

We thank the referees for their valuable comments. We respond below each comment in blue highlighted text and indicate the corresponding changes to the manuscript where relevant.

#### Anonymous Referee #1

##### General comments

This manuscript describes laboratory experiments using the Filter Inlet for Gases and Aerosols/Chemical Ionization Mass Spectrometry (FIGAERO-CIMS) technique that aim to investigate the nature of the components of IEPOX-derived secondary organic aerosol (IEPOX-SOA). Specifically, the work addresses the inconsistency between GCMS approaches that have identified semi-volatile molecular components and volatility measurements that have indicated that the bulk of IEPOX-SOA must be made up of much lower volatility molecular components. The main claim is that a desorption signal that corresponds to  $C_5H_{12}O_4$  has two maxima, one that arises from a semi-volatile source (presumably from 2-methyl tetrols directly evaporating) and one that arises from the thermal decomposition of a low volatility source and a desorption signal that corresponds to  $C_5H_{10}O_3$ , which also arises from the thermal decomposition of a low volatility source. Because knowledge of the molecular composition of IEPOX-SOA is critical to the development of accurate SOA mechanistic models, this work will be of great interest to readers of Atmospheric Chemistry and Physics. However, I believe that a number of uncertainties remain in the interpretation of both the present work and past studies, and that a revised manuscript should more directly address these issues.

##### Specific comments

Because of a lack of authentic standards, there continues to be no proof whatsoever that either the GC/MS signals previously attributed to C5-alkene triols or the present CIMS signals attributed to C5-alkene triols actually correspond to these species. Indeed, Watanabe et al. 2018 showed that these species are among the least thermodynamically favored among a variety of possible  $C_5H_{10}O_3$  isomers. I suggest that the manuscript be revised to simply refer to a  $C_5H_{10}O_3$  thermal decomposition product and refrain from associating this product with any particular molecular form.

This is a good point. We have changed and clarified wording, specifically on lines 123-125, 294, and 511, however we do think it useful in various places to connect this component to tracers of IEPOX SOA reported in the literature with the same elemental composition.

Similarly, while I find the argument fairly convincing that the semi-volatile  $C_5H_{12}O_4$  component is probably the 2-methyl tetrols themselves, I don't think the low volatility thermal decomposition product can be assumed to be the 2-methyl tetrols.

Agree, our point was supposed to be that there is a semi-volatile component with the composition  $C_5H_{12}O_4$ , likely the tetrol, but also an additional lower volatility component that decomposes into  $C_5H_{12}O_4$  during the thermal desorption as reported in field measurements by Lopez-Hilfiker et al. [2016]. We have adjusted the wording on lines 294, and 337-338.

The proposed oligomerization mechanism given in Figure 7 would benefit from more detailed discussion. Rather than a more obvious mechanism directly involving IEPOX, the authors are proposing two types of reactions: 1) acid-catalyzed etherification reactions of organosulfates to form ether-linked oligomers and 2) acid-catalyzed sulfate esterification reactions to form sulfate-linked oligomers. The

authors don't provide any literature precedents for these types of reactions. Therefore, I think the authors should provide a rationale for these somewhat unusual reaction types.

We have clarified that the schematic in Figure 7 is a hypothetical set of net transformations to explain the slower shifts in IEPOX SOA volatility and thermogram shape presented in Figure 6. We think a majority of the IEPOX SOA is low volatility, and agree most is indeed formed promptly through IEPOX aqueous phase chemistry to form the organosulfate, or even polyols. These other hypothetical reactions are to offer an explanation for the slower evolution of IEPOX-derived SOA volatility/composition taking place in the absence of IEPOX during isothermal evaporation experiments and at longer times in the batch mode experiments when prompt SOA formation has slowed or even ceased but the SOA continued to age.

Along the same lines, the overall interpretation would benefit from estimates of the thermal desorption behavior of the proposed oligomer components. Did the authors suggest two isomers of a monosulfate dimer as their major proposed molecular species because C<sub>10</sub>H<sub>22</sub>SO<sub>10</sub> is expected to have roughly the observed thermal desorption behavior?

As stated above, we are unfortunately not able to measure these oligomer (or monomer organosulfate) species as we suspect they are decomposing completely during our analysis. In our response to Yee et al., the final comment, we have estimated  $c^*$  based on the EVAPORATION group contribution method [Compernelle et al., 2011] for some of these hypothetical structures and find that they are exceedingly low and thus subject to thermal decomposition during the desorption process before evaporation rates would be sufficient to desorb them from the filter in detectable amounts. We refer the reviewer to other work by the Surratt group proposing and observing the presence of polyol esters [Lin et al., 2014; Surratt et al., 2006; Zhang et al., 2011].

#### Technical comments

Line 87: There should be a reference to Hu et al. 2016 ACP 16, 11563-11580 here.

Reference added.

Line 128: There is something wrong with the grammar in this sentence. Please revise.

We changed the sentence to:

*The data presented herein were taken at the Pacific Northwest National Laboratory (PNNL) as part of the Secondary Organic Aerosol Formation from Forest Emissions Experiments (SOAFFEE) campaign held during the summer of 2015.*

Line 464: I'm not sure why there is a reference to Atkinson, 1987 here. There are two measurements of IEPOX + OH rate constants: Bates et al. 2014 and Jacobs et al. 2013, ES&T 47, 12868-12876, which differ by a factor of two. The choice of rate constant should be explicitly discussed.

Thank you for pointing this out. The model is very simple so we use one gas-phase OH reaction rate which applies to both the IEPOX and 2-methyltetrol. We used the Atkinson SAR method to determine the OH reaction rate with both 2-methyltetrol and IEPOX. The rate found by the Atkinson method was within the range of values found by Bates et al. and Jacobs et al. We have added the references for

Bates & Jacobs and reworded the sentence (see below) to describe our rate-selection process more clearly and now also include the rate.

*We also include a loss of gas-phase species (2-methyltetrol and IEPOX) due to reaction with OH at  $1.8 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  [Atkinson, 1987], consistent with previous studies for the IEPOX + OH rate constant [Bates et al., 2014; Jacobs et al., 2013].*

Overview:

This study sheds new light on the question of volatility and chemical composition of secondary organic aerosol derived from IEPOX, a ubiquitous biogenic aerosol component. IEPOX is known to react in aqueous aerosol to form commonly observed products such as methyltetrols and organosulfates, and compounds with the molecular formula  $C_5H_{10}O_3$  (C5 alkene triols, methyl-tetrahydrofuran-diols, or both) have also been observed in IEPOX SOA. The total reactivity of IEPOX in the aerosol phase and its uptake are known to be highly dependent on aerosol acidity, sulfate content, organic coating, and other parameters, but a detailed chemical understanding of the composition of the resulting organic aerosol is still lacking. Most observations of ambient IEPOX-derived SOA suggest that the majority of the SOA is of lower volatility than the individual species described above, suggesting a greater presence of oligomers and organosulfates and relatively small contributions from methyltetrols, alkene triols, or MeTHF-diols. This work bridges that apparent gap by showing that observed alkene triols or MeTHF-diols are artifacts formed during the thermal decomposition of lower volatility material, as is a portion of the signal observed at the same mass as methyltetrols, while another portion that likely arises from the methyltetrols themselves is volatile and undergoes evaporation from the particle phase on the timescale of 1 hour.

The authors reach these conclusions by observing the uptake of trans-b-IEPOX onto acidified ammonium bisulfate seed aerosol in a series of controlled chamber experiments. They evaluate the evolution of particle chemical composition and component volatility using a high-resolution time-of-flight I- chemical ionization mass spectrometer outfitted with a filter inlet for gases and aerosols, which enables the separation of isobaric compounds by thermal desorption. Thermograms taken at varying humidities and timepoints during the experiments support the assertion that methyltetrols form quickly via direct hydrolysis following IEPOX uptake, and are then both transformed to lower-volatility species and evaporated into the gas phase, where they can be lost to walls or further photooxidation. The remaining IEPOX-derived SOA is therefore of very low volatility, likely including oligomers of the tetrols and organosulfates. Finally, the authors use a simple box model to illustrate how these results might play out under ambient conditions, and show that models using either aqueous uptake or volatility basis set schemes should be modified to account for the high uptake probability of IEPOX followed by re-volatilization of methyltetrols.

While the description of the experiments performed herein and the conclusions drawn from thermal desorption measurements is straightforward and represents a valuable contribution to our understanding of the volatility and chemical composition of IEPOX derived SOA, the extrapolation to ambient conditions remains tenuous and deserves further attention. Additional comparison to ambient results (e.g. Hu et al 2016) would help convince the reader that the results from these chamber studies are borne out in the atmosphere and are relevant to processes that occur in isoprene- and sulfate rich settings. The brief comparison on lines 221-232 is not sufficient, and if anything brings up more questions than it answers as to the validity of comparing field to laboratory results. Does Lopez-Hilfiker et al. suggest that a further 50% of IEPOX SOA observed in ambient consists of tracers that don't even correlate with those identified here, in addition to the fraction that correlates with them but isn't explicitly  $C_5H_{12}O_4$  or  $C_5H_{10}O_3$ ? What are those other tracers and what could explain their absence in these experiments? Ambient particles likely contain much more variability in organic compounds in the

condensed phase with which tetrols and other IEPOX-derived species might oligomerize or otherwise interact. How would that affect the conclusions here and our ability to put simple parameterizations into models? Is there any evidence that products of such cross-reactions result in similar observed compounds upon thermal decomposition?

See the response to comments by Yee et al., opening statement and section II c. To summarize point by point here:

1. We further discuss the ambient measurements on lines 281-289, and now cite Hu et al. 2016 on lines 89-90 and 377.
2. Due to the underestimated contribution from furan diols, the stated 50% explanation of the IEPOX PMF factor mass from the AMS is a conservative underestimate which is discussed within the reference.
3. We agree, with more complexity in the atmosphere it is possible and even likely that other species will oligomerize with IEPOX itself or its reaction products, leading to a more complex picture discussed herein. If these monomeric units oligomerize with different species in the atmosphere, forming different linkages, this will affect their lifetime. The different linkages may also affect the compounds observed upon thermal desorption as noted. However, we measure these monomers in the atmosphere, as have numerous other studies, and rather few other components in our mass spectra correlate with these specific tracers over time, suggesting that the products of a broader set of cross reactions either decompose into the same monomeric composition, are not significant contributors, or are for some reason not strongly correlated with the other IEPOX tracers. However, this complexity does not change the main conclusions of our work or implications for modeling, mainly that IEPOX SOA components with the formula  $C_5H_{12}O_4$  likely represent a major prompt product of IEPOX reactive uptake, but are semi-volatile and thus can partition to the gas-phase, and otherwise remaining components detected as  $C_5H_{12}O_4$  or  $C_5H_{10}O_3$  in the particle phase are likely decomposition of lower volatility oligomers or organosulfates.

Technical comments:

L 136: Is it possible that ethyl acetate interferes at all?

We do not have evidence that it is taken up into the aerosol and would not expect it to as its volatility is very high and solubility rather low. In the continuous flow experiments, the ethyl acetate evaporated completely well before the experiment was over and IEPOX was still present in the chamber. Also, given the similarity between the ambient tracers and chamber SOA composition, it would seem there isn't a major effect.

L 141-143: How does this uncertainty carry through to the conclusions you draw in this study? Since most of your analysis is independent of IEPOX mass, these uncertainties may not affect any major conclusions, but greater discussion of the uncertainties associated with the I- CIMS measurements is warranted. What is the potential for differences in sensitivities to the various compounds measured herein? Is the sensitivity to any given compound known to be constant over the course of a thermogram?

Please see our response to Yee et al. for more detail. Briefly: the I-CIMS is able to measure the species of interest here, namely  $C_5H_{10}O_3$  and  $C_5H_{12}O_4$ , regardless of structure [Iyer et al., 2016]. However, whether the  $C_5H_{10}O_3$  is an alkene triol or furan diol will affect the sensitivity and thus estimates of mass concentration. We use calibrations to authentic triols and diols to constrain these estimates, and generally use instrument response to  $C_5$  triols which is higher per ng than it is for the diols so that our mass concentration estimates are lower limits. Calibration uncertainties are typically 30-50% based on repeated tests, and usually systematic in nature because precision within any individual calibration test is high. We primarily focus on qualitative behavior or intrinsic relative behaviors (e.g.  $T_{max}$ ) in this paper, and thus relative sensitivities do not affect our conclusions.

L 144: What were the concentrations of ammonium bisulfate and sulfuric acid, and what size particles did their atomization generate?

We have added this information in lines 148-157, and copied below.

*Wet, polydisperse acidic ammonium sulfate seed was generated by atomizing an ammonium bisulfate solution acidified with additional  $H_2SO_4$ . The solution was made by mixing ammonium sulfate (0.1308 g) with sulfuric acid (8.02 mL of 0.2465 M) and diluting to a total volume of 1 L with ultrapure water. The average molar  $NH_4^+ : SO_4^{2-}$  ratio measured by the AMS was approximately 0.93 for all experiments, though due to the experimental procedure some interference from organic sulfate formation may exist. The measured  $NH_4^+ : SO_4^{2-}$  ratio is significantly higher than was present in the atomized solution, implying that excess gas-phase ammonia present in the chamber partially neutralized the injected seed. The seed surface area concentrations were approximately 37,600 and 24,000-27,000  $cm^{-3}$  and the volume weighted mode diameters were 106 and 244-254 nm in continuous and batch modes, respectively. Continuous flow experiments were conducted at 50% RH, while the RH of batch mode experiments was either 30% or 50%.*

L 211-214: This sentence is confusing and may be missing a verb or clause.

Agreed, “when” was changed to “with”.

L 216: Speaking of vapor wall losses, how might the wall loss of the re-evaporated 2-methyltetrols affect the results of this study? If you have a large sink to the walls, might Henry’s law equilibrium effectively pull more tetrol out of the particles that would otherwise occur?

Indeed, this effect of vapor wall loss is quite possible. Operating in continuous flow mode helps achieve a steady state that mitigates effects of reversible vapor wall loss somewhat. In the batch mode experiments, we do not see a significant loss of the low- $T_{max}$ /semi-volatile mode over the experimental time scale. That said, attempts to quantify the IEPOX SOA yield, which was not a goal of this study, do need to consider vapor wall loss of the semi-volatile product. We have added this issue to the implications section when we discuss the evolution of IEPOX SOA and the associated simple box-model (lines 481-490), and copied below.

It is not clear how much vapor wall loss affects the results of this study or if we are underestimating or overestimating IEPOX SOA in the chamber. In the atmosphere, photochemical losses of the semi-volatile tetrol in the gas-phase due to reaction with OH (not present in the chamber) would shift more tetrol out of the particle phase than in our chamber experiments (no OH). Moreover, the much smaller aqueous

volume of ambient aerosol particles in the atmosphere compared to that in the chamber would also lead to more of the tetrol re-partitioning to the gas phase than in the chamber. Thus, while vapor wall loss in the chamber likely lowers particle phase tetrol, that effect might be partially or entirely offset by other processes/conditions which enhance particle phase tetrol in the chamber compared to the atmosphere.

*Vapor wall loss is not considered in the model, which might be resulting in more tetrol evaporating from the particles in our measurements than would occur in the atmosphere. However, operating in continuous flow mode helps to mitigate these issues, and in batch mode we do not observe a significant loss of the low- $T_{\max}$ /semi-volatile mode. In the atmosphere, photochemical losses of the tetrol and the smaller aqueous volume of the aerosol would lead to partitioning of the tetrol out of the aerosol. Thus, while vapor wall loss in the chamber likely leads to lower particle-phase tetrol, the effect would be offset by these processes in the atmosphere, and so not considering vapor wall loss in the model should not significantly affect our results.*

Figure 4: Should there be units on UHP N2?

No, it is simply indicating when there was and was not flow (i.e. on or off). We added an explanation for this to line 307 and the figure caption.

L 335: Is the assumption of no particle-phase diffusion limitations a safe one? How might phase separation or organic coatings change these estimates?

Due to the rapid (1 hour) and nearly complete evaporation of the low  $T_{\max}$ /high volatility mode of the C<sub>5</sub>H<sub>12</sub>O<sub>4</sub> species, we have no indication that there is a limitation. Thus, while there may well be organic coatings, we can reasonably conclude there is not a sufficient diffusion limitation to evaporation. The observed evaporation rates are consistent with the expected saturation vapor concentration or solubility calculated or inferred from independent methods.

L 339-342: How close do you expect these estimates of the Henry's law constant to be? A variation of two orders of magnitude seems strikingly large.

The quoted range reflects the range of possible values based on the input uncertainties. The COSMOtherm computation estimates are  $4.9 \times 10^8 - 1.1 \times 10^{10}$  M atm<sup>-1</sup> while the value derived from the observed evaporation rate is more constrained to be  $1-2 \times 10^8$  M atm<sup>-1</sup>. As for saturation vapor concentration estimates, we would treat these quantities as order-of-magnitude estimates given the challenges associated with deriving them both computationally and experimentally in the extremes (low vapor pressures or very high solubilities), and for multifunctional compounds where predictions are especially uncertain [D'Ambro *et al.*, 2017]. In the end,  $>1 \times 10^8$  M atm<sup>-1</sup> is probably sufficient for atmospheric modeling.

L 460: Since other reported values (e.g. Figure 8) are in ug/m3, it would be helpful to report the same units for the starting IEPOX concentration

We added the value in ug/m3 after the value in ppb.

L 460-461: Why were 90% and 10% chosen? How certain are these branchings, and how wide a range might they span in ambient conditions? How sensitive are the simulation results to changes in these numbers, and in the other parameters used?

We have made an educated guess based on previous measurements to the branching ratio, and previous measurements of the IEPOX SOA yield, and thus they are not all that certain. Rather, we use the model as stated, for a simple conceptualization of how  $C_5H_{12}O_4$  would behave in the atmosphere. It's quite possible that this branching is correct, but may span to 50/50, but likely not much higher than 50% OS production based on previous work. The simulation should not be overly sensitive to the branching ratio as the aerosol concentration quickly converges to being dominated by the OS due to the semi-volatile nature of the tetrol product at a rate mainly determined by the solubility or saturation vapor concentration of the tetrol and its gas-phase loss rates.

L 463-464: What rates are used for the gas-phase reactions with OH?

We have added the rate,  $1.8 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , to the manuscript on line 472.

L 499: Hyphen in the wrong place on "2 methyl-tetrol"?

Yes, fixed now.

*Reference:*

Hu, W., Palm, B. B., Day, D. A., Campuzano-Jost, P., Krechmer, J. E., Peng, Z., de Sá, S. S., Martin, S. T., Alexander, M. L., Baumann, K., Hacker, L., Kiendler-Scharr, A., Koss, A. R., de Gouw, J. A., Goldstein, A. H., Seco, R., Sjostedt, S. J., Park, J.-H., Guenther, A. B., Kim, S., Canonaco, F., Prévôt, A. S. H., Brune, W. H., and Jimenez, J. L.: Volatility and lifetime against OH heterogeneous reaction of ambient isopreneepoxydiols-derived secondary organic aerosol (IEPOX-SOA), *Atmos. Chem. Phys.*, 16, 11563-11580, <https://doi.org/10.5194/acp-16-11563-2016>, 2016.

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