

We thank the commenters for their careful reading of our manuscript and helpful comments. Our point-by-point responses are below the comments, highlighted in blue.

Most of the comments by Dr. Yee et al. are centered around how the FIGAERO-CIMS measurements described in our manuscript relate to specific chemical compounds reported by other measurement techniques (e.g. GC/MS), especially given that the FIGAERO-CIMS does not separate by structure/isomer. We think it is therefore helpful to start by summarizing some aspects of FIGAERO-CIMS as a top-down constraint on molecular components and how those inform our main scientific conclusions in this study.

Our goal in this study is not to explain the measurement of specific compounds, such as C₅-alkene triols reported by other instruments, but rather to draw conclusions about the presence of C₅-alkene triols and related isomers generally in ambient SOA and specifically in SOA generated from reactive uptake of IEPOX. We have clarified that our work in no way comments on the potential for C₅-alkene triols to be present in the gas-phase, nor that other measurement techniques may measure C₅-alkene triols from sources other than IEPOX SOA. However, as we discuss below, if C₅-alkene triols and related isomers are in SOA, then the FIGAERO-CIMS would measure them, and this constraint provides insight into the nature of C₅-alkene triols, C₅-furan diols, and related isomers in ambient SOA and IEPOX-derived SOA specifically.

We do not have any reason to expect that the FIGAERO-CIMS using Iodide adduct ionization is not sensitive to C₅-alkene triols, and furan diols, based on direct calibrations of compounds with nearly identical structures shown in part in this manuscript and others [Iyer et al., 2016; Lopez-Hilfiker et al., 2016]. Thus, we fully expect to measure C₅-alkene triols and furan diols [Iyer et al., 2016] should they exist in the particle phase. While FIGAERO-CIMS does not speciate across isomers, the signal at C₅H₁₀O₃ is a top-down constraint on the sum-total of C₅-alkene triols, furan diols, hydroxy hydroperoxides, dihydroxy epoxides, hydroxy carboxylic acids, and dihydroxy carbonyls.

Importantly, we have yet to find a structure with the C₅H₁₀O₃ composition that is not detected by FIGAERO-CIMS. We have calibrated to IEPOX, ISOPOOH, alkane triols, and a furan diol with this specific composition, as well as similar hydroxy acids and hydroxy carbonyls [Lee et al., 2014]. Thus, the behavior of C₅H₁₀O₃ components in the FIGAERO-CIMS is a constraint on the behavior of commonly measured IEPOX SOA tracers. We think it useful to make this point in the manuscript, that commonly measured tracers of IEPOX SOA reported by other techniques, such as the C₅-alkene triols and furan diols, would fall into this category and be measured by FIGAERO-CIMS.

Summarizing the above, if C₅-alkene triols, furan diols, IEPOX, or ISOPOOH are present in the aerosol, the C₅H₁₀O₃ signal in the FIGAERO-CIMS accounts for that carbon. We likely underestimate the amount of furan diols due to a slightly higher sensitivity to triols, on which we base our conversion of C₅H₁₀O₃ signal to mass concentrations and is a reason we have a low-bias compared to the AMS. That is, stating that the FIGAERO-CIMS accounts for ~50% of IEPOX PMF factor mass from the AMS is a conservative estimate because we currently underestimate contributions from furan diols. It is also possible that the AMS factor is not completely specific to IEPOX derived SOA.

Given that i) we do not observe multiple or broad desorption profiles of C₅H₁₀O₃ (which would possibly imply multiple isomers), ii) that we replicate the field measured desorption profile of C₅H₁₀O₃ in the laboratory using only IEPOX reactive uptake, and iii) that the C₅H₁₀O₃ desorption profile is only consistent with a species having much lower volatility than that of a freely partitioning C₅-alkene triol or furan diol (or IEPOX, ISOPOOH, etc), we conclude that such isomers do not exist in organic aerosol

freely and are instead artifacts of thermal decomposition of a much lower volatility product such as organosulfates, or associated IEPOX-derived oligomers, known independently to also form from IEPOX reactive uptake.

If such components of IEPOX SOA thermally decompose in the FIGAERO, a reasonable hypothesis is that they thermally decompose in other analytical methods that also similarly heat the sample, potentially leading to the same detected tracers ($C_5H_{10}O_3$ isomers). We have reframed our conclusions to make clear that this extrapolation to other methods is a hypothesis that can be tested, and that to some degree has been, and is supported by independent experiments by Cui et al. [2018]. More direct comparisons could certainly provide better tests of specific isomers desorbing from IEPOX SOA or other types of organic in different analytical methods.

In light of the uncertainty surrounding the molecular structure(s) that actually lead to observations of C5-alkene triols in chromatography based techniques and $C_5H_{10}O_3$ 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

Reference added.

- 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?

We have added a reference to Hu et al. [2016] on line 377 when discussing the volatility of the ambient aerosol.

- 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.

For Figure 7, we are highlighting possible pathways that could explain the time-evolution of our measurements (Figure 6), and effective volatility of IEPOX SOA components that we measured. We have added a statement to this effect on lines 430-432 (copied below) and changed the figure caption to highlight that these are hypothetical processes, albeit based on evidence in other publications. As for hydrolysis, we are evaporating the aerosol at the same RH as their formation, i.e. 50% RH, so we do not believe we would be driving more hydrolysis than would be occurring in the chamber. We have removed the statement about hydrolysis from the abstract.

“...illustrated in Figure 7 which shows hypothetical reaction pathways and oligomers that could explain the observed time-evolution of detected products.”

- 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 $C_5H_{12}O_4$ and $C_5H_{10}O_3$ explain 50% of IEPOX-SOA factor mass, not just $C_5H_{12}O_4$ and $C_5H_{10}O_3$.

Figure 1 in Lopez-Hilfiker et al. [2016] shows that the sum of FIGAERO-CIMS tracers varies from explaining ~50-90% of the AMS IEPOX-PMF factor. Figure S3 shows that $C_5H_{10}O_3 + C_5H_{12}O_4$ make up >80% of the total sum of tracers (which includes 6 additional ions). Thus our wording on lines 227-230 that the FIGAERO-CIMS $C_5H_{10}O_3 + C_5H_{12}O_4$ make up ~50% of IEPOX SOA mass measured by the AMS is accurate with reference to Lopez-Hilfiker et al. [2016]. See also above discussion of the IEPOX SOA reported by the FIGAERO-CIMS in Lopez-Hilfiker et al. [2016] being a conservative estimate.

- 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?

We have added a reference to Lin et al., ES&T 2014 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 $C_5H_{12}O_4$ is "presumably" 2-methyltetrols) yet in other areas claim unwarranted certainty in the chemical structure of $C_5H_{12}O_4$ and $C_5H_{10}O_3$. 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 $C_5H_{10}O_3$ 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 decomposition (<50%), so is it fair to say predominant? Maybe just predominant for chamber conditions tested here?

As discussed above, our measurement of $C_5H_{10}O_3$ would include C5-alkene triols and 3-MeTHF-3,4-diols, as well as other related isomers. We have changed the wording throughout the manuscript to use the measured formula for the tracers and indicate that they are presumably, but not definitively, the 2-methyltetrols and C5-alkene triols or 3-MeTHF-3,4-diols. We can't think of another structure other than the 2-methyltetrols for $C_5H_{12}O_4$ appearing from authentic IEPOX reacting in the dark in the presence of only aqueous acidic aerosol and no oxidants. We'd happily add a reference to other isomers that would have that composition under those conditions should we be made aware of them.

- 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..."

We have changed the wording to now read: "Species with these compositions 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 $C_5H_{10}O_3$ 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-

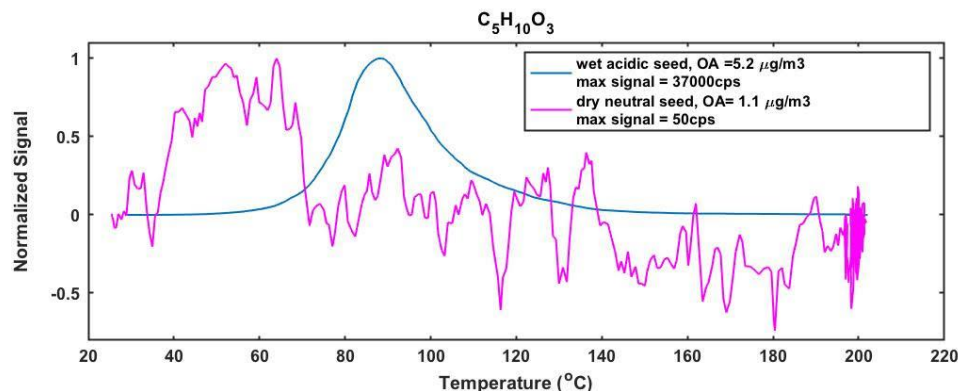
497. Considering there are other potential chemical conditions under which C₅-alkene triols may be observed, but not tested here there should be room left for these possibilities, even if less abundant in the atmosphere including:

We basically agree that there are likely multiple sources of C₅H₁₀O₃ during a thermal desorption and this is what we're trying to convey in figure 7. While the isothermal evaporations are evidence that C₅H₁₂O₄ exists partly as a monomer in the particle phase, we don't have any evidence that isomers of C₅H₁₀O₃ from IEPOX uptake exists in a monomer form in the particle phase. Due to the simplicity of the inputs (IEPOX + acidified ammonium sulfate + aqueous seed), there are limited combinations of monomeric units possible in these chamber experiments, hence why two species (C₅H₁₂O₄ & C₅H₁₀O₃) make up such a large portion of our measurements. In addition, the fact that our chamber and ambient thermograms for C₅H₁₀O₃ ([Lopez-Hilfiker *et al.*, 2016], figure 1) are rather narrow suggests that what we are measuring also likely comes from compound/s that have similar bond strengths that are breaking within a fairly narrow temperature range to produce C₅H₁₀O₃ (see also Shobesberger *et al.* [2018]). As noted above, these components have nearly the same effective volatility (T_{\max}) as measured by the FIGAERO in chamber generated IEPOX SOA and in ambient OA measured in the field. Thus, the field measurements made with the same instrument and setup [Lopez-Hilfiker *et al.*, 2016], are very similar to the chamber results, and this similarity is the support for concluding more generally about the sources of C₅H₁₀O₃ in IEPOX SOA.

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_natural and dry_acidic conditions)
4. D'Ambro *et al.*, ACP, 2017, DOI: 10.5194/acp-17-159-2017 (Fig. 4 shows C₅H₁₀O₃ observation)

We respectfully disagree that the above references represent counter examples to our conclusions. IEPOX can undergo the same ring-opening chemistry and oligomerization in aqueous ammonium sulfate particles which likely have a pH of 4-5 based on aerosol thermodynamic modeling, and will depend on RH [Gaston *et al.*, 2014], only slower. In references 2 and 3, "dry" does not necessarily mean "solid" as the acidification used likely leads to ammonium bisulfate or even sulfuric acid solutions which remain deliquesced even if some ammonium sulfate effloresces at low RH. We show below that the C₅H₁₀O₃ reported in reference 4, which did use effloresced ammonium sulfate seed, is present at nearly 2 orders of magnitude lower mass fraction of the OA with a desorption profile markedly different than the IEPOX tracer discussed in this work.



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)

As noted above, we agree that C₅H₁₀O₃ components could arise from other pathways. But, reference 1 under non-IEPOX pathways is based on the same set of experiments as in reference 4 above, and as noted the C₅H₁₀O₃ in that system behaves nothing like what we describe for the IEPOX system nor what we observe in ambient SOA. As for isoprene ozonolysis leading to sulfate esters, we cannot comment as we have not conducted similar experiments, but our ambient measurements would suggest they either decompose in the FIGAERO the same as IEPOX-derived organosulfates or they are a small contribution to ambient SOA.

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?

We refer to the general discussion above about the top-down constraint provided on these isomers with the FIGAERO CIMS. We have not attempted direct comparisons but agree such could be useful. However, we don't think such comparisons are required to make our conclusions given that the FIGAERO CIMS is sensitive to these isomers, and that using similar or even authentic standards of them demonstrates how different the IEPOX SOA and ambient OA components with the same composition behave during a thermal desorption. For example, we directly compare the thermal desorption of pure 3-MeTHF-3,4-diols to thermal desorptions of the IEPOX SOA components and show they are entirely

inconsistent with these isomers being present as free monomers in the aerosol. Our best explanation is thermal decomposition. The new experiments described here illustrate that another possible explanation, monomers trapped by highly viscous OA, is unlikely due to the rapid and nearly complete evaporation of the species measured at $C_5H_{12}O_4$.

- 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.

We stress that our goal is not to denigrate any particular instrument or method. Moreover, we further stress that even though we conclude $C_5H_{10}O_3$ components are detected in the FIGAERO CIMS analysis of IEPOX SOA due to thermal decomposition, those tracers are highly useful for source apportionment of OA. And we agree that the suite of instruments are useful and necessary for making progress on understanding the sources and properties of SOA.

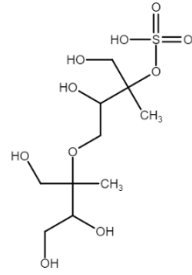
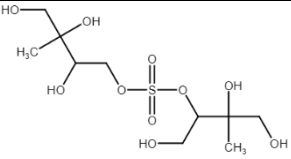
We have made it clearer that our results suggest a hypothesis that other methods that utilize heat in the workup procedures or online analyses would detect IEPOX SOA tracers which are the result of thermal decomposition of low volatility components. We also make it clearer that, using the FIGAERO CIMS specifically, we find no evidence for IEPOX SOA components with an elemental composition of $C_5H_{10}O_3$ and desorption profile consistent with a free monomer partitioning based on its solubility or saturation vapor pressure. The resulting section, which also address points from IIIa above, are on lines 516-523 and below.

We further confirm that the observed properties of $C_5H_{10}O_3$ are not consistent with the structure of C_5 -alkene triols and/or 3-MeTHF-3,4-diols, and thus these structures cannot be components of IEPOX SOA but are likely artifacts of thermal decomposition during analytical workup. A direct intercomparison is required to definitively determine whether all instruments are measuring the same species and that prior estimates of IEPOX SOA have not been overestimated due to "double counting" carbon in these tracers which might be derived from organosulfates and oligomers measured separately.

The evidence presented herein, as well as in independent experiments [Cui et al., 2018], indicates that the $C_5H_{10}O_3$, regardless of structure, as well as a significant portion of the $C_5H_{12}O_4$, are not actual components of the SOA but rather derived from other related components during the analysis. Therefore, we do not recommend that these species be included as products in mechanistic models of IEPOX SOA formation and evolution.

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

We do not have direct measurements of the species that decompose and lead to the detection of C₅H₁₀O₃ as they do not survive our analysis. However, we can estimate the c* of the dimer species in Figure 7 based on group contribution methods [Compernelle *et al.*, 2011]. The very low c* supports the idea that these species with their weaker ether and sulfate bridges will likely undergo decomposition prior to volatilization.

Structure	SMILES	Estimated c* (μg/m ³)
	<chem>CC(CO)(OCC(O)C(C)(CO)OS(O)(=O)=O)C(O)CO</chem>	0.0001
	<chem>CC(O)(CO)C(O)COS(=O)(=O)OC(CO)C(C)(O)CO</chem>	0.00006

References

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