Response to reviewer's comments (# 1)

The reviewer said in general comment: The authors greatly improved the quality of the paper.
Author Comment: We feel the comments of Reviewer 1 have aided in improving the quality.

Comment # 1. If the authors want to use acronym they should be consistent (e.g. OS vs OSs) and use them. […] Please go through the article and make it consistent.
Response: This was updated as suggested by the reviewer. We replaced "OSs" with "OS" throughout the manuscript.

Comment # 2. Line 14, page 2. It needs to be rephrased. […] Instead, they should clearly mention that it is probably due to the re-evaporation of the 2-MT as recently suggested. (Isaacman-VanWertz et al., 2016 ES&T).
Response: We agree with the reviewer's comment. We added the appropriate reference and changed the sentence as suggested:

"While many of these are formed through multiphase chemistry (e.g. IEPOX channel), we cannot exclude their gas phase formation at least for 2-methyltetrols – probably in part through the re-evaporation processes (Isaacman-VanWertz et al., 2016) – and for 2-methylglyceric acid, as these compounds have been linked to gas phase reaction products from the oxidation of isoprene (Kleindienst et al., 2009) and in ambient $PM_{2.5}$ (Xie at al., 2014)."

Isaacman-VanWertz, G, Yee, L. D., Kreisberg. N. M, Wernis, R., Moss, J. A, Hering, S. V, de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Riva, M., Surratt, J. D., Viegas, J., Manzi, A., Edgerton, E., Baumann, K., Souza, R., Artaxo, P., Goldstein, A. H.: Ambient gas-particle partitioning of tracers for biogenic oxidation, Environ. Sci. Technol., 50, 9952–9962, 2016.

Comment # 3. The authors claimed that they cannot estimate the aerosol acidity because they didn't have any particle phase measurement providing the concentrations of inorganic species. […] In this previous study the same authors estimated the aerosol acidity, so why don't they use their previous study to determine the aerosol acidity if the parameter (besides the RH) were identical?
Response: The aerosol acidity in Lewandowski et al., 2015 was measured (not estimated) as nmol H^+ per m^3 air sample volume, an acidity measure that gives air concentration (nmol m^{-3}) rather than an aerosol pH. We did report the aerosol acidity in the main manuscript as nmol H^+ per m^3 in tables 3 and 4 caption for ER667 and ER662 experiments. The average aerosol acidity level estimated for acidic seed and non-acidic seed experiments was 275 nmol m^{-3} and 54 nmol m^{-3}, respectively.

As reported in Lewandowski et al., 2015:

"The [H+] air was calculated by dividing the measured aqueous concentration of hydrogen ions by the volume of air collected, as described by Surratt et al. (2007). While this method provides a simple, easily repeatable measure of bulk acidity, it does not fully capture the actual acidity of individual aerosol particles, which is more likely to be of physical significance in these chemical systems. Nevertheless, in the absence of a true aerosol pH measurement, the [H+] air approach appears to provide a useful surrogate measure under sufficiently constrained experimental conditions."

See also our previous response to the same reviewer (comment # 5) that reads:

"We agree with the reviewer that aerosol pH levels or aerosol liquid water concentrations would be of tremendous value to the interpretation of the results. We also generally agree with the reviewer's assessment to use modeling work (i.e., ISORROPIA (Fountoukis and Nenes, 2007); or AIM (Wexler and Clegg, 2002)) of the aerosol acidity and liquid water content, unfortunately, we do not have sufficient composition information to do the modeling with these models (ISORROPIA or AIM) appropriately. While chamber temperature, RH and particle sulfate loading are known for each reaction step, particle phase ammonium and nitrate were not measured in these experiments. And, although not strictly necessary, no gas-phase ammonia or nitric acid concentrations are available (and, as high-NOx experiments, nitric acid concentrations should be non-trivial), further complicating model predictions."

Comment # 4. The experiments performed using AS as seed aerosols are a bit strange. At RH < 40% the seed aerosols should be effloresced and be metastatic (i.e., a crystal). However, the results presented in this study clearly show that the RH matter, which is a bit surprising (e.g., Fig. MS at 9% vs 19%). How do the authors explain such results? […] One explanation might be the larger wall losses due to humid walls but that would imply that 2mGAd are not formed in particle phase.

Response: We agree with the reviewer that the aerosol liquid water was probably negligible in the neutral seed case. We attribute this decrease in the 2-methyltetrol, 2-MGA, and 2 MGA dimer to a decrease in the organic aerosol level as observed by Lewandowski et al., 2015. We now include a sentence to state this specifically and mention the possibility that chamber wall-effects may play a role in this decrease as suggested by the reviewer.

We changed the relevant paragraph to improve the readability as given on page 15-16 to:

"The major SOA components detected were 2-methyltetrols, 2-methylglyceric acid and its dimer, whose maximal estimated concentrations exceeded 800, 350 and 300 ng m^{-3} respectively under low-humidity conditions of RH 9% (Figure 2. At the two lowest humidities, aerosol liquid water is expected to be very low and the decrease in these compounds may not be controlled by aerosol liquid water but possibly by the SOC levels associated with the particles (Lewandowski et al., 2015), although chamber-related wall effects due to water vapor might also play some role. Among compounds detected with LC-MS (Figure 3) are organosulfates derived from acid-catalysed multiphase chemistry of IEPOX (MW 216) and MAE/HMML (MW 200) (Surratt et al., 2010; Lin et al., 2012, 2013; Nguyen et al., 2015). Other components were significantly less abundant. In most cases, increasing the humidity resulted in decreased yields of the products detected, although some compounds were observed at higher concentrations at RH

49% compared to RH 9% (i.e. m/z 199: Figure 3). As found in Table 1, total SOC decreased with increased humidity. Generally, the influence of RH on the product yields was modest consistent with Dommen et al. (2006) and Nguyen et al. (2011), who saw a negligible effect of relative humidity on SOA yield in photooxidation of isoprene in the absence of acidic seed aerosol. By contrast, here the 2-methyltetrols, 2-methylglyceric acid, and 2-methylglyceric acid dimer were found in significantly larger quantities at RH 9% compared to RH 49%. Two recent studies (Lin et al., 2014; Riva et al., 2016) reported an increase in aerosol mass with increasing RH. Riva et al., (2016) also reported an increase in 2-methyltetrols concentrations with increasing RH. However, the initial conditions for those two studies differed substantially from that in the present study. Here, isoprene is oxidized in the presence of NOx and seed aerosol (acidic and non-acidic) under a wide range of RH. In contrast, in Riva et al. and Lin et al. studies, the reactants were hydroxyhydroperoxide (ISOPOOH) and IEPOX oxidized under NOx-free conditions at two levels of RH. In addition, organosulfates, 2-methyltetrols and SOA yields derived from isoprene photooxidation typically have been enhanced under acidic conditions (Surratt et al., 2007a,b, 2010; Gomez-Gonzalez et al., 2008; Jaoui et al., 2010; Zhang et al., 2011). Organosulfates were also formed in non-acidic experiments, probably through radical-initiated reactions in wet aerosol particles containing sulfate moieties (Noziere et al., 2010; Perri et al., 2010). The NOS and OS compounds detected here could have been formed via such a mechanism."

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Response to reviewer's comments (# 2)

Comment # 1. Q16: Data in Table 4 and Figures 4-5 should be presented and discussed in more detail. Provided response "The presence of 2-methyltetrols and 2-methylglyceric acid and their sulfated analogues in isoprene SOA at a wide range of RH conditions, suggests that SOA water content does not affect significantly their formation" only partly answers the request, but at least please correct to "does not significantly".

Response: This was updated as suggested by the reviewer.

Comment # 2. Q20: ISOPROPIA should be ISORROPIA

Response: The name has been corrected in accordance with the reviewer's

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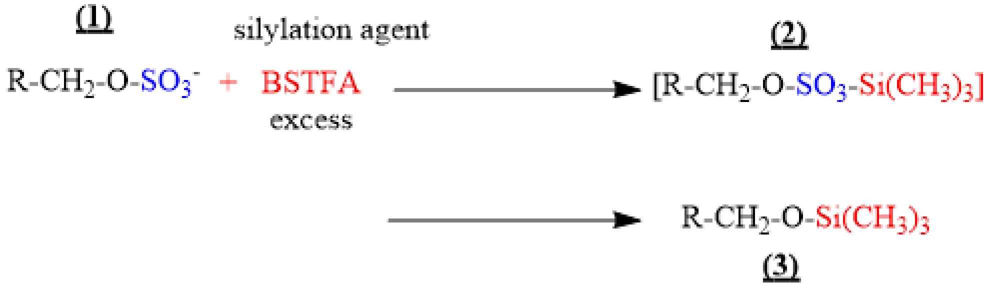
Reviewer's comments (# 3)

This reviewer said in the general comments:

"I thank the authors for revising their manuscript and considering some of my initial comments. Unfortunately, there appears to be some major deficiencies remaining that must be addressed before full publication in ACP can be considered. My largest concern relates to the fact that extreme care must be given when applying GC/Ei-MS (or other thermal analytical methods) to the chemical characterization of isoprene SOA (and likely to other types of SOA in general)**"**

Response. In analytical chemistry, derivatization mainly silylation has been used since the late 1950's in gas chromatography and mass spectrometry for the derivatization of a wide variety of compounds with a wide range of functional groups. Silylation of a polar compound results in reduced polarity, enhanced volatility and increased thermal stability, and enables the GC-MS analysis of many compounds otherwise involatile or too unstable for these techniques. GC/EI-MS analysis of derivatized compounds is not a thermal analytical method as suggested by the reviewer. We showed clearly in our previous revision (see response to comment # 9 from the same reviewer: revision 1) that thermal degradation of accretion isoprene products does not happen in our system using GC-MS analysis of silylated isoprene reaction products. It is possible that the reviewer may be confusing desulfation with thermal decomposition associated with silylation of organosulfate compounds as shown in Reaction 1 below:

Reaction 1: Desulfation reaction of organosulfates upon silylation



Although, desulfation reaction is used regularly mainly in carbohydrates chemistry on sulfated polysaccharides (e.g. glycosaminoglycans) using a variety of desulfation agents (Takano et al., 1992; Kolender et al., 2004; Bedini et al., 206; Bedini et al. 2017 (review)), we are not aware of any study related to desulfation reaction occurring with small organosulfate molecules found in ambient particulate matter. Takano et al. showed the occurrence of desulfation when a silylation reagent was added to carbohydrate sulfates and observed that only primary sulfated alcohols were desulfated (formation of compound 3 from compound 1: Reaction 1). However, sulfated secondary alcohols and other organosulfates were not desulfated (formation of Compound 2 from Compound 1 by Reaction 1). Although some speculation has been reported in the literature of artifacts associated when PM organosulfates are subjected to derivatization, no literature data could be found because of the absence of organosulfate authentic standards. Therefore, more analytical work on desulfation reaction of organosulfates associated with ambient PM is necessary. (References below.)

The reviewer general comment, and Points 1, 2, and 6 make essentially the same argument. The reviewer appears to use this review to promote the LC-MS technique described by Cui et. 2018 over the method used in this manuscript. It is not clear if the main reviewer argument is with the derivatization only when organosulfate are present, although ambient PM can contain hundreds of non-sulfated organic compounds. In our response below by addressing each of the comments separately, we will hope to highlight the main shortcoming of the reviewer arguments, mainly associated with Cui et al. 2018: purity of the standards used, comparison between GC-MS and LC-MS, CIMS-FIGAERO techniques. That said, to reflect the reviewer comments and concerns, and considering the paper by Cui et al. (2018), we have added the following sentences and references to the manuscript on page 6, line 15:

"Silylations of polar compounds result in reduced polarity, enhanced volatility and increased thermal stability, and enables the GC-MS analysis of many compounds otherwise involatile or too unstable for these techniques. Therefore, appropriate caution should be taken, for example, with desulfation reactions associated with primary organosulfates (Takano et al., 1992; Kolender et al., 2004; Bedini et al., 2006; Bedini et al., 2017; Cui et al., 2018), and corrections might be warranted when analyzing methyltetrols."

Takano, R., Matsuo, M., Kamei-Hayashi, K., Hara, S., and Hirase, S. A.: Novel regioselective desulfation method specific to carbohydrate 6-sulfate using silylation reagents, Biosci. Biotech. Biochem., 56 (10), 1577-1580, 1992.

Kolender, A. A., Matulewicz, M. C.: Desulfation of sulfated galactans with chlorotrimethylsilane. Characterization of b-carrageenan by ^{1}H NMR spectroscopy, Carbohydr. Res., 339, 1619–1629, 2004.

Bedini, E., Laezza, A., Ladonisi, A.: Chemical derivatization of sulfated glycosaminoglycans, EurJOC., https://doi.org/10.1002/ejoc.201600108, 2016.

Bedini, E., Laezza, A., Parrilli, M.: A review of chemical methods for the selective sulfation and desulfation of polysaccharides, Carbohydr. Polym., 174 (15), 1224-1239, 2017.

Cui, T., Zeng, Z., dos Santos, E. O., Zhang, Z., Chen, Y., Zhang, Y., Rose, C. A., Budisulistiorini, S. H., Collins, L. B., Bodnar, W. M., de Souza, R. A. F., Martin, S. T., Machado, C. M. D., Turpin, B. T., Gold, A., Ault, A. P., and Surratt, J. D.: Development of a hydrophilic interaction liquid chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol (IEPOX)-derived secondary organic aerosol, Environ. Sci.: Processes Impacts, DOI: 10.1039/c8em00308d, 2018.

Comment #1. "I would argue we (as a research community) need to get away from using GC/EI-MS with prior derivatization for chemically characterizing isoprene SOA, and possibly for other SOA systems. Importantly, a new HILIC/ESI-HR-QTFOMS recently published by Cui et al. (2018, ESPI) from the Surratt group can measure both 2-methyletrols and organosulfates with the SAME non-thermal analytical method without the need of prior derivatization. Further, this is all done in negative ESI mode. Yes, the 2-methyltetrols can be measured by HILIC/ESI-HR-QTOFMS in the negative ion mode and can be resolved from the organosulfates! This is exciting. Furthermore, they showed that 2-methyltetrols measured by GC/MS with prior derivatization was so much higher than HILIC/ESI-HR_QTOFMS, and further showed with authentic standards that the IEPOX-derived organosulfates (i.e., 2-methyltetrol sulfates and 3-methyltetrol sulfates) decomposed into 2-methyltetrols and C5-alkene triols!!! This has to be considered here in this study! Thus, artifacts of GC/EI-MS must be acknowledged and this could affect the interpretation of the current results."

Response. We disagree with the reviewer regarding the statement "get away from using GC-MS with prior derivatization". The author appears to be using this review as a medium to promote advantages of the LC technique described by Cui et al, 2018 and in the process, recommend the abandonment of a technique used by many researchers over nearly three decades. We believe that the reviewer should show caution in promoting a method published a month ago which has not been tested independently by the scientific community for a broader range of SOA derived organosulfates. We do see the method referenced by the reviewer (Cui et al., 2018) a step forward to analyze a set of ambient aerosol compounds from isoprene methyltetrols and their corresponding organosulfates. However, as we highlight below, several analytical inconsistencies can be associated with this method, and we feel that some of the data presented in Cui et al. paper does not support many of the arguments of the reviewer's comments. The paper of Cui et al. 2018 is dependent on two important compounds synthesized: (1) Methyltetrols (MT) are used as the starting materials to synthesize methyltetrols organosulfates (MT-OS); (2) MT-OS used for comparing GC-MS and LC-MS methods. The data provided in Cui et al. 2018 appears not to support the purity or the standard procedure of organic chemistry synthesis of MT-OS.

Synthesis

MT: There is lack of comprehensive experimental data (^{1}H NMR, ^{13}C NMR) therefore the purity could not be verified in Cui et al. paper of MT. The procedure used should be described, mainly the purification method since up to four stereoisomers can be formed, in the SI and/or in the main manuscript and ^{1}H NMR data should be provided for the intermediates as well the MT synthesized (see for example Lessmeier et al. 2018 for methyltetrols synthesis).

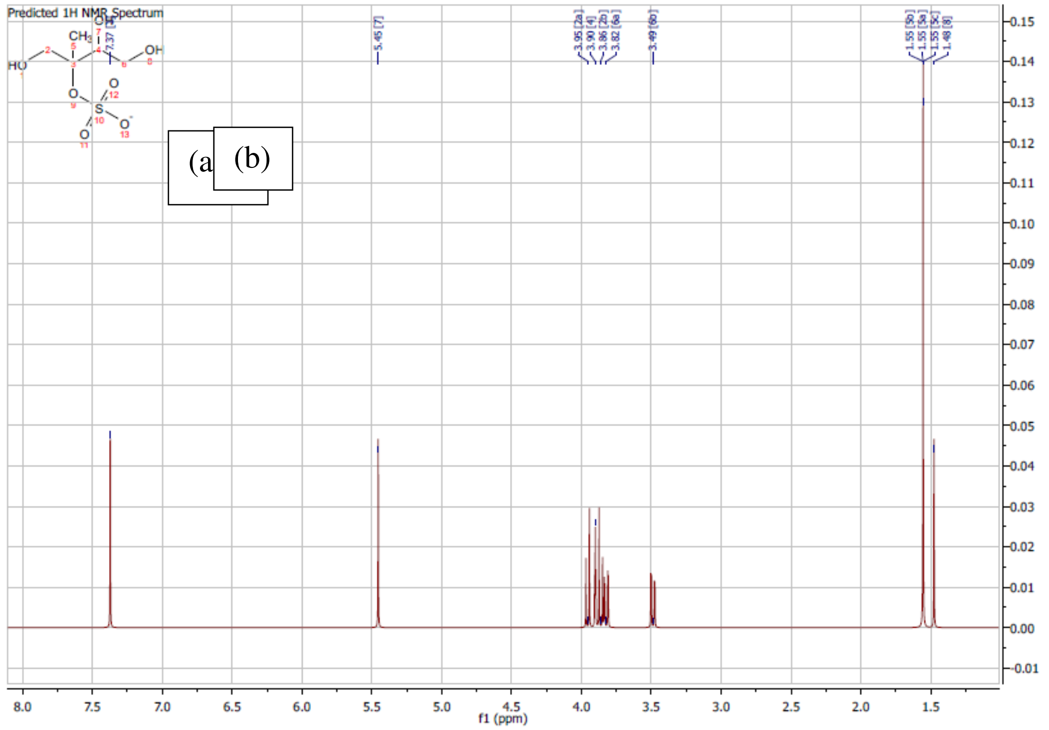
Lessmeier J., Dette H. P., Godt A., and Koop T. Physical state of 2-methylbutane-1,2,3,4-tetraol in pure and internally mixed aerosols. Atmos. Chem. Phys., 18, 15841–15857, 2018.

MT-OS: The synthesis of 2-MT-sulfate (from synthesized MT) described by Cui et al. 2018 is a three-step approach. The authors did not provide experimental data (NMR, MS, …) necessary to confirm (1) the selectivity reported in the acetylation reaction (step 1); (2) for the structure of the intermediates resulted from the sulfation reaction (step 2); and (3) the reaction of tri-acetylated 2-MT sulfate with ammonia (step 3). It appears that the action of ammonia with tri-acetylated 2-MT sulfate gives rise to deacetylation and desulfation of the sulfated group (removal of all groups therefore data should be provided), which would likely explain the origin of additional signals in the ^{1}H NMR spectrum (two singlets at 1.4 and 1.5 ppm) (Cui et al., 2018). It appears also that 3-MeTHF-3,4-diols formation might occur during any synthetic steps, the most likely during acetylation. This is consistent with Figure 1 reported in Cui et al. 2018 as well as our simulated ^{1}H NMR for 2MT-OS, 3-MT OS, MT, and methyl-THF-3,4diol (see Figure S1 below).

Purity

MT: Little if any data is presented in Cui et al. 2018 for MT purity.

MT-OS: The analysis of the ^{1}H NMR spectrum in Figure S1 of Cui et al., 2018, and our simulated ^{1}H NMR for 2-MT-OS, 3-MT-OS, MT, and 3-MeTHF-3,4diol (see Figure S1 below), it appears impurities are present in the synthesized Cui et al. 2-MT-OS. The ^{1}H NMR spectrum (Figure S1, Cui et al. 2018) shows a multiplets (singlet) arising at 2.04 ppm, corresponding to the methyl group, which exist in a vicinity of strongly electronegative substituent/group. It is consistent with the presence of OSO_3H moiety in the 2-MT sulfate. However, the existence of the two preceding multiplets at 1.54 and 1.47 ppm (Figure S1, Cui et al. 2018) indicate the presence of impurities bearing methyl group(s). Our simulated ^{1}H NMR spectra for MT, 2-MT-OS, 2-MT triacetylated, and 3-MeTHF-3,4-diol derivative (see Figure S1), clearly shows that the source of these multiplets are methyl groups which originate from either the 2-MT and/or 3-MeTHF-3,4-diol molecule. It is evident that the vicinity of the methyl group in 2-MT is less electronegative than in 2-MT sulfate giving rise to a characteristic shift towards the lesser values. Moreover, the peak integration in the ^{1}H NMR of the synthesized ammonium 1,3,4-trihydroxy-2-methylbutan-2-yl sulfate (i.e., 2-MT-OS, Figure S1; Cui et al., 2018) is not consistent with the structure of this compound. It is our contention, that Cui et al., 2018 did not provide sufficient analytical data proving the purity and structural assignment (95.5% reported) of the other organosulfate (3-MT-OS) synthesized.



The reviewer main argument is based on Cui et al., 2018 paper. The authors of that paper did not provide consistent analytical data associated with the purity of the methyltetrols as well as the methyltetrols organosulfates. They based their purity on only one ^{1}H NMR spectrum provided in the SI. They should provide for example ^{13}C NMR spectra as well as GCMS data for the methyltetrols (starting materials used to the synthesize of MT-OS) as well as the ^{13}C NMR and ^{1}H NMR spectra for the MT-OS. In addition, the ^{1}H NMR spectrum provided in the SI show that impurities are present in their synthesized 2-MT-OS and is not consistent with the purity reported in their paper of 99% for 2MT-OS. The size of the two peaks between 1.4 and 1.6 ppm could not be associated with the organosulfates synthesized, therefore, we believe caution should be taken when referring to Cui et al. 2018 and conclusions associated to the discrepancies between GC-MS and LCMS. For example, Cui et al. 2018 conclude that "*We also demonstrate that conventional GC/EI-MS analyses overestimate 2-methyltetrols by up to 188%, resulting (in part) from the thermal degradation of methyltetrol sulfates. Lastly, C_5-alkene triols and 3-methyltetrahydrofuran-3,4-diols are found to be largely GC/EI-MS artifacts formed from thermal degradation of 2-methyltetrol sulfates and 3-methyletrol sulfates, respectively, and are not detected with HILIC/ESI-HR-QTOFM*S." We find this statement as speculative since C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols are also formed when no acid seed is present therefore other pathways leading to these compounds should not be ignored. We should not rule out that the overestimation presented by Cui et al. 2018 could also result from the impurities introduced with the starting materials MT.

We disagree with the reviewer comment related to the "GC/EI-MS for the chemical characterization of isoprene SOA". We are not sure if the reviewer issue is with the GC/EI-MS or with the derivatization itself. We believe that "thermal decomposition" does not occur in our case since silylated isoprene species are sufficiently volatile and unlikely to decompose in the injector/column of the GC-MS. This method is used for over 30 years by scientists and researchers not only for small molecules but also for high molecular weight species. The derivatization main purpose is avoiding thermal decomposition of labile species by making them more volatile. We believe that the reviewer refers to the derivatization itself and not the GC/EI-MS, although the Surratt group (since the reviewer refer to this group) used this technique in their published work. We do not come to the same conclusion for the work of Cui et al 2018 that GC-MS thermal decomposition is the main factor contributing to discrepancies between LC-MS and GC-MS. Cui et al. 2018 does not report how the comparison between GC-MS and LC-MS was done. The silylation reaction need to be done under water free condition, since organosulfates were synthesized in aqueous solution and no recoveries were reported on the extraction from the chamber, and C data were also not reported. For example, these compounds when water is evaporated can lead to lactone formation.

Possible shortcomings should not be ignored when using HILIC/LC-MS including: (1) HILIC analysis is often not reproductible and can be time consuming due to long times needed between analyses for column re-equilibration. (2) Lower separation power of LC-MS (ESI/APCI) compared to GC-MS method when complex systems are analyzed. (3) The software often used in the HRMS can assign a number of possibly ambiguous formulae to a given peak.

Comment #2. "Table 2: The C5H10O3 compounds in Table 2 are NOT IEPOX isomers. They are in fact 3-MeTHF-3,4-diols, which are now known to be thermal degradation products from organosuflates (as shown recently in Cui et al., 2018, ESPI). Further, Lin et al. (2012, ES&T) and Zhang et al. (2012, ACP) from the Surratt group showed that GC/MS measures these ions at m/z 262 and 118 as 3-MeTHF-3,4-diols. This was proven with the use of authentic standards. These are not the correct assignments shown here. Furthermore, these compounds are decomposition products of low-volatility products, such as the IEPOX-derived organosulfates (Cui et al., 2018, ESPI)."

Response. These compounds were observed also in isoprene/NOx system (see Figure 1 in the main paper) without acidic seed aerosol used, therefore there is no organosulfates in the system. Therefore, these compounds could not be degradation products of organosulfates as shown above.

Figure S1 suggests possible issues with the purity reported by Cui et al. 2018, therefore other compounds bearing methyl groups are present in the synthesized organosulfates; see the peaks between 1.4 and 1.6 ppm in Figure S1 (Cui et al. 2018). These two peaks are mostly associated with methyltetrols and/or 3-MeTHF-3,4-diols as impurities (note methyltetrols were used in the synthesis of organosulfates). Therefore, 3-MeTHF-3,4-diols are not necessarily degradation products or organosulfates as claimed by the reviewer and Cui et al. 2018 when derivatization/GCMS technique is used. The authors did not detect 3-MeTHF-3,4-diols in the LC-MS method, most probably because ESI in negative ion mode is not the appropriate analysis method for these compounds. (See following response as well.)

We do not dismiss the possible presence of 3-MeTHF-3,4-diols in our samples. In fact, we do detect them in both under acidic and non-acidic seed aerosol based on authentic standards (see mass spectrum below: Figures S2 and S3). We do detect IEPOX peaks in our samples (see Figure 1), which elutes later in our chromatogram while having similar mass spectra to the 3-MeTHF-3,4-diols. However, we felt that this was outside the scope of the paper and we have not reported all isoprene compounds we identified.

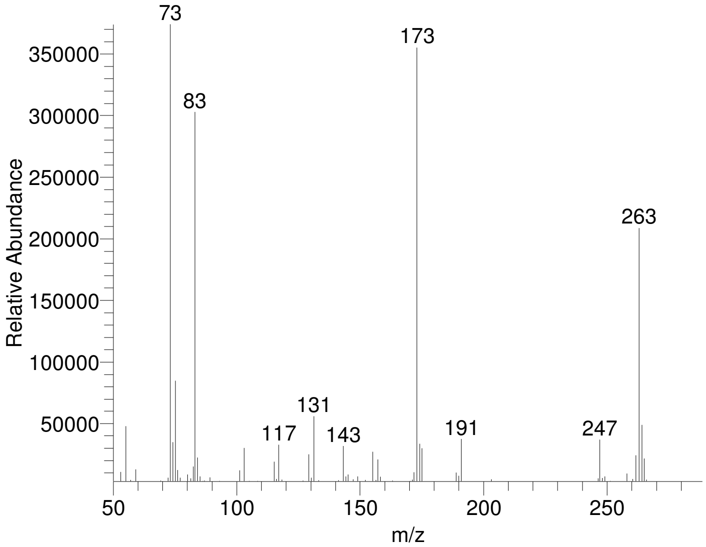


Figure S2. CI-Mass spectrum (methane) of cis-3-MeTHF-3,4-diols (standard).

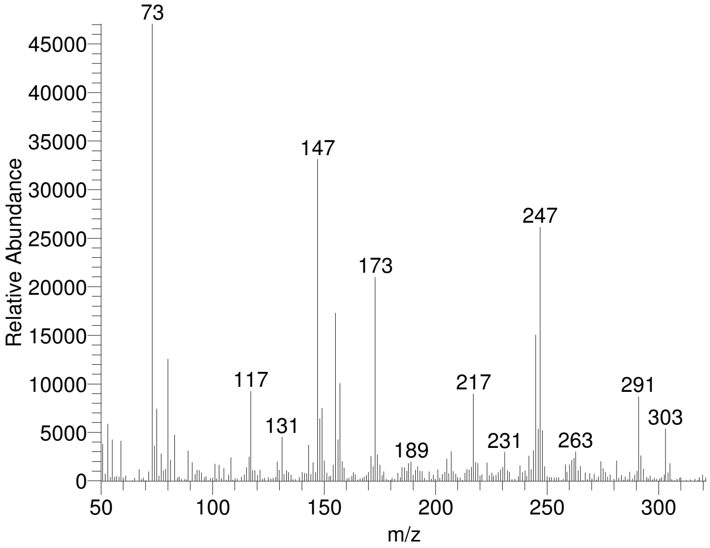


Figure S3. CI-Mass spectrum (methane) of IEPOX in isoprene SOA.

It is our contention that based on our analysis of data reported in Cui et al. 2018, that the 3-MeTHF-3,4-diols are not degradation products of organosulfates, but products from isoprene oxidation.

In addition, Lin et al. 2012, reports that "reactive uptake on the acidified sulfate aerosols through catalyzed intramolecular rearrangement of IEPOX leads to cis- and trans-3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols) in the particle phase." Cui et al. 2018, presumptively from the same group, reports that 3-MeTHF-3,4-diols are reaction artifacts from IEPOX derived organosulfates. Although the paper of Cui et al. speculates that 3-MeTHF-3,4-diols are artifacts of GC/EI-MS analysis. It is not clear which statement is correct. Furthermore, the paper of Hu et al. 2015, shows the presence of C_5-alkene triols in the Southeast U.S.A. during SOAS field study without invoking decomposition arguments.

For the $C_5H_{10}O_3$ compounds, several structures can be associated with this formula including IEPOX (and isomers), and 3-MeTHF-3,4-diols (and isomers). It is not clear what arguments the reviewer makes in stating that these are 3-MeTHF-3,4-diols. Our results show the presence of both IEPOX and 3-MeTHF-3,4-diols in isoprene SOA as well as in gas phase. Due to the number of products we identify in this system, we report only the main products consistent with the objective of this study. Therefore, we did report IEPOX in Table 2 and not 3-MeTHF-3,4-diols. 3-MeTHF-3,4-diols eluting earlier in the chromatogram than IEPOX. Figures S2 and S3 shows mass spectra associated with 3-MeTHF-3,4-diols (standard) and IEPOX (isoprene SOA). Both IEPOX and 3-MeTHF-3,4-diols do indeed have similar fragmentation patterns.

Lin YH, Zhang Z, Docherty KS, Zhang H, Budisulistiorini SH, Rubitschun CL, Shaw SL, Knipping EM, Edgerton ES, Kleindienst TE, Gold A, Surratt JD. Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed reactive uptake studies with authentic compounds. Environ Sci Technol., 2011.

W. W. Hu, P. Campuzano-Jost, B. B. Palm, D. A. Day, A. M. Ortega, P. L. Hayes, J. E. Krechmer, Q. Chen, M. Kuwata, Y. J. Liu, S. S. de Sá, K. McKinney, S. T. Martin, M. Hu, S. H. Budisulistiorini, M. Riva, J. D. Surratt, J. M. St. Clair, G. Isaacman-Van Wertz, L. D. Yee, A. H. Goldstein, S. Carbone, J. Brito, P. Artaxo, J. A. de Gouw, A. Koss, A. Wisthaler, T. Mikoviny, T. Karl, L. Kaser, W. Jud, A. Hansel,K. S. Docherty, M. L. Alexander, N. H. Robinson, H. Coe, J. D. Allan, M. R. Canagaratna, F. Paulot,and J. L. Jimenez. Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements. Atmos. Chem. Phys., 15, 11807-11833, 2015.

Comment #3. “Page 2, Line 6: Again, this statement "although the SOA yield of isoprene tends to be low," is misleading. This is true if you look back at the prior literature from Kroll et al. (2005, GRL), Kroll et al. (2006, ES&T), Edney et al. (2005, AE), but if you consider the multiphase chemistry of its oxidation products (especially IEPOX), then using the SOA yield approach in determining amount of SOA possilbe from isoprene is not a good way to model it. Specifically, the EPA CMAQ model no longer uses the Odum 2-product model approach to constrain the products from isoprene oxidation. Specifically, it models SOA from isorpene as a multiphase chemical processes by modeling the reactive uptake of IEPOX and other important products.”

Response. Isoprene yields (even when heterogenous chemistry is considered) reported in these references are low compared to other important biogenic compounds (i.e. alpha-pinene, d-limonene…), and we do not see this as misleading. We do recognize the possibility of heterogenous chemistry in isoprene SOA formation (our group is still involved in heterogenous isoprene chemistry), although many unresolved difficulties are remaining (i.e. mechanistic, analytical, rate constants…) in the role of heterogenous chemistry in isoprene aerosol formation and presently outside of the scope of this work. We emphasize that isoprene SOA yield (ratio of aerosol mass formed to the isoprene reacted), is a “bulk” property, measured and reports in the literature account for many processes involved in the chemistry leading to the aerosol formation including heterogenous chemistry. Therefore, the role of one compound or other (i.e. IEPOX) tends to be immaterial to the aerosol bulk property (i.e. yield).

Comment #4. “Page 2, Line 11: change "products include" to "products, including...."
Response. This was updated as suggested by the reviewer.

Comment #5. Page 2, Line 11: change "reported including" to "previously reported include"
Response. This was updated as suggested by the reviewer.

Comment #6. **“**Page 2, Lines 14-15: Previous analytical work suggests as you heat isoprene SOA you see the off gassing of 2-MTs and C5-alkene triols, especially in thermodunders and FIGAERO-CIMS (Lopez-Hilfiker et al., 2016, ES&T). As shown in the FIGAERO-CIMS, the 2-methyltetrols and C5-alkene triol peaks didn't make sense due to their location in the low-volatility section of the thermograms. Thus, as this study showed, 2-methyltetrols and C5-alkene triols were likely thermal degradation products of lower volatility compounds in isoprene SOA. Importantly, the Cui et al. (2018, ESPI) from the Surratt Group recently demonstrated with authentic standrads that the 2-methyletrol sulfates (2MT-OS) and 3-MT-OS degrade in GC/MS with prior derivatization into C5-alkene triols and 2-methyltetrols! This is a huge deal, as it appears that most of the isorpene SOA is in the organosulfate forms of IEPOX (including sulfated oligomers). This has important consequences for the results presented here. Previous statements about artifacts from GC/MS can NO LONGER be neglected and these authors must recognize this now in their analyses.”
Response. Here the reviewer is interpreting the Lopez-Hilfiker et al. (2016) data and trying to apply it to our data having different conditions and analysis method. The relationship of the FIGAERO CIMS instrument and our method is at best tenuous. The FIGAERO inlet is specifically designed to heat a laboratory or ambient sample collected on a specialized filter (Lopez-Hilfiker et al, 2014). The active heating program volatilizes the components of the collected aerosol to produce gas-phase constituents which are then measured by chemical ionization mass spectrometry. The method has been tested against laboratory sample and ambient field samples. The approach has been described in detail by Lopez-Hilfiker et al. (2014).

The purported relationship of the real-time FIGAERO CIMS approach for studying ambient aerosol and off-line approach for studying laboratory aerosol is unclear to us. First, our collection process is conducted entirely at ambient temperature unlike the FIGAERO CIMS, which uses an active temperature ramp designed to decompose the constituents volatilized from the aerosol sample. As remarked by Lopez-Hilfiger et al. (2014) regarding the instrument operation, “lower volatility components are likely larger molecular weight dimer, trimers, or other oligomeric or extremely low volatility compounds which thermally decompose during desorption.” As best we can tell from the figure of Lopez-Hilfiker et al. (2016), the decomposition temperature for the isoprene-derived organic sulfates in an ambient sample is in the range 100-150 C. The suggestion that there is a temperature decomposition in our collection is unfounded given the collection is conducted at ambient temperature. The derivatization reaction, which occurs in a condensed phase, is extremely rapidly in forming the TMS derivatives leaving little, if any time, for decomposition to occur with the modest heating employed to ensure quantitative conversion. The same derivative conversions have been found when the BSTFA reaction takes place at room temperature over a more extended period (e.g., overnight). As noted by Lopez-Hilfiker et al., (2014), the FIGAERO system is “designed” to enhance decomposition of the analytes. By contrast, our method is designed to retain the analytes in their original (undecomposed) form. Thus, we feel that the reviewer’s argument is unsupported. Again, this is a single paper from which the reviewer wishes to make overly broad statements applied to our paper.

The reviewer's comment that methylketols are degradation products of isoprene organosulfates is not consistent with our data. First, we detect methyltetrols in systems that do not have organosulfates and therefore it is unreasonable to think they are degradation products of organosulfates. Second, we responded to the same reviewer (first revision) that when isoprene SOA was silylated, both methyltetrols and dimers were detected as the silylated derivatives, therefore thermal degradation is unlikely to be occurring.

Comment # 7. **"**Page 3, Lines 31-33: The authors should note that "Subsquent studies..." is not correct for the fact they cite Zhang et al. 2011 (ACP). Zhang et al. (2011, ACP) was published before Nguyen et al. (2011), right? They were published very close together though."
Response. To reflect the reviewer concern, "Subsequent" was replaced by "other"

Comment #8. **"**Page 5, Lines 28-30: What was the average RH? Especially during the day ?"
Response. We added the RH as suggested by the reviewer.

Comment #9. **"**Page 5, Line 32: As shown by the many previous studies (e.g., Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&TL; etc.) sulfate aerosol is the most important field parameter to report over SO2 concentrations. Its the sulfate particles that provide the surface for the multiphase chemical reactions to occur on."
Response. Only SO2 were measured in this study.