

Interactive comment on “Chemical composition of isoprene SOA under acidic and non-acidic conditions: Effect of relative humidity” by Klara Nestorowicz et al.

Klara Nestorowicz et al.

jaoui.mohammed@epa.gov

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Response to reviewer's comments (# 1)

This reviewer said in his general comments:

This paper reports the formation of organosulfates and other oxygenated compounds in secondary organic aerosols (SOA) generated in an indoor smog chamber from isoprene oxidation in the presence of seed aerosols. For several OSs, chemical structures are proposed on the basis of high-resolution tandem mass spectra. Isoprene accounts for a large part of VOCs in the global atmosphere, and its photooxidation has been

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found to contribute to SOA formation. However, relatively few studies have been focused on the oxidation of isoprene under various relative humidities (RH), and there is still uncertainty on its chemical mechanisms and contribution to SOA formation. While this study might provide valuable information for a better understanding of the chemical pathways from the photooxidation of isoprene, the results presented here are not sufficiently supported by the analytical method and/or do not present a real novelty. In addition, the authors should have a closer look at the literature since some of their results (e.g. 2-methyltetrols) are not consistent with the existing literature. Therefore, additional information/references and major revisions would have to be provided in order to consider this article for publication.

Response: It is not clear what the reviewer means with “sufficiently supported”. We disagree with the statement that the analytical methods used in this study does not support the findings in this paper. The aim of this paper is to investigate changes of the main reaction products observed in isoprene secondary organic aerosol (2-methyltetrols, 2-methylglyceric acid, organosulfates etc.) as a function of relative humidity and acidity. Relatively few studies have been focused on the oxidation of isoprene under various relative humidities (RH) mainly focusing on bulk aerosol properties, there is still uncertainty on its chemical mechanisms and contribution to SOA formation. This is the first study to focus on a wide range of isoprene SOA products evolution with relative humidity under acidic and non-acidic conditions.

The comments raised by the reviewer above are addressed in detail below.

Comment # 1. Page 2, lines 8-10: Too simplified, as written gas-phase oxidation of isoprene leads directly to the formation of isoprene-derived SOA products such as 2-methyltetrols. Please detail.

Response: We changed the following sentences from:

“The primary removal of ISO in the atmosphere is through the gas-phase reactions with hydroxyl radicals (OH), nitrate radicals (NO₃) and ozone (O₃) which result in

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the formation of numerous oxidized SOA components, including 2-methyltetrols, 2-methylglyceric acid, C5-alkene triols and C4/C5 organosulfates (OSs).”

To

“The primary removal mechanism for isoprene is by gas-phase reactions with hydroxyl radicals (OH), nitrate radicals and, to a lesser extent, ozone. These processes result in the formation of gas and aerosol products include numerous oxidized SOA components. Aerosol species reported including 2-methyltetrols, 2 methylglyceric acid, C5-alkene triols and organosulfates (OSs) (i.e. Edney et al., 2005; Surratt et al., 2007a, 2010; Riva et al., 2016; Spolnik et al., 2018). 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 and 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 et al., 2014).”

Comment # 2. Page 3, line 5: Why did the authors use Kleindienst et al. 2007 as a reference to explain the formation of organosulfate?

Response: The reviewer is correct. This was corrected as suggested by the reviewer.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, 41, 517–527, 2007a.

Comment # 3. Page 3, lines 13-22: Other groups have investigated the impact of RH on the SOA formation from isoprene oxidation: e.g. Abbatt’s (isoprene + OH at different RH) & Surratt’s groups (reactive uptake of IEPOX under different RH, acidity, : :; isoprene +O₃ at different RH and seed).

Response: More than 20 new references were added to the revised manuscript. The following references were added on page 3.

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Wong J. P.S., Lee A.K.Y. and Abbatt J.P.D.: Impacts of Sulfate Seed Acidity and Water Content on Isoprene Secondary Organic Aerosol Formation, *Environ. Sci. Technol.*, 49, 13215–13221, 2015.

Surratt, J. D.; Lewandowski, M.; Offenberg, J. H.; Jaoui, M.; Kleindienst, T. E.; Edney, E. O. and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41, 5363– 5369, 2007b.

Riva, M.P., Budisulistiorini, S. H.P., Zhang, Z., Gold, A. and Surratt, J. D.: Chemical Characterization of Secondary Organic Aerosol Constituents from Isoprene Ozonolysis in the Presence of Acidic Aerosol, *Atmos. Environ.*, 130, 5-13, 2016.

Spolnik G., Wach P., Rudzinski K.J., Skotak K., Danikiewicz W. and Szmigielski R., Improved UHPLC-MS/MS Methods for Analysis of Isoprene-Derived Organosulfates, *Anal. Chem.*, 90 (5), 3416-3423, 2018.

Also, as suggested by reviewer # 3, we added the following references on page 2, line 24 (original manuscript): (Lin et al., 2013; Budisulistiorini et al., 2016; Rattanavara et al., 2016; Gaston et al., 2014; Riedel et al., 2015; Zhang et al., 2018).

Lin Y.H., Knipping E.M., Edgerton E.S., Shaw S.L. and Surratt J.D.: Investigating the influences of SO₂ and NH₃ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches. *Atmos. Chem. Phys.*, 13, 8457–8470, 2013.

Budisulistiorini S.H., Baumann K., Edgerton E.S., Bairai S.T., Mueller S., Shaw S.L., Knipping E. M., Gold A. and Surratt J.D.: Seasonal characterization of submicron aerosol chemical composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia, and Look Rock, Tennessee. *Atmos. Chem. Phys.*, 16, 5171–5189, 2016.

Zhang Y., Chen Y., Lambe A.T., Olson N.E., Lei Z., Craig R.L., Zhang Z., Gold A., Onasch T.B., Jayne J.T., Worsnop D.R., Gaston C.J., Thornton J.A., Vizuete W., Ault

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A.P. and Surratt J.D.: Effect of the Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX). *Environ. Sci. Technol. Lett.*, 5, 167–174, 2018.

Comment # 4. Page 3, lines 23-24: Couvidat et al. did not incorporate heterogeneous chemistry (i.e. reactive uptake) or the impact of acidity in their model. Pye et al. (2013) and Marais et al. (2016) demonstrate that replacing a reversible partitioning approach with reactive uptake to aqueous aerosol improves agreement with observations. Please revise.

Response: As suggested by the reviewer, we changed the following sentence on page 3 lines 23-24 (original manuscript) from:

“The results obtained in the smog chamber experiments are not compatible with modelling predictions that ISO SOA yield would increase under humid conditions (Couvidat et al., 2011).”

To

“The results obtained from the chamber experiments have been in agreement with recent model approaches, when reactive uptake to aqueous aerosol is used rather than a reversible partitioning approach (Pye et al., 2013; Marais et al., 2016).”

Pye, H. O. T., Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y-H., Surratt, J. D., Zhang, Z., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation, *Environ. Sci. Technol. Lett.*, 2, 38–42, 2013.

Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D.A., Hu, W., Krechmer, J., Zhu, L., Kim, P.S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G.M., Arkinson, H.L., Pye, H.O.T., Froyd, K.D., Liao J. and McNeill, V.F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene:

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application to the southeast United States and co-benefit of SO₂ emission controls, *Atmos. Chem. Phys.*, 16, 1603–1618, 2016.

Comment # 5. Page 4, lines 18-19: “moderately acidic sulfate aerosol” does not have a real scientific meaning. Please determine the aerosol acidity and liquid water content using thermodynamically model.

Response: To reflect the reviewer comment, we changed the following sentence (page 4, lines 18-19 original manuscript) from

“The second experiment (ER662) was similar but run in the presence of a moderately acidic sulfate aerosol at constant concentration.”

To

“The second experiment ER662 (acidic) was similar but run in the presence of acidic seed aerosol at constant concentration.”

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-NO_x experiments, nitric acid concentrations should be non-trivial), further complicating model predictions.

Comment # 6. Page 4, lines 30-31: Please add additional information. What was the sampling time for the filters? How much mass was collected?

Response: The following sentence (page 4, lines 30-31: original manuscript) was

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changed from:

“Chamber filter samples were collected for SOA products analysis at 16.7 L min⁻¹ using 47-mm glass fiber filters (Pall Gelman Laboratory, Ann Arbor, MI, USA).”

To

“Chamber filter samples were collected for 24 h at 16.7 L min⁻¹ using 47-mm glass fiber filters (Pall Gelman Laboratory, Ann Arbor, MI, USA).”

Comment # 7. Page 5, lines 17-19: how many filters were analyzed? It is important to know if the tracers were identified in 1, 10 or 100 samples. Please provide some statistical information.

Response: The chemical analyses were performed for 10 ambient PM_{2.5} samples. The statistical analysis for such a small number of filters gives rise to high uncertainty, and thus was not applied here. Moreover, the statistical correlation for tracers was out of the scope of the paper.

To reflect the reviewer concern we changed section # 3 (page 5, lines 17-28 original manuscript) to:

“Twenty ambient PM_{2.5} samples were collected, onto pre-baked quartz filters using a high-volume aerosol sampler (DH-80, Digitel), from two sites (ten samples each) having strong isoprene emissions: (1) a regional background monitoring station in Zielonka, in the Kuyavian-Pomeranian Province in the northern Poland (PL; 53°39' N, 17°55' E) during summer 2016 campaign, and (2) a regional background monitoring station in Godow, PL located in the Silesian Province (49°55' N, 18°28' E) in summer 2014 campaign. Sampling times were 12 and 24 hours, respectively. Major tree species at both sites are European oak (*Quercus robur* L.); European hornbeam (*Carpinus betulus* L.); *Tilia cordata* (*Tilia cordata* Mill); European white birch (*Betula pubescens* Ehrh); and European alder (*Alnus glutinosa* Gaertn). The Zielonka station is in a forested area while the Godow station is located near a coal-fired power station

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in Detmarovice (Czech Republic). Godow is also close to the major industrial cities of the Silesian region in Poland, and thus aerosol samples collected in Godow were influenced by anthropogenic sources. Several chemical and physical parameters were measured at the two sites. The relative humidity during sampling was up to 86% in Zielonka and 94% at Godow. Both locations were influenced by NO_x concentration, modestly in Zielonka at 1.3 μg m⁻³ and at a level of 30 μg m⁻³ in Godow, represented by the nearest monitoring station at Zywiec, PL. The SO₂ levels at Zielonka were approximately 0.6 μg m⁻³ and 3.0 μg m⁻³ at Godow. At each site, OC/EC values were determined for each filter using a thermo-optical method (Birch and Cary, 1996). The organic carbon value at Zielonka was approximately 1.7 μg m⁻³ and 5.4 μg m⁻³ at Godow, although aerosol masses were not determined.”

Comment # 8. Page 6. Line 3-19: Additional information/explanation are needed in the analytical protocol to validate the results: - Temperature and pressure in the rotavapor? Did the authors evaluate the losses of the most volatile compounds → tetrols/IEPOX/...? - The authors mentioned that internal standards were used. What is the extraction efficiency/recovery? Why did the author realize this step for the GC-MS analysis only? Extraction/recovery efficiencies have to be provided for both methods.

Response: This section (Page 6, line 3-19) refers to LCMS analysis. The temperature of rotavapor bath was 28 °C at the pressure of 150 mbar. We did not evaluate the recovery of methyltetrols/IEPOX/organosulfates due to lack of authentic standard. However, recoveries were done on other compounds, and the extraction efficiency for the LC/MS analysis of organosulfates was in the range of 94-101%.

The section related to LC-MS (page 6, lines 3-17) was changed to:

“For the LC/MS analysis, from each filter, two 1 cm² punches were taken and twice extracted for 30 min with 15 mL aliquots of methanol using a Multi-Orbital Shaker (PSU-20i, BioSan). High purity methanol (LC-MS ChromaSolv-Grade; Sigma-Aldrich, PL) was used for the extraction of SOA filters, reconstitution of aerosol extracts, and prepa-

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ration of the LC mobile phase. The two extracts were combined and concentrated to 1 mL using a rotary evaporator operated at 28 °C and 150 mbar (Rotavapor[®] R215, Buchi). They were then filtered with 0.2 μm PTFE syringe and taken to dryness under a gentle stream of nitrogen. High-purity water (resistivity 18.2 MΩ·cm⁻¹) from a Milli-Q Advantage water purification system (Merck, Poland) was used for the reconstitution of aerosol extracts and preparation of the LC mobile phase. The residues were reconstituted with 180 μL of 1:1 high purity methanol/water mixture (v/v), then agitated for 1 min. Recoveries were not taken for compounds analysed in this study, due to lack of authentic standards, however recovery of 94 -101% were measured for appropriate surrogate compounds. Extracts were analyzed by ultra-high performance liquid chromatography/electrospray ionization/time-of-flight high resolution mass spectrometry (UHPLC / ESI (-) QTOF) HRMS equipment consisting of a Waters Acquity UPLC I-Class chromatograph coupled to a Waters Synapt G2-S high resolution mass spectrometer. The chromatographic separations were performed using an Acquity HSS T3 column (2.1 × 100 mm, 1.8 μm particle size) at room temperature. The mobile phases consisted of 10 mM ammonium acetate (eluent A) and methanol (eluent B). To obtain appropriate chromatographic separations and responses, a gradient elution program 13 min in length was used. The chromatographic run commenced with 100% eluent A over the first 3 min. Eluent B increased from 0-100% from 3 to 8 min, held constant at 100 % from 8 to 10 min, and then decreased back from 100-0% from 10 to 13 min. The initial and final flow was 0.35 mL min⁻¹ while the flow from 3 to 10 min was 0.25 mL min⁻¹. An injection volume of 0.5 μL was used. The Synapt G2-S spectrometer equipped with an ESI source was operated in the negative ion mode. Optimal ESI source conditions were 3 kV capillary voltage, 20 V sampling cone at a FWHM mass resolving power of 20,000. High resolution mass spectra were recorded from m/z 50-600 in the MS or MS/MS modes. All data were recorded and analyzed with the Waters MassLynx V4.1 software package. During the analyses, the mass spectrometer was continuously calibrated by injecting the reference compound, leucine enkephalin, directly into the ESI source.”

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Comment # 9. Page 6, line 27: The authors report a SOA yield of 0.32% and conclude: “The values of SOA yields agree with previous smog chamber studies”. It is not exact and some studies have reported SOA yields 10 times higher (Carlton et al., 2009 ACP). The authors should discuss and compare their results in more details. In addition, to really compare apple to apple the authors should discuss the impact of NO/VOC ratio, which can greatly impact isoprene SOA formation (Xu et al., 2014).

Response: SOA yield reported in the literature for isoprene photooxidation vary considerably (Carlton et al., 2009). It is very difficult to compare the reported SOA yields as noted by the reviewer, largely because literature data were reported at different conditions, and isoprene SOA yields are highly sensitive to reaction conditions and/or experimental design and conditions (e.g. temperature, relative humidity, NO_x level (NO/VOC ratio), concentration and type of seed aerosol, OH concentration. . .). Our experiments were conducted in the presence of NO_x and yields reported under these conditions correspondent to the lowest end compared to those measured under NO_x-free condition. Since the objective of this study is not bulk SOA parameter analysis, and to reflect the reviewer concerns, we changed the following sentence (page 6, line 27 original manuscript) from

“The average OM/OC ratio was 1.92 ± 0.13 and the average laboratory SOA yield measured in this experiment was 0.0032 ± 0.0004 . The values of SOA yields agree with previous smog chamber studies (Edney et al., 2005; Kroll et al., 2006; Dommen et al., 2006; Surratt et al., 2007; Zhang et al., 2011).”

To

“The average OM/OC ratio was 1.92 ± 0.13 , and the average laboratory SOA yield measured in this experiment was 0.0032 ± 0.0004 . For the non-acidic experiment, the carbon yield values range from a low 0.001 (stage 5, Table 1) at the highest relative humidity to a high of 0.004 at the lowest relative humidity (stage 1, Table 1). For the acidified experiment, carbon yield declined from above 0.011 at the lowest relative

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humidity (8%) to 0.001 at the highest relative humidity (44%). Although the relative humidity considered for both acidic and non-acidic experiments do not correspond precisely, an increase of SOC was observed under acidic conditions at approximately the same relative humidity. The values of SOA yields agree with previous chamber studies reported in the literature under the same nominal conditions in the presence of NO_x (Edney et al., 2005; Dommen et al., 2006; Surratt et al., 2007; Zhang et al., 2011)."

Comment # 9. Page 7, Table 1: The initial concentration of NO is higher than the steady-state concentration of NO_x (= NO + NO₂). Why? What was the NO₂ concentration? The authors should also discuss the different regimes NO/NO₂ (→ impact SOA yields).

Response: Our smog chamber experiments were run as a flow reactor and the initial NO is higher than the steady state conditions (Table 1 is correct). The initial NO_x (NO + NO₂) injected into the chamber was only NO and no NO₂ was added to the chamber. To reflect the reviewer concern, we added to Table 1 caption: "Initial NO_x was 100% NO". The NO/NO₂ effect on SOA yields is important, however, we do believe that is out of the scope of this study.

Comment # 10. Page 8, lines 1-2: Why did the authors look only at the organosulfates? The authors should compare the quantification of the acids from LC/ESI(-)-MS vs GC-MS and polyol LC/ESI(+)-MS vs GC-MS. Indeed, it is now recognized that all thermal analyses (i.e. GC-MS, FIGAERO, SV-TAG) lead to a subsequent fragmentation of the oligomers. Isoprene-derived SOA is assumed to be mainly made out of oligomers especially under acidic conditions. The authors have the information/analytical tools to provide more insights on this topic.

Response: The primary objective of this study is the characterization of organosulfates/nitro-organosulfates, and organic acids/polyols ... using two complementary methods LC-MS and GC-MS, respectively. We agree with the reviewer about a comparison between the two analytical techniques, unfortunately at the time of these

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analysis no comparison was done between these two methods for the organic acids. However, we are working to synthesizing some isoprene reaction products that will be used for such comparison.

Please see our response to reviewer 3 comment # 9 related to thermal decomposition of oligomers.

Comment # 11. Page 8, lines 3-4: Please add references

Response: We added the following three references:

Darer, A.I., Cole-Filipiak N.C., O'Connor A.E. and Elrod M.J.: Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates. *Environ. Sci. Technol.* 45, 1895-1902, 2011.

Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M.R., Gascho, A., Weingartner, E., Prevot, A. S. H., Verheggen, B., and Baltensperger, U.: Laboratory observation of oligomers in the aerosol from isoprene/NO_x photooxidation, *Geophys. Res. Lett.*, 33(13), L13805, 2006.

Szmigielski R., Evidence for C₅ organosulfur secondary organic aerosol components from in-cloud processing of isoprene: Role of reactive SO₄ and SO₃ radicals, *Atmos. Environ.*, 130, 14-22, 2016.

Comment # 12. Page 8, lines 8-9: Organosulfate at m/z 230 was previously identified from the oxidation of unsaturated aldehydes.

Response: The MW 230 organosulfate was previously detected from photo-oxidation of 2-E-pentenal – one of a key green plant volatile (Shalamzari et al., ACP, 2016), however to the best of our knowledge, has never been detected from photo-oxidation of isoprene. We added the following sentence to the revised manuscript and reads

"An organosulfate with MW 230, but with a distinct structure, was recently reported in the literature from the photooxidation of 2-E-pentanal (Shalamzari et al., 2016)."

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Shalamzari M., Vermeylen R., Blockhuys F., Kleindienst T.E., Lewandowski M., Szmigielski R., Rudzinski K.J., Spolnik G., Danikiewicz W., Waenhaut W. and Claeys M.: Characterization of polar organosulfates in secondary organic aerosol from the unsaturated aldehydes 2-E-pentenal, 2-E-hexenal, and 3-Z-hexenal, *Atmos. Chem. Phys.*, 16, 7135–7148, 2016.

Comment # 13. Page 8, Table 2: Please verify the structures/formulae and specify the compounds already identified in isoprene-derived SOA.

Response: The reviewer is correct; the structure was corrected. Table 2 was updated and now contains one additional column describing compounds identified previously as well as the corresponding references.

Comment # 14. Page 11, lines 13-14: It is confusing. They are particle phase products. As written it can be understood that 2MT and 2MG are formed in the gas phase as secondary products. In addition, 2-MT should be a tertiary product not a secondary. ISO->ISOPOOH-> IEPOX$\xrightarrow{\text{H}}$ 2-MT.

Response: For the formation of 2-methyltetrols and 2-methylglyceric acid either in the gas phase or particle phase, please see our respond to reviewer # 3 comment # 2. We do agree with the reviewer that 2-methyltetrols are not secondary oxidation products from isoprene, therefore we changed the following sentence (page 11, lines 13-14) from

“The formation of second generation compounds of ISO SOA such as 2-methyltetrols (mT) and 2-methylglyceric acid (2-mGA) is well documented in the literature.”

To

“The formation of isoprene SOA products such as 2-methyltetrols (mT) and 2 methylglyceric acid is well documented in the literature.”

Comment # 15. Page 12, lines 1-17: Need to use it to compare quantification. While the authors mentioned that the detailed analysis was performed using LC-MS in positive

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and negative modes, only the negative mode is presented in this study, why? The authors could have used the benefit of deploying two complementary techniques by comparing the concentrations obtained from both methods. But instead, they are giving qualitative data and do not seem to be eager to tackle the “analytical limitations” (page 15, line 6). The authors need to revise their analytical methods and use the full potential of the methods used in this study: - Comparison LC/ESI(-)-MS vs GC need to be proposed for the acids using similar standards. - Comparison LC/ESI(+)-MS vs GC need to be proposed for the polyols using similar standards. - Additional standards commercially available (e.g. erythritol, organosulfate: : :) can be used. Indeed the authors used only one acid to quantify a wide range of compounds. What can be the impact? - Which fraction of the SOA can be explained by the compounds identified in the different experiments? What does the relative abundance mean? Is it normalized by the volume of air collected? The authors mentioned that they did not quantify the organosulfates but in the SI the concentrations are reported...Please explain Finally, the results presented are not well constrained. Therefore conclusions proposed based on the concentrations appear speculative: “The major SOA components detected were 2-methyltetrols, 2-methylglyceric acid and its dimer, whose maximal concentrations exceeded 800, 350 and 300 ng/m³ respectively under low-humid conditions of RH 5-9% (Fig. 2).”

Response: We performed LC-MS measurements only in the negative ion mode. It is now corrected in the abstract that only negative mode was done using LC-MS. The aim of this study was not to compare both analytical methods but to detect and follow the evolution of isoprene SOA components formed under various RHs. While GC/MS was applied for quantitation of selected isoprene SOA components, LC/MS was used for more qualitative analysis with a trial to do a semi-quantitation. Since no authentic standards are available for the compound of interest in this study at the time of analysis, LC/MS responses were reduced for comparative analysis based on the contribution of a given peak to the total ion current defined as a normalization level. Due to lack of authentic standards, the quantitative analysis using GC-MS should be regarded as

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indicative of the trend of isoprene products as the RH/acidity change. See also our response to comment # 10.

However, we do believe that this comparison should be done, and we are working on 1,3-butadiene oxidation products to do such comparison since the major oxidation products (threitol, erythritol, threonic acid . . .) do exist commercially.

We changed this part (page 12, line 1-17: original manuscript) to

“The LC-MS analyses focused mainly on the formation of the variety of organosulfates, nitroxy- and nitrosoxy-organosulfates. Mass spectra and proposed fragmentation pathways of newly identified components are presented in section 3.4.

3.2 Effect of relative humidity and acidity on products formation 3.2.1 Non-acidic aerosol

Table 3 and Figures 2 – 3 present the estimated amounts of polar oxygenated products detected with GC-MS and LC-MS techniques in samples from ER667 photooxidation experiments with non-acidic aerosol seeds under various RH conditions. Six products were quantified (as sums of respective isomers) based on the response factor of ketopinic acid using GS-MS. Nine other compounds were detected qualitatively using LC-MS, with chromatographic responses representing the amounts of respective analytes. Therefore, the results should be understood as a tendency of product occurrence in the chamber experiments rather than the real amounts formed. Table 3 does not contain data on 2-methyltartaric acid organosulfate (MW 244) because it occurred in the samples merely in trace amounts.”

Comment # 16. Page 14, lines 10-12: The authors found that concentration of 2-MT increase at lower RH. It is not consistent with previous works (Lin et al., 2014 ES&T; Riva et al., 2016 ES&T). Please explain.

Response: Riva et al. (2016), and Lin et al. (2014) found that aerosol mass increases as the RH increases, results not consistent with our findings in this paper as well as in

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Lewandowski et al. (2015), and Surratt et al. (2007a). In addition, Riva et al. (2016) report an increase in 2-methyltetrols relative concentration as the RH increases from dry condition (RH ~ 5%) to wet condition (RH ~ 55 %), again not consistent with our findings here as well as in Surratt et al. (2007a). The experimental conditions of Riva et al. (2016) and Lin et al. (2014) studies were fundamentally different than those in the present study. In our study, isoprene was oxidized in the presence of NO_x and seed aerosol (acidic or non-acidic), however hydroxyhydroperoxide (ISOPOOH) was used as the reactant in the case of Riva et al. study, and IEPOX as the starting reactant for Lin et al. Lin et al. investigated the reactive uptake and multiphase chemistry of isoprene epoxydiols (mainly their focus was on light absorbing compounds: brown carbon) from IEPOX uptake on acidic sulfate aerosol). In addition, both Lin et al. and Riva et al. experiments were conducted under NO_x-free conditions. Note Li et al used two types of seed (MgSO₄, and (NH₄)₂(SO₄)) and similar behaviour was observed in their studies. We do believe that such comparison is difficult between our results and those of Riva et al. and Lin et al., because different pathways may be responsible for SOA formation.

Under acidic condition, as the RH decreases (water content decreases), the acidity increase, which is consistent with the increase of aerosol mass observed in our study. Therefore, a decrease in RH lead generally in an increase in products abundances (as the aerosol mass increases) at lower RH, consistent with our findings. High concentrations of 2MT and 2-MG at lower RH could be due to enhanced contribution of acid-catalysed multiphase chemistry of IEPOX.

We added the following sentences (page 14, line 14) to the revised manuscript and read:

“Two recent studies (Lin et al., 2014; Riva et al., 2016) reported an increase in aerosol mass with increasing RH. Riva et al., (2016) reported also an increase in 2-methyltetrols concentrations with increasing RH. These two studies were fundamentally different than those in the present study. In our study, isoprene was oxidized in the

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presence of NO_x and seed aerosol (acidic and non-acidic) under a wide range of humidity, however hydroxyhydroperoxide (ISOPOOH), and IEPOX were used as reactant in Riva et al., and Lin et al. studies under two RH and free-NO_x conditions.”

Lin Y.H., Budisulistiorini S. H., Chu K., Siejack R.A., Zhang H., Riva M., Zhang Z., Gold A., Kautzman K.E. and Surratt J.D.: Light-Absorbing Oligomer Formation in Secondary Organic Aerosol from Reactive Uptake of Isoprene Epoxydiols., *Environ. Sci. Technol.*, 48, 12012–12021, 2014.

Riva M., Budisulistiorini S.H., Chen Y., Zhang Z., D'Ambro E.L., Zhang X., Gold A., Turpin B.J., Thornton J.A., Canagaratna M.R. and Surratt J.D.: Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxyhydroperoxides. *Environ. Sci. Technol.*, 50, 9889–9899, 2016.

Comment # 17. Page 15, Table 4: Concentration of IEPOX-1 is much higher under certain conditions. Please comment? Variability of the measurements?

Response: There was a typing error, and this was now corrected. We thank the reviewer.

Comment # 18. Page 17, lines 10-14: What is new here? It has already been reported that acidity enhances the formation of isoprene-SOA components such as tetrols, organosulfates. Please add the references and further highlight the novelty.

Response: The first section on page 17 was changed to reflect the reviewer concerns: “Early chamber studies on isoprene ozonolysis by Jang et al. (2002) and Czoschke et al. (2003) showed enhanced SOA yields in the presence of acidified aerosol seeds. Recent laboratory results showed that the acidity of aerosol seeds plays a major role in the reactive uptake of isoprene oxidation products by particle phases (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Gaston et al., 2014; Riedel et al., 2015). In our study, SOC produced in acidic-seed experiments was always higher than in non-acidic seed ones under the corresponding RH conditions, while the difference di-

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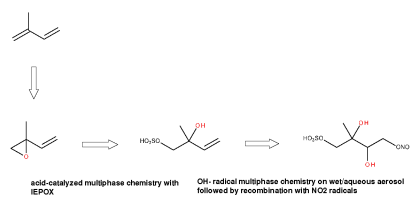
minished with increasing RH to a negligible value of 0.3 $\mu\text{g C m}^{-3}$ at RH 44 – 49% (Table 1 and Figure S1, Supplementary Information; Surratt et al., 2007a). However, the formation of the individual organic compounds did not follow the same pattern. As an example, Figure 6 shows a comparison of the concentrations of 2-methylglyceric acid under acidic and non-acidic condition as a function of relative humidity. Acidic seed aerosol has a greater effect on 2-methylglyceric acid at lower RH. Some of the compounds produced in higher quantities in the acidic seed experiments included 2-methylglyceric acid, 2-methyltetrols, furanetriol-OS, 2-methyltetrol-NOS, 2 methylthreonic acid NOS, furanone-OS, while some other in the non-acidic seed experiments including IEPOX-2, 2 methylglyceric acid OS, 2-methylthreonic acid OS. Yields of the remaining compounds followed an inconclusive pattern (SI: Figures S1, S2, and S3; Table S1). Thus, this study shows the effect of relative humidity on the formation of a wide range of isoprene SOA products cannot easily be predicted, although the majority increases with decreasing relative humidity both under acidic and non-acidic conditions.”

Comment # 19. Page 22, lines 13-18: How would this product be formed? Which kind of chemistry?

Response: The chemistry of the formation of the MW 245 product is not clear to us at present and deserves the further research. We can speculate that it could arise from a complex chain of reactions as indicated below:

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Fig. 1. Authors response to reviewer 1 comments

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