

## Response to reviewer's comments (# 2)

This reviewer said in the general comments:

**“The manuscript presents interesting new work on elucidation of isoprene SOA formation and the influence of aerosol acidity and relative humidity.** The results are generally interesting, but the presentation needs considerable improvement before publication can be considered, in order to provide a less fragmented paper. The structure of the manuscript could be improved by moving the detailed characterization (3.3) to an earlier part of results and discussion, and then end with a general discussion of the findings in relation to current literature.”

**Response.** As noted in our response to the next comment, the revised manuscript was carefully edited for English as well as in terms related to results associated with recent advances on isoprene SOA chemistry (see also our detailed response to the three reviewers). We do believe that the revised manuscript now is clear and comprehensive. Section 3.3 presents a comparison between smog chamber and the field samples, and we do believe that this section should be after the discussion of the chamber and field samples sections.

This reviewer goes on to say

**“In general the use of English language should be improved. It is not the task of the reviewer to do this, and the authors should carefully read the manuscript to improve this.”**

**Response.** The revised manuscript was carefully edited for English as well as terms related to results associated with recent advances on isoprene SOA chemistry.

**Comment # 1.** Please define abbreviations the first time they appear, also in the abstract.

**Response.** This was updated as suggested by the reviewer.

**Comment # 2.** Abstract: I suggest adding some concluding remarks at the end of the abstract.

**Response.** The abstract was edited and additional conclusions were added to the abstract in the revised manuscript:

**“Abstract.** The effect of acidity and relative humidity on bulk isoprene aerosol parameters has been investigated in several studies, however few measurements have been conducted on individual aerosol compounds. While the focus of this study has been the examination of the effect of acidity and relative humidity on secondary organic aerosol (SOA) chemical composition from isoprene photooxidation in the presence of nitrogen oxide (NO<sub>x</sub>), a detailed characterization of SOA at the molecular level have been also conducted. Experiments were conducted in a 14.5 m<sup>3</sup> smog chamber operated in flow mode. Based on a detailed analysis of mass spectra obtained from gas chromatography-mass spectrometry of silylated derivatives in electron impact and chemical ionization modes, and ultra-

high performance liquid chromatography/electrospray ionization/time-of-flight high resolution mass spectrometry, and collision-induced dissociation in the negative ionization modes, we characterized not only typical isoprene products, but also new oxygenated compounds. A series of nitroxy-organosulfates (OS) were tentatively identified on the basis of high resolution mass spectra. Under acidic conditions, the major identified compounds include 2-methyltetrols (2MT), 2-methylglyceric acid (2MGA) and 2MT-OS. Other products identified include epoxydiols, mono- and dicarboxylic acids, other organic sulfates, and nitroxy- and nitrosoxy-OS. The contribution of SOA products from isoprene oxidation to PM<sub>2.5</sub> was investigated by analysing ambient aerosol collected at rural sites in Poland. Methyltetrols, 2MGA and several organosulfates and nitroxy-OS were detected in both the field and laboratory samples. The influence of relative humidity on SOA formation was modest in non-acidic seed experiments, and robust under acidic seed aerosol. Total secondary organic carbon decreased with increasing relative humidity under both acidic and non-acidic conditions. While the yields of some of the specific organic compounds decreased with increasing relative humidity others varied in an indeterminate manner from changes in the relative humidity.”

**Comment # 3. Introduction:** The use of references needs significant improvement. References are missing for several statements (e.g. Page 2 line 4 "Isoprene is the most abundant nonmethane hydrocarbon...").

**Response.** As noted above, the paper was carefully updated for references and almost the majority of requests/suggestions raised by the three reviewers were incorporated in the revised manuscript. The following references were added to the revised manuscript:

Xie M., Hannigan M.P., Barsanti K.C., Gas/Particle Partitioning of 2-Methyltetrols and Levoglucosan at an Urban Site in Denver, Environ. Sci. Technol., 48, 2835–2842, 2014.

Kleindienst T.E., Lewandowski M., Offenberg J.H., Jaoui M., Edney E.O., The formation of secondary organic aerosol from the isoprene + OH reaction in the absence of NO<sub>x</sub>, Atmos. Chem. Phys., 9, 6541–6558, 2009.

Lin Y.-H., E. M. Knipping, E. S. Edgerton, S. L. Shaw, and J. D. Surratt. Investigating the influences of SO<sub>2</sub> and NH<sub>3</sub> 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., 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 A.P., 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.

Riva, M., Budisulistiorini, S.H., Zhang, Z., Gold, A., 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.

Riva M., Sri Budisulistiorini H., Zhang Z., Gold A., Thornton J.A., Turpin B.J., Surratt J.D., Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the presence of acidified aerosols. *Atmos. Environ.*, 152, 314-322, 2017.

**Comment # 4.** There is no need to introduce an abbreviation in the text for isoprene. There are already plenty of abbreviations in the manuscript, and this one only makes the text more difficult to read. Furthermore it is used inconsistently.

**Response.** We agree with reviewer, we deleted most of the use of the isoprene abbreviation (ISO) from the revised manuscript. Virtually all abbreviations for use as a noun have been eliminated, except for secondary organic aerosol (SOA) and organosulfate (OS). Abbreviations are used mostly for adjectives, e.g. SOA formation. The only use of ISO is in combination with SOA when used as an adjective, e.g., ISO-SOA.

**Comment # 5.** Page 2 Line 10: Please add relevant references.

**Response.** See comment # 1 from reviewer #3. We changed the sentences on page 2, lines 8-10 incorporating additional references. They read now:

“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, C<sub>5</sub>-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<sub>2.5</sub> (Xie et al., 2014).”

The new references were added to the reference section.

**Comment # 6.** Page 2 line 26: It would be relevant to refer to the following studies: Riva et al., *Environ. Sci. Technol.*, 2016, 50 (11), pp 5580–5588 Zhang et al., *Environ. Sci. Technol. Lett.*, 2018, 5 (3), pp 167–174.

**Response.** As suggested by the reviewer, we added the following references to the revised manuscript:

Riva, M., Budisulistiorini, S.H., 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.

Riva M., Budisulistiorini S.H., Zhang Z., Gold A., Thornton J.A., Turpin B.J., and Surratt J.D.: Multiphase reactivity of gaseous hydroperoxide oligomers produced from isoprene ozonolysis in the presence of acidified aerosols. *Atmos. Environ.*, 152, 314-322, 2017.

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 A.P., 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 # 7.** Page 2 Line 29-31. This sentence is hard to understand and need references.

**Response.** To reflect the reviewer concern, we changed the following sentence from:

“The most common in the atmosphere and investigated were organosulfates derived from the oxidation of ISO that were identified both in smog chamber experiments and in field studies.”

To

“The most common isoprene organosulfates have been identified both in smog chamber experiments and in field studies (Surratt et al., 2007a; 2008, 2010; Gomez-Gonzalez et al., 2008; Shalamzari et al., 2013; Tao et al., 2014; Hettiyadura et al., 2015; Spolnik et al., 2018).”

**Comment # 8.** Page 3 Line 26: Define SOC. I think "e.g." should maybe be "i.e."

**Response.** The reviewer is correct. We deleted from the revised manuscript “e.g.”. Note SOC is now defined in the revised manuscript when it appears the first time. SOC: secondary organic carbon.

**Comment # 9.** P3. Line 30- 31: Other research groups were the first to develop analysis of organosulfates using LC/MS. I suggest to remove "developed in our laboratories" from the sentence. Section 2.2.

**Response.** We changed the following sentence from:

“Two techniques developed in our laboratories were used: (1) analysis of organosulfates compounds based on LC/MS (Szmigielski, 2016, Rudzinski et al., 2009) and (2) analysis of non-sulfate compounds based on derivatization techniques followed by GC-MS analysis (Jaoui et al., 2004).”

To

“Organosulfate compounds were analyzed using LC/MS measurements (Szmigielski, 2016; Rudzinski et al., 2009; Darer et al., 2011; Surratt et al., 2007a), while non-sulfate oxygenated compounds were examined using derivatization followed by GC-MS analysis (Jaoui et al., 2004).”

Additional references were added to the revised manuscript.

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.

Surratt, J.D., Kroll J.H., Kleindienst T.E., Edney E.O., 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, 2007.

**Comment # 10.** Please add information on sampling time and tree species in the area. In several instances "emission" should be replaced by "concentration".

**Response.** We changed the following sentence to reflect the reviewer concerns from:

“Ambient fine aerosol samples (PM<sub>2.5</sub>) were collected onto pre-baked quartz-fiber filters using a high-volume aerosol samplers (DH-80, Digitel) at the regional background monitoring station in Zielonka, located in the Kuyavian-Pomeranian Province in the northern Poland (53°39'N, 17°55'E) during the 2016 summer campaign, and at the regional background monitoring station in Godow, located in the Silesian Province in southern Poland (49°55'N 18°28'E) in summer 2014. At both sites, strong emission of isoprene occurred. The Zielonka station is located in the forested rural area while the Godow station is located near a coal-fired power station in Detmarovice (Czech Republic) and close to big industrial cities of the Silesian agglomeration (Poland). Therefore, SOA collected in Godow can be influenced by anthropogenic aerosol precursors. The relative humidity level during sampling in Zielonka was 86%, SO<sub>2</sub> emission was estimated at 0.6 µg/m<sup>3</sup> and 25 OC value was 1.68 µg/m<sup>3</sup>. The relative humidity level during sampling in Godow was 94%, SO<sub>2</sub> emission was estimated at 3.0 µg/m<sup>3</sup> (approximate value from the nearest sampling station - Zory) and OC value was 5.43 µg/m<sup>3</sup>. Both locations were influenced by NO<sub>x</sub> emission – slightly in Zielonka at 1.3 µg/m<sup>3</sup> and 30.0 µg/m<sup>3</sup> in Godow (approximate value from the nearest sampling station - Zywiec).”

To

“Twenty ambient PM<sub>2.5</sub> 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 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 temperature range during sampling at both sites range from 27-28 °C. The relative humidity during sampling was up to 86% in Zielonka and 94% at Godow. Both locations were influenced by NO<sub>x</sub> concentration, modestly in Zielonka at 1.3 µg m<sup>-3</sup> and at a level of 30 µg m<sup>-3</sup> in Godow, represented by the nearest monitoring station at Zywiec, PL. The SO<sub>2</sub> levels at Zielonka were approximately 0.6 µg m<sup>-3</sup> and 3.0 µg m<sup>-3</sup> at Godow. At each site, OC/EC values was 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<sup>-3</sup> and 5.4 µg m<sup>-3</sup> at Godow, although aerosol masses were not determined.”

**Comment # 11.** P. 6 Line 7: Define the abbreviation.

**Response.** This was done as requested by the reviewer.

**Comment # 13.** P. 7 Line 7- page 8 line 5: This should be moved to the experimental section.

**Response.** We do believe that this section should remain here because it provides a discussion on the mass spectra behavior of the products.

**Comment # 14.** Table 2 needs references to studies where these compounds were first identified.

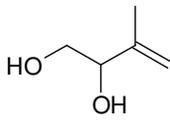
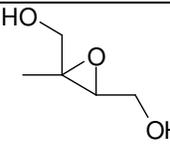
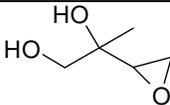
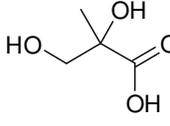
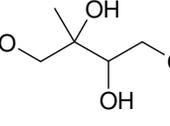
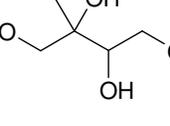
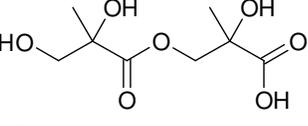
**Response.** We added one column to Table 2, providing references associated with the compounds reported in Table 2. The revised Table 2 is shown below with the new references:

**Table 2.** Products detected in SOA samples from chamber experiments using GC-MS and LC-MS.

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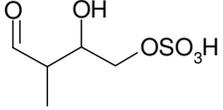
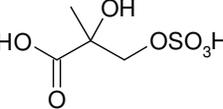
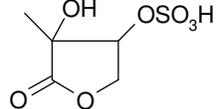
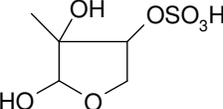
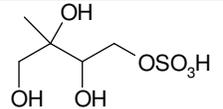
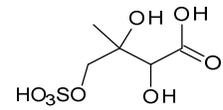
**GC-MS**

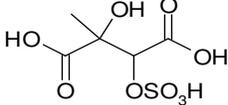
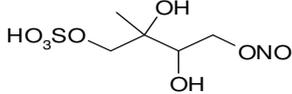
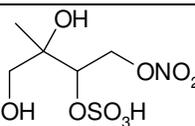
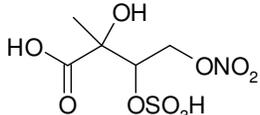
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Chemical Formula	<i>m/z</i> BSTFA Derivative (methane-Cl)	MW MW <sub>BSTFA</sub> (g mol <sup>-1</sup> )	Tentative Structure* and Chemical Name	References
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	247, 231, 157, 147, 73	102 246	 3-methyl-3-butene-1,2-diol (C <sub>5</sub> -diol-1)	Wang et al. 2005 Surratt et al., 2006
C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	263, 247, 173, 83, 73,	118 262	 2-methyl-2,3-epoxy-but-1,4-diol (IEPOX-1)	Paulot et al., 2009 Surratt et al., 2010 Zhang et al., 2012
C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	263, 247, 173, 83, 73	118 262	 2-methyl-3,4-epoxy-but-1,2-diol (IEPOX-2)	
C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	337, 321, 293, 219, 203	120 336	 2-methylglyceric acid (2-MG)	Claeys et al., 2004 Surratt et al., 2006 Edney et al., 2005 Szmigielski et al. 2007
C <sub>5</sub> H <sub>12</sub> O <sub>4</sub>	409, 319, 293, 219, 203	136 424	 2-methylthreitol (2-MT)	Claeys et al., 2004 Wang et al., 2004 Edney et al., 2005 Surratt et al., 2006 Nozière et al., 2011
C <sub>5</sub> H <sub>12</sub> O <sub>4</sub>	409, 319, 293, 219, 203	136 424	 2-methylerythritol (2-MT)	
C <sub>8</sub> H <sub>14</sub> O <sub>7</sub>	495, 321, 219, 203, 73	222 510	 2-methylglyceric acid dimer	Surratt et al., 2006 Szmigielski et al. 2007

			(2-MG dimer)	
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**LC-MS**

Chemical Formula	<i>m/z</i> Main Ions	MW (g mol <sup>-1</sup> )	Tentative Structure and Chemical Name*	References
C <sub>5</sub> H <sub>10</sub> O <sub>6</sub> S	197, 167, 97, 81	198	 IEPOX-derived organosulfate	Tao et al., 2014
C <sub>4</sub> H <sub>8</sub> O <sub>7</sub> S	199, 119, 97, 73	200	 2-methylglyceric acid organosulfate (2-MG OS)	Surratt et al., 2007a Gomez-Gonzalez et al., 2008 Shalamzari et al., 2013 Riva et al., 2016
C <sub>5</sub> H <sub>8</sub> O <sub>7</sub> S	211, 193, 113, 97	212	 2(3 <i>H</i> )-furanone, dihydro-3,4-dihydroxy-3-methyl organosulfate	Surratt et al., 2008 Hettiyadura et al., 2015 Spolnik et al., 2018
C <sub>5</sub> H <sub>10</sub> O <sub>7</sub> S	213, 183, 153, 97	214	 2,3,4-furantriol, tetrahydro-3-methyl-organosulfate	Hettiyadura et al., 2015 Spolnik et al., 2018
C <sub>5</sub> H <sub>12</sub> O <sub>7</sub> S	215, 97	216	 2-methyltetrol organosulfate (2-MT OS)	Surratt et al., 2007a Gomez-Gonzalez et al., 2008 Surratt et al., 2010
C <sub>5</sub> H <sub>10</sub> O <sub>8</sub> S	229, 149, 97, 75	230	 2-methylthreonic acid organosulfate	This study

C <sub>5</sub> H <sub>9</sub> O <sub>9</sub> S	243, 163, 145, 101	244	 2-methyltartaric acid organosulfate	This study
C <sub>5</sub> H <sub>11</sub> NO <sub>8</sub> S	244, 226, 197, 183, 153, 97	245	 2-methyltetrol nitrosoxy-organosulfate	This study
C <sub>5</sub> H <sub>11</sub> NO <sub>9</sub> S	260, 197, 183, 153, 97	261	 2-methyltetrol nitroxyorganosulfate	Surratt et al., 2007a Surratt et al., 2008
C <sub>5</sub> H <sub>9</sub> NO <sub>10</sub> S	274, 211, 193, 153, 97	275	 2-methylthreonic acid nitroxy-organosulfate	This study

\* For more stereo-chemically complex molecules a representative isomer is shown.

## References

Claeys M., Graham B., Vas G., Wang W., Vermeylen R., Pashynska V., Cafmeyer J., Guyon P., Andreae M.O., Artaxo P., Maenhaut W., Formation of secondary organic aerosols through photooxidation of isoprene. *Science*, 303, 1173-1176, 2004.

Edney E.O., Kleindienst T.E., Jaoui M, Lewandowski M, Offenbergl J.H, Wang W, Claeys M., Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO<sub>x</sub>/SO<sub>2</sub>/air mixtures and their detection in ambient PM<sub>2.5</sub> samples collected in the eastern United States., *Atmos. Environ.*, 39, 5281-5289, 2005.

Wang W., Kourtchev I., Graham B., Cafmeyer J., Maenhaut W., Claeys M., .Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass spectrometry, *Rapid Commun. Mass Spectrom.*, 19, 1343-51 2005.

Surratt J.D., Murphy SM, Kroll J.H., Ng N.L., Hildebrandt L, Sorooshian A, Szmigielski R, Vermeylen R, Maenhaut W, Claeys M, Flagan RC, Seinfeld JH. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene., *J. Phys. Chem. A*; 110, 9665–9690, 2006.

Szmigielski R, Surratt JD, Vermeylen R, Szmigielska K, Kroll JH, Ng NL, Murphy SM, Sorooshian A, Seinfeld JH, Claeys M., Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry. *Journal of Mass Spectrometry*, 42, 101, 2007.

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.

Gomez-Gonzalez Y.G., Surratt J.D., Cuyckens F., Szmigielski R., Vermeylen R., Jaoui M., Lewandowski M., Offenberg M., Kleindienst T.E., Edney E.O., Blockhuys F., Van Alsenoy Ch., Maenhaut W., Claeys M., Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, *J. Mass Spectrom.* 43, 371–382, 2008.

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J.H., Lewandowski, M., and Jaoui, M.: Organosulfate Formation in Biogenic Secondary Organic Aerosol, *J. Phys. Chem. A.*, 112, 8345–8378, 2008.

Paulot, F., Crouse J. D., Kjaergaard, H.G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O., Unexpected epoxide formation in the gas-phase photooxidation of isoprene, *Science*, 325, 730–733, 2009.

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Note, the reference section of the revised manuscript was updated.

**Comment # 15.** Figure 1: Why are all these chromatograms shown, when they are not discussed in detailed in the text? I suggest to reduce the figure to one or two chromatograms - if they are discussed.

**Response.** Figure 1 presents GC-MS Extracted Ion Chromatograms (EIC) obtained for ER667 isoprene photo-oxidation originated under non-acidic seed aerosol at 5 RH. All chromatograms in this figure were acquired using the same analytical method, therefore Figure 1 provides a direct visual comparison of the evolution of reaction products at the 5 RH. The identifications of 2-methylerythronic acid, 2-methylthreonic acid, and 2-methyltartaric acid are tentative and further work is being conducted to understand their role in isoprene SOA, therefore they were deleted from the present manuscript for clarity purpose. An effort is underway to synthesize these compounds in our laboratory.

**Comment # 16.** P11.L10: What do you mean by "attained"? C2 Table 3: Add percentage for RH (RH9 -> RH9%). Data in Table 4 and Figures 4-5 should be presented and discussed in more detail.

**Response.** We changed the following sentence from:

“According to attained chromatographic separations a number of isomers of analyzed compounds were distinguished, i.e. IEPOX-1 and IEPOX-2 or 4 isomers of 2-methyltetrols, however, only some of them are marked on the figure.”

To

“According to acquired chromatograms shown in Figure 1, several isomers associated with the compounds analyzed can be distinguished, i.e. IEPOX-1 and IEPOX-2, 4 isomers of 2-methyltetrols and their relative contributions to SOA masses at various relative humidity levels.”

Tables 3 and 4 were updated as requested by the reviewer.

We added the following sentence on page 15, line 7 (original manuscript) to the revised manuscript to reflect the reviewer concern:

“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.”

**Comment # 17.** Page 17 Line 9: Please write this as a complete sentence.

**Response.** We changed the following sentence on page 17, line 9 from:

“Figure 6 compares the results for 2-methylglyceric acid – combined effect of RH and H<sub>2</sub>SO<sub>4</sub> was stronger than that 10 of RH alone. Some of the compounds were produced in higher quantities in the acidic seed experiments (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 (IEPOX-2, methylthreonic acid, 2-methylglyceric acid OS, 2-methylthreonic acid OS). Yields of the remaining compounds followed a mixed pattern (supplementary information: see Figs S1, and S2, and Table S1).”

To

“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 relative humidity. 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 # 18.** Figures 7-14. Some of these should be moved to Supplementary. Instead of experiment number it would be more useful to the reader to list whether an experiment was non-acidic or acidic.

**Response.** We moved Figures 9, 10, 13, and 14 to the supplementary information. We changed accordingly the numbering of the remaining figures. We also incorporate when appropriate in the revised manuscript if an experiment is non-acidic or acidic instead of experiment number.

**Comment # 19.** Page 21: please add figure number to the mass spectrum.

**Response.** The mass spectrum is part of Figure 15 as is the case of Figure 16.

**Comment # 20.** Conclusion: How much do the quantified compounds make-up of the total SOA mass? It is important to keep this in mind, when discussing the effects of acidity and RH.

**Response.** Given the relatively limited organic quantification available in these experiments due unfortunately to lack of authentic standards as well using ketopinic acid as surrogate for quantitative analysis, it is difficult to assess their contribution to SOA mass accurately. In this paper, only estimates were provided as noted in the main manuscript.

We have also added the following paragraphs prior to the summary section, which includes an additional review of the limitations of the quantitative analysis presented in the paper, including areas requiring additional investigation in future work, which includes discussion of the need for using authentic standards, and modeling work. The two paragraphs are:

“While these experiments provide an analysis of a wide range of isoprene reaction products in the aerosol phase as a function of RH and acidity, they also include a number of shortcomings that need to be addressed in future work. Perhaps the most significant is the use of authentic standards to assess the contribution of these products to SOA mass at different RH. In addition, when the relative humidity is varied, it is important to measure aerosol liquid water content directly or estimated using thermodynamic models, such as ISOPROPIA (Fountoukis and Nenes, 2007) or AIM (Wexler and Clegg, 2002), and other gas and particle composition (e.g. inorganic species). Liquid water inorganic species measurements were not available for this study.

The use of these marker compounds for ambient air quality models can follow the approach of Pye et al. (2013). In such an approach, the model is run using a base case chemical mechanism for isoprene, where there is no adjustment for acidity and relative humidity. A comparison can then be made with the same model having such an adjustment incorporated within the isoprene mechanism. The markers can then serve as constraints to the PM observations. For the U.S. the Community Multiscale Air Quality (CMAQ) model is frequently used for ozone and PM ambient concentrations (Pye et al., 2013). For Poland, a similar approach can be used with a European model having the appropriate meteorology and chemical mechanism (Miranda et al. 2015).”

The following references were added to the reference section.

Miranda, A., Silveira, C., Ferreira, J., Montheiro, A., Lopes, D., Relvas, H., Borrego, C., and Roebeling, P.: Current air quality plans in Europe designed to support air quality management policies. *Atmospheric Pollution Research*, 6, 434-443, 2015.

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