 3
        2. Riva et al., ES&T 2016, DOI: 10.1021/acs.est.6b02511, as C5-alkene triols are observed as reported in Figure 1
    iii. isoprene ozonolysis leading to structures proposed as sulfate esters of C5-alkene triols as in Riva et al., Atmos. Env. 2016, DOI: 10.1016/j.atmosenv.2015.06.027)

III. The connection of FIGAERO-CIMS measurement of C5H10O3 being equivalent to the same C5-alkene triols signal reported from GC-MS is not clear unless an intercomparison was done previously. If done, then please cite the reference:

A. Lines 494-497: Claim of confirmation that C5-alkene triols and/or 3-MeTHF-3,4-diols are all artifacts of thermal decomposition is too strong given that it has not been established if what the FIGAERO CIMS measures as these compounds (C5H10O3) is actually the same as what other techniques (GC/MS) would assign to be C5-alkene triols and/or 3-MeTHF-3,4-diols. Where is there direct comparison of FIGAERO-CIMS measured C5H10O3 and other techniques measured C5-alkene triols and/or 3-MeTHF-3,4-diols to prove that the compound/s is/are the same?

B. Further, this means the conclusive statement in lines 522-523 is not supported to broadly overgeneralize that GC/MS methods are incorrect. As there are a variety of ways in which GC/MS methods are employed to measure isoprene-derived tracers as well as how the samples are handled and treated before GC/MS analysis, it does not seem appropriate to mention this here without performing proper intercomparisons or going into more specifics as to why all GC/MS methods would lead to thermal decomposition of these products. Thus, statements about specific tracers being "artifacts" or somehow not being useful measurements are misleading and unnecessary. It seems more productive to focus on what the community can learn from the different methods, and what the different tracers teach us, rather than denigrating a particular measurement approach because it sees a combination of products that may include pieces that decompose from larger molecules. For example, the UPLC/HILIC/GC/MS methods provide more specific information (more highly speciated EI mass spectrum of individual tracers that elute from chromatography columns) than the direct CIMS (sum of isomers as a function of desorption temperature) or AMS (EI mass spectrum of the total), but using all the observations we can learn more (not less) about the chemical composition, sources, and transformation processes in organic aerosols.

IV. For some of the structures (organosulfates/polymers) proposed to lead to C5H10O3 via decomposition, can you estimate their C*/Tmax and do they make sense with the observed thermograms?