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 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 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 PM₂.₅ (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.


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.


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; Rattanavaraha et al., 2016; Gaston et al., 2014; Riedel et al., 2015; Zhang et al., 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).”


**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-NOx 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 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 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\textsubscript{x} concentration, modestly in Zielonka at 1.3 µg m\textsuperscript{-3} and at a level of 30 µg m\textsuperscript{-3} in Godow, represented by the nearest monitoring station at Zywiec, PL. The SO\textsubscript{2} levels at Zielonka were approximately 0.6 µg m\textsuperscript{-3} and 3.0 µg m\textsuperscript{-3} 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\textsuperscript{-3} and 5.4 µg m\textsuperscript{-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 \( \rightarrow \) 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 cm\textsuperscript{2} 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 preparation 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 M\textOmega\cdot cm\textsuperscript{-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.”

**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, NOx level (NO/VOC ratio), concentration and type of seed aerosol, OH concentration…). Our experiments were conducted in the presence of NOx and yields reported under these conditions correspondent to the lowest end compared to those measured under NOx-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 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 NOx (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 NOx (= 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 NOx (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 NOx 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 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:


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).”


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—> 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 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-methylgligeric 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 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 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 NOx 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 NOx-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 presence of NOx 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-NOx conditions.”


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 diminished with increasing RH to a negligible value of 0.3 µg 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, furanetrol-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:
acid-catalyzed multiphase chemistry with IEPOX

OH- radical multiphase chemistry on wet/aqueous aerosol followed by recombination with NO2 radicals
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 (NOx), a detailed characterization of SOA at the molecular level have been also conducted. Experiments were conducted in a 14.5 m³ 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$_{2.5}$ 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 flowing references were added to the revised manuscript:


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 organicsulfate (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, 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 PM₂.₅ (Xie at al., 2014).”

The new references were added to the reference section.


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


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.


**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:

“Twenty ambient PM$_{2.5}$ samples were collected, onto pre-baked quartz-fiber 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 of northern Poland (53$^\circ$39'N, 17$^\circ$55'E) during the 2016 summer campaign, and at the regional background monitoring station in Godow, located in the Silesian Province in southern Poland (49$^\circ$55'N 18$^\circ$28'E) in summer 2014. At both sites, strong emission of isoprene occurred. The Zielonka station is located in the forested rural area while the Godow station is located near a coal-fired power station in Detmarovice (Czech Republic) and close to big industrial cities of the Silesian agglomeration (Poland). Therefore, SOA collected in Godow can be influenced by anthropogenic aerosol precursors. The relative humidity level during sampling in Zielonka was 86%, SO$_2$ emission was estimated at 0.6 µg/m$^3$ and 25 OC value was 1.68 µg/m$^3$. The relative humidity level during sampling in Godow was 94%, SO$_2$ emission was estimated at 3.0 µg/m$^3$ (approximate value from the nearest sampling station - Zory) and OC value was 5.43 µg/m$^3$. Both locations were influenced by NO$_x$ emission – slightly in Zielonka at 1.3 µg/m$^3$ and 30.0 µg/m$^3$ in Godow (approximate value from the nearest sampling station - Zywiec).”
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 NOx 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 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⁻³ and 5.4 µg m⁻³ 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.

<table>
<thead>
<tr>
<th>Product</th>
<th>GC-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldolase</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td></td>
</tr>
</tbody>
</table>

6
<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>m/z BSTFA Derivative (methane-CI)</th>
<th>MW BSTFA (g mol⁻¹)</th>
<th>Tentative Structure* and Chemical Name</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅H₁₀O₂</td>
<td>247, 231, 157, 147, 73</td>
<td>102 246</td>
<td>3-methyl-3-butene-1,2-diol (C₅-diol-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wang et al. 2005, Surratt et al., 2006</td>
</tr>
<tr>
<td>C₅H₁₀O₃</td>
<td>263, 247, 173, 83, 73</td>
<td>118 262</td>
<td>2-methyl-2,3-epoxy-but-1,4-diol (IEPOX-1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Paulot et al., 2009, Surratt et al., 2010, Zhang et al., 2012</td>
</tr>
<tr>
<td>C₅H₁₀O₃</td>
<td>263, 247, 173, 83, 73</td>
<td>118 262</td>
<td>2-methyl-3,4-epoxy-but-1,2-diol (IEPOX-2)</td>
<td></td>
</tr>
<tr>
<td>C₅H₆O₄</td>
<td>337, 321, 293, 219, 203</td>
<td>120 336</td>
<td>2-methylglyceric acid (2-MG)</td>
<td>Claeys et al., 2004, Surratt et al., 2006, Edney et al., 2005, Szmigielski et al. 2007</td>
</tr>
<tr>
<td>C₅H₁₂O₄</td>
<td>409, 319, 293, 219, 203</td>
<td>136 424</td>
<td>2-methylthreitol (2-MT)</td>
<td>Claeys et al., 2004, Wang et al., 2004, Edney et al., 2005, Surratt et al., 2006, Nozière et al., 2011</td>
</tr>
<tr>
<td>C₅H₁₂O₄</td>
<td>409, 319, 293, 219, 203</td>
<td>136 424</td>
<td>2-methylerthritol (2-MT)</td>
<td></td>
</tr>
<tr>
<td>C₅H₈O₇</td>
<td>495, 321, 219, 203, 73</td>
<td>222 510</td>
<td>2-methylglyceric acid dimer</td>
<td>Surratt et al., 2006, Szmigielski et al. 2007</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>m/z Main Ions</td>
<td>MW (g mol⁻¹)</td>
<td>Tentative Structure and Chemical Name*</td>
<td>References</td>
</tr>
<tr>
<td>------------------</td>
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<td>---------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>C₅H₁₀O₅S</td>
<td>197, 167, 97, 81</td>
<td>198</td>
<td>IEPOX-derived organosulfate</td>
<td>Tao et al., 2014</td>
</tr>
<tr>
<td>C₄H₈O₇S</td>
<td>199, 119, 97, 73</td>
<td>200</td>
<td>2-methylglyceric acid organosulfate (2-MG OS)</td>
<td>Surratt et al., 2007a, Gomez-Gonzalez et al., 2008, Shalamzari et al., 2013, Riva et al., 2016</td>
</tr>
<tr>
<td>C₅H₈O₇S</td>
<td>211, 193, 113, 97</td>
<td>212</td>
<td>2(3H)-furanone, dihydro-3,4-dihydroxy-3-methyl organosulfate</td>
<td>Surratt et al., 2008, Hettiyadura et al., 2015, Spolnik et al., 2018</td>
</tr>
<tr>
<td>C₅H₁₀O₇S</td>
<td>213, 183, 153, 97</td>
<td>214</td>
<td>2,3,4-furantriol, tetrahydro-3-methyl-organosulfate</td>
<td>Hettiyadura et al., 2015, Spolnik et al., 2018</td>
</tr>
<tr>
<td>C₅H₁₀O₇S</td>
<td>215, 97</td>
<td>216</td>
<td>2-methyltetrol organosulfate (2-MT OS)</td>
<td>Surratt et al., 2007a, Gomez-Gonzalez et al., 2008, Surratt et al., 2010</td>
</tr>
<tr>
<td>C₅H₁₂O₇S</td>
<td>229, 149, 97, 75</td>
<td>230</td>
<td>2-methylthreonic acid organosulfate</td>
<td>This study</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>Mass (Da)</td>
<td>Charge (n)</td>
<td>Molecular Structure</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------</td>
<td>------------</td>
<td>---------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>C₉H₅O₉S</td>
<td>243, 163, 145, 101</td>
<td>244</td>
<td><img src="image" alt="2-methyltartaric acid organosulfate" /></td>
<td>This study</td>
</tr>
<tr>
<td>C₇H₁₁NO₉S</td>
<td>244, 226, 197, 183, 153, 97</td>
<td>245</td>
<td><img src="image" alt="2-methyltetrol nitrosoxyorganosulfate" /></td>
<td>This study</td>
</tr>
<tr>
<td>C₇H₁₁NO₉S</td>
<td>260, 197, 183, 153, 97</td>
<td>261</td>
<td><img src="image" alt="2-methyltetrol nitroxyorganosulfate" /></td>
<td>Surratt et al., 2007a</td>
</tr>
<tr>
<td>C₅H₇NO₁₀S</td>
<td>274, 211, 193, 153, 97</td>
<td>275</td>
<td><img src="image" alt="2-methylthreonic acid nitroxyorganosulfate" /></td>
<td>This study</td>
</tr>
</tbody>
</table>

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

**References**


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:

“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 on 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 Cregg, 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.


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

Response to reviewer’s comments (# 3)

This reviewer said in the general comments:

“This manuscript measures the chemical composition changes (as well as bulk SOA yields) of isoprene SOA produced under acidic and non-acidic conditions as a function of relative humidity. The kind of results presented here could certainly be of value to the atmospheric and aerosol research communities. However, as I will stress in some of my major comments below, I think one thing that is missing is a stronger connection to current models that explicitly predict isoprene SOA formation through acid-catalyzed multiphase chemical processes. Of these processes, the acid-catalyzed multiphase chemistry of IEPOX on acidic (and wet) sulfate aerosol has been shown to be one of the dominant sources of isoprene SOA in atmospheric PM samples (e.g. Claeys et al., 2004, Science; Lin et al., 2013, ACP; Budisulistiorini et al., 2015, ACP, etc. etc.). The acid-catalyzed multiphase chemistry of high-NOx SOA precursors, such as HMML/MAE, have been shown to yield very little SOA in atmospheric PM samples (e.g., Lin et al., 2013, ACP; Budisulistiorini et al., 2015, ACP; Rattanavaraha et al., 2016, ACP). Since IEPOX has been shown to be so important to forming SOA in atmospheric PM samples, recent work has been really aimed at measuring reactive uptake (or multiphase chemical) kinetics of IEPOX on differing aerosol types as a function of aerosol acidity and RH (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters). Recently, how RH affects both aerosol acidity and aerosol-phase state (morphology) has been examined to determine how the reactive uptake kinetics changes (Zhang et al., 2018, ES&T Letters). These studies have helped to further develop models, such as CMAQ (Pye et al., 2013, ES&T), GAMMA (McNeill 2015, ES&T), and GEOS-Chem (Marais et al. 2016, ACP), that now explicitly predict 2-methylterols and organosulfates derived from the acid-catalyzed multiphase chemistry of IEPOX as well as predicting 2-methylglyceric acid and organosulfates derived from multiphase chemistry of MAE/HMML. Since there are now models to predict many of the SOA constituents you measure here, I think you need to present your data in a clearer way in how this can improve future modeling efforts. This is a major shortcoming of the present work and why I strongly suggest this manuscript requires revision before full publication in ACP can be considered.”
Response. First, we would like to thank this reviewer for the time and effort spent in reading and evaluating this manuscript. While the results presented in this paper could certainly benefit from additional information regarding modeling work, we do not believe that this information is vital to the comparisons presented. Although, we do agree with the reviewer’s assessment of the importance of modeling.

Multiphase chemistry (e.g. relative uptake of IEPOX on aerosol particles) has been shown to be important in forming SOA in atmospheric PM samples (e.g. Gaston et al., 2014; Riedel et al., 2015), and as noted in our response to reviewer # 2, comment # 20, it is important to measure directly or have an accurate estimate of aerosol liquid water content in order to accurately “model” the formation of isoprene reaction products formed under a wide range of RH. Liquid water inorganic species measurements were not available for this study. Air quality modeling to improve organic PM predictions using the organic markers as constraints is both outside the scope of this paper and, in any case, is not at the stage to help improve model results. How such modeling might function is given in the last paragraph of the Results and Discussion.

We have added now the following paragraph to address this issue just before the Summary section in the revised manuscript:

“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 Cregg, 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 provided that absolute concentrations can be assigned. 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 reviewer goes on to say:

“Another major problem with this manuscript is it is poorly written in many sections (including grammar issues and improper citations) and fails to connect their results to recent advances on isoprene SOA chemistry. I’ve made suggestions below in the major comments section on how some of this can be improved. One of the authors who is a native English speaker should really carefully review the written text for these authors before resubmitting the revised draft. I found the poor writing distracting while reading the manuscript.”

Response. The revised manuscript was carefully edited for appropriate scientific-English terminology as well as to explicate certain sections or paragraphs that may have lacked clarity or been perplexing. The results have been augmented to reflect recent advances in isoprene SOA chemistry.

Major revisions.

Comment #1. “Page 2, Lines 4-6: Best to cite Guenther et al. 2006, Guenther et al., 1995 for this sentence and remove its citation in the first sentence. Along with the Goldstein and Galbally (2007) in the first sentence (lines 2-4), the authors could cite Hallquist et al. (2009, ACP).”

Response. This was corrected as suggested by the reviewer. Guenther et al., 2006 was added to the reference section.

Comment #2. “Page 2, Lines 8-10: Again, greater care is needed with this sentence. 2- methyltetrols, 2-methylglyceric acid, and organosulfates all form from multiphase chemistry and NOT gas-phase oxidation chemistry. However, I think the authors mean to say that certain oxidation products from isoprene + OH, isoprene + NO3, or isoprene + O3 undergo subsequent multiphase chemical reactions to yield these important SOA constituents.”

Response. We did not understand the reviewer concerns here. We refer to isoprene removal through gas phase chemistry and not to its oxidation products. We agree somewhat with the reviewer that 2- methyltetrols, 2-methylglyceric acid, and organosulfates are formed only through multiphase chemistry but we cannot exclude their gas phase formation also, at least for the 2-methyltetrols and 2-methylglyceric acid. For examples, 2-methyltetrols and 2-methylglyceric acid were detected in our laboratory in the gas phase from the chamber
oxidation of isoprene and as indicated in the associated mechanism (Kleindienst et al., 2009). Our chamber data are consistent with isoprene oxidation products 2-methyltetrols and 2-methylglyceric acid presence either in the gas phase, in the particle phase, or both. 2-Methyltetrols were also reported in ambient samples in the gas phase (Xie et al., 2014). During a recent inter-comparison study during 2013 SOAS field study, using four “real-time” instruments (FIGAERO-HRTof-CIMS with acetate ionization source; FIGAERO-HRTof-CIMS with iodide ionization source; semi-volatile thermal desorption aerosol GC-MS (SV-TAG); high-resolution thermal desorption proton-transfer reaction mass spectrometer (HR-TD-PTRMS)) for gas/particle partitioning of organic species, Thomson et al. (2016) show the difficulties of these instruments in the interpretation of complex ambient samples. Note that the formation of 2-methyltetrols and 2-methylglyceric acid and other isoprene/momoterpene products in the gas or particle phase through multiphase chemistry remain poorly constrained.

However, to reflect the reviewer comment, 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 the formation of numerous oxidized SOA components, including 2-methyltetrols, 2-methylglyceric acid, C5-alkene triols and C4/C5 organosulfates (OSs). These compounds were identified in ambient PM2.5 (particulate matter with diameter < 2.5 μm) in several places around the world while SOA generated from isoprene was reported to account for up to 20 – 50% of the overall SOA budget (Claeys et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).” which is changed 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 PM2.5 (Xie at al., 2014). Moreover, these compounds were identified in ambient PM2.5 in several places around the world, and SOA from isoprene often accounts for 20–50% of the overall SOA budget (Claeys et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).”
The following references were added to the reference section.


Comment #3. “Page 2, Line 12: correct the spelling of "Claeys" here.”
Response. We thank the reviewer for this. This has been corrected.

Comment #4. “Page 2, Line 18: Probably worth citing Surratt et al. (2006, JPCA) and Surratt et al. (2010, PNAS) for the NOx concentration having an affect on the isoprene SOA composition”
Response. This was updated as suggested by the reviewer.

Comment #5. “Page 2, Lines 22-24: Citations to the published literature are needed for this sentence.”
Response. To reflect the reviewer comment, we added the following references on page 2, line 24 (original manuscript): (Lin et al., 2013; Budisulistiorini et al., 2016; Rattanavaraha et al., 2016; Gaston et al., 2014; Riedel et al., 2015; Zhang et al., 2018).

These new references were added to the revised manuscript.

Budisulistiorini S.H., Baumann K., Edgerton E.S., Bairai S.T., Mueller S., Shaw S.L., Eladio M. Gold
K.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.

Zhang Y., Chen Y., Lambe A.T., Olson N.E., Lei Z., Craig R.L., Zhang Z., Gold A., Onasch T.B.,
Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived

Rattanavaraha, W., Chu, K., Budisulistiorini, S. H., Riva, M., Lin, Y.-H., Edgerton, E. S., Baumann,
Gold, A. and Surratt, J. D.: Assessing the impact of anthropogenic pollution on isoprene-derived secondary
organic aerosol formation in PM$_{2.5}$ collected from the Birmingham, Alabama, ground site during the 2013

Gaston C. J., Thornton J. A. and Ng N. L.: Reactive uptake of N$_2$O$_5$ to internally mixed inorganic and
organic particles: the role of organic carbon oxidation state and inferred organic phase separations, Atmos.

Gold A., and Surratt J. D.: Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and
Riedel et al., 2015.

**Comment #6.** “Page 2, Lines 24-26: The authors need to also include the fact that the acid catalyzed
multiphase chemistry (or reactive uptake) of IEPOX also highly depends on the aerosol phase state. As recently
shown by Zhang et al. (2018, ES&T Letters) the reactive uptake of IEPOX is adversely affected if aqueous
sulfate aerosol is coated with viscous SOA. This causes a substantial diffusion barrier that the IEPOX can’t
react in the aqueous acidic core. This recent work is also supported by initial findings presented in Gaston et al.
(2014, ES&T) and Riva et al. (2016, ES&T).”

**Response.** We added the following sentences to the revised manuscript on page 2, line 25 (original
manuscript) and read:

“However, this type of multiphase chemistry following the uptake of IEPOX can be highly
dependent on the aerosol phase state and the presence of aerosol coatings from viscous SOA constituents (Zhang et al., 2018). Such coatings can cause a substantial diffusion barrier to the availability to an acidic core.”

Comment #7. “Page 2, Line 26-27: Acid-catalyzed reactions of isoprene ozonolysis products have also been recently reported by Riva et al. (2015, Atmos. Environ.) and Riva et al. (2017, Atmos. Environ.). These are worth mentioning here.”

Response. We have added the Riva et al., 2016 (we believe the reviewer is referring to 2016 Riva et al. paper and not to a 2015 paper) and Riva et al., 2017 references to the revised manuscript.


Comment #8. “Page 3, Line 5: Don’t the authors mean Surratt et al. (2007, ES&T) and not Kleindienst et al. (2007)? This seems strange to me.”

Response. This is corrected as suggested by the reviewer.

Comment #9. “Chemical Artifacts (Potentially Serious Issue): Since filters were collected and extracted and derivatized for GC/EI-MS, can the authors comment on any potential artifacts? The reason this is so important is that recent work by Lopez-Hilfiker et al. (2016, ES&T) showed that IEPOX-derived SOA had a much lower volatility than expected. It turned out that they provided evidence that 2-methyltetrols and C5-alkene triols are likely thermal degradation products from accretion products (oligomers and organosulfates). Can the authors rule out that these novel GC/MS products are not simply thermal degradation products of accretion products found with the SOA?”

Response. Artifact peaks associated with silylation (BSTFA) derivatization elute early in the chromatogram and are clearly recognizable from isoprene oxidation products (e.g. by the interpretation of their mass spectra and their occurrence in blank and background samples), which elute after artifact peaks. In addition, BSTFA
artifacts were identified in our work by acquiring blank and/or background chamber, as well as from analyzing about a hundred of standards derivatized in our laboratory, including methyltetrols, and IEPOX.

The point brought by the reviewer associated with accretion products is very important. Lopez-Hilfiker et al. (2016) analyzing samples collected during the 2013 SOAS field study, hypothesize that 2-methyltetrols and C5-alkene triols are likely thermal decomposition products from accretion products. These authors analyzed thermograms originated from filters collected on FIGAERO-CIMS system (PM1), and measured the bulk aerosol composition. The possibility of artifacts in our methods or in the FIGAERO-CIMS must always be recognized, and they are typically checked but not necessarily reported. In prior work, we have addressed possible sample handling problems and do not believe that further work is required on our behalf. We feel that the potential issues using the CIMS-FIQAERO instrument might need further exploration to address that instrument-specific formation artifacts and analyte losses (e.g. thermal decomposition, using vacuum and its effect on more volatile compounds losses).

Our data provide strong evidence that 2-methylglyceric acid, 2-methyltetrols and C5-triols exist in our systems as monomers as well as dimers. (See compounds observed as dimer in the figures below as well as Jaoui et al., 2008). The derivatization technique used in this study in not associated with thermal decomposition as speculated by Lopez-Hilfiker et al. (2016). As an example, the figure below shows the presence of monomers: 2-methylglyceric acid and 2-methyltetrols as monomers as well as and dimers (2-methyltetrols_2-methylglyceric acid dimers) in the same or similar system (Jaoui et al. 2008; also SOA from isoprene + ozone). This is consistent that silylation reactions does not leading to isoprene dimers through thermo-decomposition by the extraction and derivatization procedure given that we detect dimers and monomers as TMS-derivative. In addition, we conducted two derivatizations on isoprene SOA extract using the same amount of the extract for each derivatization. Both derivatizations underwent the same steps except one was heated to 70 °C for 1 hour (same technique used in this study), and the second was left for 24 hours at room temperature (no heat). The results show that chromatograms acquired from both derivatization were essentially identical, confirming that the BSTFA derivatization does not lead to thermal decomposition of the TMS-dimer isoprene products. In fact, the silylation derivatization can be a useful tool for identifying the presence of oligomers in SOA as shown in the figure.
Figure 1. Total (top) and extracted (bottom) ion chromatograms of an isoprene ozone experiment showing the presence of monomeric and dimers oxidation products using silylation reaction (BSTFA) using the same protocol used in the paper.
Figure 2. Mass spectra associated with isoprene monomer 2-methylglyceric acid and dimers observed simultaneously in isoprene SOA.
Comment #10. “Page 5, Lines 23-28: How were OC and SO2 emissions estimated from the Poland sites? This needs to be clarified in the experimental section.”

Response. We changed “section 2.2.” to reflect the reviewer comments and read:

“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 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 SO$_2$ levels at Zielonka were approximately 0.6 µg m$^{-3}$ and 3.0 µg m$^{-3}$ 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$^{-3}$ and 5.4 µg m$^{-3}$ at Godow, although aerosol masses were not determined.”

Comment #11. “Table 1: It would be easier if you could label on Table 1 what the sulfate mass concentrations were in there. Also, why didn’t the authors consider running a thermodynamic model like ISORROPIA to estimate aerosol acidity. That way you can estimate what the aerosol acidity is as a function of RH. Obviously, as RH is increasing it is adding more water to your particles that you atomize the same way at each test condition, and thus, your pH is becoming less acidic.”

Response. To address the reviewer comment, we updated the caption of Table 1, and now reads:

“Table 1. Initial and steady state conditions, yields and OM/OC data for chamber experiments on isoprene
photooxidation in the presence of acidic and non-acidic seed aerosol. The initial NOx was entirely nitric oxide. Experiment ER667 was conducted at a low-concentration ammonium sulfate seed (~1 μg m⁻³). Experiment ER662 was conducted with a higher concentration of inorganic seed (~30 μg m⁻³) generated from a nebulized solution for which half the sulfate mass was derived from sulfuric acid and the other half from ammonium sulfate (Lewandowski et al., 2015). As for using thermodynamic models for aerosol acidity, see the responses to reviewers from Lewandowski et al., 2014, and our response to reviewer #2, comment 20. A copy of Lewandowski et al. 2015 response to similar comment is provided below and reads:

“In the varied RH experiments, where [H⁺]ₐir measurements are of limited value (since the maximum dissociated H⁺ in the extracts remains unchanged, but actual aerosol pH is expected to change with liquid water content), 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. Unfortunately, we do not have sufficient composition information to do the modeling with 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. Additionally, as with the SOAS field measurements reported in Guo et al., 2014, we have a significant aerosol fraction composed of isoprene-related organic aerosol to contend with, which can further contribute to aerosol phase water content, but is not accounted for in the models. Given these limitations, we believe that any modeled pH levels or aerosol liquid water concentrations that we could generate from our existing data would be suspect and potentially counterproductive to the analysis (due more to our under-analysis of the aerosol composition than to any limitations inherent in the models). While we readily admit that humidity provides, at best, an indirect measure of the physically important aerosol parameters of interest in these comparisons, it is nevertheless the most reliable measurement surrogate that we have to work with in this data set.”

See our response to reviewer 2, comment #20 for addition text added to the revised manuscript.

Comment #12. “Page 8, Lines 3-5: Citations are warranted to prior studies that characterized these ions as characteristic ions for organosulfates and nitrooxy organosulfates.”

Response. We added the following references.


Comment #13. “IEPOX-1 and IEPOX-2 is VERY STRANGE: IEPOX-1 and IEPOX-2 don’t make any sense to me. Do the authors mean they are the isomers of 3-MeTHF-3,4-diols? These were first characterized by authentic standards in Lin et al. (2012, ES&T) by the Surratt Group at UNC. 3-MeTHF-3,4-diols.”

Response. We are not sure what the reviewer is referring here. IEPOX-1 and IEPOX-2 are defined in Table 2 with their structure and nomenclature. These compounds are reported in the literature during the last six years and are isomers of 3-MeTHF-3,4-diols. To reflect the reviewer comment, we added Lin et al., 2012 reference to the revised manuscript.


Comment #14. “Table 2 - LC/MS section: MW 230 is the wrong structure. I’m surprised by the carelessness here.”

Response. We thank the reviewer. This was corrected.

Comment #15. “Page 11, Lines 19-20: You’re specific about the other tracers precursors (i.e., IEPOX and MPAN). Why not be more specific here for these recently reported new SOA tracers?”

Response. See response to comment 15, reviewer # 2.

Comment #16. “Page 12, Lines 13-14: What are the uncertainties of using ketopinic acid to quantify all eight isoprene SOA constituents measured by GC/EI-MS?”
Response. Due to lack of authentic standards, we used ketopinic acid for all samples, as we have in past studies, to estimate the changes associated with each compound reported in this study as the RH or acidity changes. As noted in Figures 2, 4, Tables 3, 4 captions, these are necessarily estimates. Without authentic standards, it is difficult to estimate the uncertainties of using ketopinic acid. (See Jaoui et al., (2005) for a further discussion of this point.

Comment #17. “Page 12, Lines 16-17: The fact that you measure 2-methyltartaric acid organosulfate at levels above baseline in your LC/ESI-MS makes me wonder how important this compound really is to isoprene SOA formation. More specifically, what is the exact precursor to this species that forms from the gas-phase oxidation of isoprene?”

Response. See our response to comment #15, reviewer #2.

Comment #18. “Page 14, Lines 5-7: The terminology "the most abundant were organosulfates derived from 2-methyltetrols (MW 216) and 2-methylglyceric acid (MW 200)" is incorrect. This should really state "Organosulfate monomers derived from acid-catalyzed multiphase chemistry of IEPOX (MW 216) and MAE/HMML (MW 200)" to more accurately reflect their sources (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T; Lin et al., 2013, PNAS; Nguyen et al., 2015, PCCP). For the IEPOX-derived organosulfates, they are being termed 2-methyltetrol sulfates and 3-methyltetrol sulfates to reflect the possible isomers that form from the multiphase chemistry of the IEPOX isomers (i.e., cis- and trans-beta-IEPOX and delta-IEPOX). Recall, Bates et al. (2014, JPCA) showed that the cis- and trans-beta-IEPOX isomers are the predominant isomers that form in the gas phase, with trans-beta-IEPOX being the most abundant. The beta-IEPOX isomers likely lead to the 2-methyltetrol sulfate isomers.”

Response. The whole paragraph (page 14, line 4-14: original manuscript was updated and now reads:

"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-humid conditions of RH 9% (Figure 2). Among compounds detected with LC-MS (Figure 3) are organosulfates derived from acid-catalyzed 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 RH 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). Total SOC decreased with increased RH (Table 1). Generally, the influence of RH on the product yields was mild, with the exception of 2-methyltetrols, 2-methylglyceric acid, and 2-methylglyceric acid dimer which were produced in significantly larger amounts at RH 9% compared to RH 49%. This is generally consistent with Dommen et al. (2006) and Nguyen et al. (2011), who saw a negligible effect of relative humidity on SOA formation in photooxidation of isoprene in the absence of acidic seed aerosol. 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 presence of NOx and seed aerosol (acidic and non-acidic) under a wide range of humidity, however hydroxyhydropeoxide (ISOPOOH), and IEPOX were used as reactant in Riva et al., and Lin et al. studies under two RH and free-NOx conditions.”

Comment #19. “Page 14, Lines 17-18: I’m not in agreement with this statement. Precursors for organosulfates typically form in the gas phase from the oxidation of isoprene. Such precursors like IEPOX have large Henry’s law constants, and thus, can partition into any aerosol water that might be present in the aerosol phase. Thus, the detection of these organosulfates could simply result from the fact that there is enough water on these particles (especially if organics condense and then take up water). I think the authors are unable to rule out this possibility based on their data.”

Response. In our sentence on page 14, lines 17-19 that reads “However, 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 we detected could also occur via this mechanism.”

We did not understand the reviewer concerns here. We refer in this sentence to the formation of organosulfates in the non-acidic seed aerosol and how they may be formed, that is, from where the sulfate group originates. We do agree with the reviewer that IEPOX may be a precursor to these organosulfates in the non-acidic aerosol.

Comment #20. “The ER labelling of experiments is really not helpful to readers. Can’t you simply just call one set of experiments the acidic experiment at varying RH and the other one the non-acidic experiment at varying RH?”
Response. The ER label is associated with the chamber used to generate these data. Therefore, for quality assurance purposes and clarity these labels were kept in the revised manuscript, when appropriate. We do not feel this is too distracting for the reader.

Comment #21. “As shown in Table 4 heading, reporting [H+] air concentration isn’t really helpful to modeling. Couldn’t the authors use one of the thermodynamic models to estimate what the INITIAL pH is of these particles? If the authors recall, McNeill (2015, ES&T), Pye et al. (2013, ES&T) and Maraias et al. (2017, ACP) have developed explicit models to predict IEPOX SOA. These models have been further developed by aerosol flow tube reactors that determine the reactive uptake coefficient of IEPOX as a function of acidity (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters), RH (Gaston et al., 2014, ES&T; Zhang et al., 2018, ES&T Letters) and pre-existing SOA coatings (Gaston et al., 2014, ES&T; Zhang et al., 2018, ES&T Letters). It’s not clear to me how this data you show in Table 4 and Table 3 can help improve explicit modeling of many of these SOA products. The GAMMA, CMAQ, and GEOS-Chem models all now explicitly predict 2-methyltetrols and the organosulfates derived from the acid-catalyzed chemistry of IEPOX. In addition, some of these models, like CMAQ, now predict 2-methylglyceric acid and the organosulfate derived from MAE/HMML multiphase chemistry. I think much more care is needed by the authors to convince readers and reviewers how this data can be used to further improve these much needed models. I strongly believe these models have to explicitly model the acid-catalyzed multiphase chemistry of isoprene oxidation products that consider the interconnecting effects of aerosol acidity and aerosol phase state, which both depend on the RH condition.”

Response. We generally agree with the reviewer’s assessment of the limitations of the [H+] air measurement. See our response to comment # 11 above for running a thermodynamic model to estimate the initial pH. Also see our comment to reviewer # 2, comment # 20.

Comment #22. “Figure 4 is poorly generated. Too difficult to read. Please regenerate this figure. Why do some figures use color and others use black and white. I think your figures need to be more consistently generated.”

Response. This figure is regenerated as shown in the revised manuscript. All figures in the revised manuscript are now consistent.
Comment #23. “Figure 6: It remains unclear to me how much sulfate was present in all the conditions shown in this figure, the tables of the experimental conditions, and the experimental description. Is sulfate the same concentration in each experiment? 2-MG has been shown to be reduced in concentration if the acidity of the aerosol is high (Nguyen et al., 2015, PCCP). In fact, there is prior evidence that the nucleation of 2-MG and its corresponding oligoesters is enhanced under dry conditions (Nguyen et al., 2011, ACP; Zhang et al., 2011, AcP). I wonder, do you have evidence in your size distribution measurements of nucleation events? I ask this since it appears your sulfate seed aerosol concentrations were quite low at the start of each experimental condition.”

Response. See our response to Comment #11 above for sulfate concentrations associated with both experiments. Sulfate concentrations are internally consistent within each experiment, but the two runs use both different inorganic concentrations and different inorganic compositions, as noted in our response to comment #11. See the experimental section of Lewandowski et al. (2015) for additional text describing the experimental conditions. As all experiments start with non-trivial concentrations of inorganic material (at least one-third of the total particle mass in ER662, and at least 5% in ER667), would we expect any organic products formed to condense on existing inorganic particles rather than undergoing nucleation. However, as all sampling was conducted only after the chamber system reached steady-state conditions, transient nucleation events, should they somehow occur despite the presence of preexisting inorganic particles, would not be detected.

Comment #24. Surratt et al. (2007, ES&T) - The authors don’t compare their results to that paper. That paper showed 2-MG concentration doesn’t change with increasing aerosol acidity, but the 2-methyltetrols do.

Response. See our response to reviewer # 2, comment # 17.
Chemical composition of isoprene SOA under acidic and non-acidic conditions: Effect of relative humidity

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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 (NOx), a detailed characterization of SOA at the molecular level have been also conducted. Experiments were conducted in a 14.5 m³ smog chamber operated in flow mode. Based on a detailed analysis of mass spectra obtained from GCMS gas chromatography-mass spectrometry of silylated derivatives in electron impact and CI chemical ionization modes, and UPLC/ESI/QTOF HRMS ultra-high performance liquid chromatography/electrospray ionization/time-of-flight high resolution mass spectrometry, and collision-induced dissociation in the positive and negative ionization modes, we characterized not only typical isoprene products, but also new oxygenated compounds. The analysis showed the presence of methylthreonic acids (mTr) and methyltartaric acids (mTA), proposed recently by our groups as isoprene aging SOA markers. Furthermore, a series of nitroxy-organosulfates (OSs) were tentatively identified including 2mTr-OS, 2mTA-OS and 2mTA nitroxy-OS, on the basis of high resolution mass spectra. Under acidic conditions, the major identified compounds include 2-methyltetrols (2mMT), 2-methylglyceric acid (2mMGA) and 2mMT-OS. Other products identified include epoxydiols, mono- and dicarboxylic acids, OS other organic sulfates, and nitroxy- and nitrosoxy-OSs. The contribution of SOA products from isoprene oxidation to PM2.5 was investigated by analyzing ambient aerosol collected at rural sites in Poland. mTr, mMGA, methyltetrols, 2mMGA 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 experiments and robust under acidic seed aerosol. Total SOC secondary organic carbon decreased with increasing RH. The relative humidity under both acidic and non-acidic conditions. While the yields of most some of the specific organic compounds decreased, but the concentrations of 2mTA, IEPOX-OS, 2mGA-OS and 2mTe-OS increased with increasing RH. Some components followed this pattern while other were more abundant. Relative humidity others varied in non-acidic experiments or behaved in an indeterminate manner from changes in a mixed way, depending on RH the relative humidity.

Keywords: Isoprene, relative humidity, acidity, SOA, organosulfates
1 Introduction

Secondary organic aerosol (SOA), which is formed through complex physico-chemical reactions of volatile organic compounds (VOCs) which are emitted into the atmosphere from biogenic and anthropogenic sources, constitutes and can constitute a substantial portion of the continental aerosol mass (Guenther et al., 1995; Goldstein and Galbally, 2007; Hallquist et al., 2009). Isoprene (ISO) — of the volatile organic compounds, isoprene is the most abundant non-methane hydrocarbon emitted to the atmosphere (Guenther et al., 1995, 2006). Although the SOA formation yield of isoprene tends to be low, its high emissions can contribute substantially to a high organic aerosol loading. As a result, making it one of the most studied compounds emitted into the atmosphere for aerosol formation (Guenther et al., 1995; Henze and Seinfeld, 2006; Fu et al., 2008; Carlton et al., 2009; Hallquist et al., 2009). The primary removal of ISO in the atmosphere is through the mechanism for isoprene is by gas-phase reactions with hydroxyl radicals (OH), nitrate radicals (NO₃) and, to a lesser extent, ozone (O³) which. 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, C₃-alkene triols and C₅/C₆ organosulfates (OSs) (i.e. Edney et al., 2005; Surratt et al., 2007a, 2010; Riva et al., 2016; Spolnik et al., 2018). These 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 PM₂.₅ (Xie et al., 2014). Moreover, these compounds were identified in ambient PM₂.₅ (particulate matter with diameter < 2.5 µm) in several places around the world while, and SOA generated from isoprene was reported to account for up to 20–50% of the overall SOA budget (Clavey et al., 2004a; Wang et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006; Surratt et al., 2006; Hoyle et al., 2007).

Over the last 15 years, intensive research has been conducted to study the contribution of isoprene oxidation to SOA formation in the ambient atmosphere. The formation of isoprene SOA was An enhancement of isoprene (ISO)-SOA yields is controlled by various factors, mainly the aerosol acidity including NOX concentration (Kroll et al., 2006; Chan et al., 2010; Surratt et al., 2006, 2010) and the acidity of preexisting aerosol (Jang et al., 2002; Czoschke et al., 2003; Edney et al., 2005; Kleindienst et al., 2006; Surratt et al., 2007a, 2010; Jaoui et al., 2010; Szmigiel et al., 2010; Lewandowski et al., 2015). The strength of the acidity depends on the aerosol liquid water content and the relative humidity (RH) (Nguyen et al., 2011; Zhang et al., 2011; Lewandowski et al., 2015; Wong et al., 2015, 2015) and NOX concentration (Kroll et al., 2006; Chan et al., 2010). In addition, a number of smog which are coupled. Smog chamber experiments have revealed that the yield of isoprene SOA increases under acidic conditions in part due to the through an enhanced formation of isoprene-derived oxygenates, including organosulfates, through one mechanism isoprene reactions with OH (2009). Key formation pathways included the ISO-photooxidation in the presence of OH-radicals under low-NOX or high-NOX conditions that produced oxygenated...
compounds, mostly can form epoxydiols (IEPOX) in high yields followed by their uptake into the particle phase by SOA and subsequent acid-catalyzed reactions therein. Recent laboratory results show that the latter reactive uptake significantly depends on the acidity of the particle phase particle reactions (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Budisulistiorini et al., 2015; Rattanavaraha et al., 2016; Gaston et al., 2014a,b; Riedel et al., 2015). In addition, early smog chamber studies (Zhang et al., 2018). However, this type of multiphase chemistry following the uptake of IEPOX can be highly dependent on isoprene ozonolysis by Jang et al. (2002) and Czoschke et al. (2003) showed enhanced the aerosol phase state and the presence of aerosol coatings from viscous SOA yields in the presence of acidified aerosol seeds constituents (Zhang et al., 2018). Such coatings can cause a substantial diffusion barrier to the availability to an acidic core.

Atmospheric organosulfates are another class of organic compounds formed from atmospheric reactions of various precursors are significant, including isoprene, and have been identified as components of fine particulate matter ambient PM (Surratt et al., 2008, 2010; Stone et al., 2012; Tolocka and Turpin, 2012). The most common in the atmosphere and investigated were isoprene organosulfates derived from the oxidation of ISO that were 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; Szmigielski, 2016; Spolnik et al., 2018). For many of these polar oxygenated compounds, chemical structures, MS fragmentation patterns and formation mechanisms have been tentatively proposed (Surratt et al., 2007a,b; 2008, 2010; Gomez-Gonzalez et al., 2008; Zhang et al., 2011; Shalamzari et al., 2013; Schindelka et al., 2013; Nguyen et al., 2014; Tao et al., 2014; Hettiyadura et al., 2015; Riva et al., 2016; Spolnik et al., 2018). The commonly detected components of ISO isoprene SOA attributed to processing of isoprene oxidation products such as (e.g., IEPOX, methacrolein (MACR) and methyl ketone (MVK)) have the following MWs reported molecular weights of 154, 156, 184, 198, 200, 212, 214, 216, 260, and 334 (Surratt et al., 2007b, 2008, 2010; Gomez-Gonzalez et al., 2008; Kristensen et al., 2011; Zhang et al., 2011; Shalamzari et al., 2013; Schindelka et al., 2013; Nguyen et al., 2014; Hettiyadura et al., 2015; Riva et al., 2016). The mechanisms of organosulfate OS formation were proposed for the conditions of either acidified or non-acidified sulfate aerosol seeds (e.g. 2-methyltetrol OSs organosulfates) proposed respectively by Kleindienst et al. (2007a) and Riva et al. (2016). Whereas Kleindienst et al. (2006) reported the formation of highly oxygenated products through OH radical oxidation, Riva et al. (2016) proposed an alternative route through acid-catalyzed oxidation by organic peroxides. Isoprene organosulfates were also reported to occur in the aqueous-phase through the photooxidation or dark reactions of isoprene in aqueous solutions containing sulfate and sulfite moieties (Rudzinski et al., 2004, 2009; Noziere et al., 2010). A detailed mechanism of this transformation has been tentatively proposed based on chain reactions propagated by sulfate and sulfite radical anions (Rudzinski et al., 2009) and confirmed by mass spectrometric studies (Szmigielski, 2016). The acid-catalyzed formation of 2-methyltetrols has also been suggested in aqueous phase oxidation of ISO isoprene with H2O2 (Claeys et al., 2004b).

To date, only a few studies involving smog–chamber experiments have examined the effect of relative humidity on the formation of isoprene SOA (Dommen et al., 2006; Nguyen et al., 2011; Zhang et al., 2011;
However, the impact of relative humidity may be an important parameter, in that, it may affect the mechanism of SOA formation and hence the chemical composition, physical properties and yield of isoprene SOA (de P. Vasconcelos et al., 1994; Poulain et al., 2010; Guo et al., 2014). The chamber studies conducted by Dommen et al. (2006) and Nguyen et al. (2011) showed a negligible effect of RH on the SOA formation from the photooxidation of isoprene in the absence of sulfate aerosol seeds. However, subsequent studies revealed that isoprene-SOA formation yields under high-NOx conditions in the presence of acidified and non-acidified sulfate aerosol seeds decreased as the RH increased, with an increase in relative humidity while simultaneously the formation yield of organosulfates was enhanced (Zhang et al., 2011; Lewandowski et al., 2015). The latter observation can be explained by transformation of isoprene ISO-SOA propagated by sulfate/sulfite radical-anions in the aqueous particle phase or on the aqueous surface of aerosol particles (Zhang et al., 2011; Rudzinski et al., 2016). 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). 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). A recent study conducted in our laboratory focused on the effects of relative humidity on secondary organic carbon (SOC) formation from isoprene photooxidation in the presence of NOx (Lewandowski et al., 2015). The study indicated that relative humidity can have a profound effect on the acid-derived enhancement of isoprene SOC, while an increasing content of aerosol liquid water suppressed the level of enhancement.

A recent study conducted in our laboratory focused on the effects of relative humidity on bulk SOA formation (e.g. SOC) from ISO photooxidation in the presence of NOx (Lewandowski et al., 2015). These authors showed that humidity can have a profound effect on the acid-derived enhancement of isoprene SOC, while high content of aerosol water suppresses enhanced SOC formation by ISO photochemistry. In the present study, the main focus is to investigate at the molecular level the role of relative humidity on the chemical composition of isoprene SOA obtained under conditions of acidic and non-acidic seed aerosol. Two techniques developed in our laboratories were used: (1) analysis of organosulfate compounds based on measurements (Szmigielski, 2016; Rudzinski et al., 2009) and (2) analysis of non-sulfate oxygenated compounds by GC-MS analysis (Jaoui et al., 2004). In this study, we have explored the RH effect of a wide range of isoprene polar oxygenated products, including, 2-methyltetrols, 2-methylglyceric acid, IEPOX, organosulfates (OSs), nitroxy-organosulfates (NOSs) and other selected oxygenates in the presence of acidified and non-acidified sulfate aerosol seeds. In addition, a similar chemical analysis of PM2.5 field samples has been conducted to assess the possible link between these laboratory findings and their role in ambient SOA formation.
2 Experimental Methods

ISO and the derivatizing agent BSTFA (N,O bis(trimethylsilyl) trifluoroacetamide) with 1% trimethylchlorosilane as catalyst were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA) at the highest purity available and were used without further purification. Solvents with GC² quality were purchased from Burdick and Jackson (Muskegon, MI, USA).

2.1 Smog chamber experiments

Smog chamber experiments were conducted in a stainless-steel, fixed 14.5 m³ volume chamber with interior walls fused with a 40-µm PTFE Teflon coating. Details of chamber operation, sample collection, derivatization procedure, and gas chromatography–mass spectrometry (GC–MS) analysis method are described in more detail in Lewandowski et al. (2015), and Jaoui et al. (2004). A combination of UV-fluorescent bulbs was used in the chamber as source of radiation from the 300-400 nm with a distribution similar photolytically comparable to that of solar radiation (Kleindienst et al., 2006 1998). The reaction chamber was operated as a flow reactor with a residence time of 4 h, to produce a steady-state, constant aerosol distribution which could be repeatedly sampled at different seed aerosol acidities.

Isoprene and nitric oxide (NO) were taken from high-pressure cylinders each diluted with N₂. Isoprene was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA) at the highest purity available and used without further purification. Isoprene and NO were added to the chamber through flow controllers. The temperature in all experiments was ~ 27 °C (Table 1). Dilute aqueous solutions of ammonium sulfate and sulfuric acid as inorganic seed aerosol were nebulized to the chamber with total sulfate concentration of the combined solution held constant to maintain stable inorganic concentrations in the chamber (Lewandowski et al., 2015). NO and total oxides of nitrogen (NOₓ) were measured with a ThermoElectron NOₓ analyzer (Model 8840, Thermo Environmental, Inc., Franklin, MA). Ozone formed during the irradiation was measured with a Bendix ozone monitor (Model 8002, Lewisburg, WV). Temperature and relative humidity were measured with an Omega Digital Thermo-Hydrometer (Model RH411, Omega Engineering, Inc., Stamford, CT). Isoprene concentrations were measured by gas chromatography with flame ionization detection (Hewlett-Packard, Model 5890 GC). 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).

Two sets of experiments were conducted (Table 1) to explore the effect of humidity and acidity on isoprene SOA products. The ER667 non-acidic experiment (ER667) was conducted at four different humidity levels in the presence of ISO, NO, and ammonium sulfate as seed aerosol (1 µg m⁻³). It provided as a base case for exploring the changes and nature of SOA products in the absence of significant aerosol acidity. The second experiment (ER662 acidic) was similar but run in the presence of a moderately acidic sulfate seed aerosol at constant concentration. They included 5 and 4 stages differing in humidity levels for ER667 (9%; 19%; 30%; 39%; and 49%) and ER662 (8%; 18%; 28%; and 44%) respectively. ISO was produced in a high pressure cylinder diluted with nitrogen (N₂). ISO and NO were added to the chamber through flow controllers. Temperature for all stages in the experiments was set to about 27 °C. Dilute aqueous solutions of ammonium sulfate and sulfuric acid as inorganic seed aerosol were nebulized to the chamber with total sulfate concentration...
of the combined solution held constant in order to maintain stable inorganic concentrations in the chamber (Lewandowski et al., 2015). NO and total NOx were measured with a ThermoElectron (Model 8840, Thermo Environmental, Inc., Franklin, MA) oxides of nitrogen chemiluminescence analyzer. Aerosol concentrations are those from Lewandowski et al. (2015). Temperature and relative humidity were measured with an Omega Digital Thermo-Hygrometer (Model RH411, Omega Engineering, Inc., Stamford, CT). Chamber ISO concentrations were measured using a gas chromatograph with flame ionization detection (Hewlett-Packard, Model 5890 GC). Chamber O3 was measured with a Bendix ozone monitor (Model 8002, Lewisburg, WV, USA).

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). After sample collection, filters

2.2 Ambient aerosol samples.

Twenty ambient PM2.5 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 pendula, 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 25-28 °C. The relative humidity during sampling was up to 86% in Zielonka and 94% at Godow. Both locations were influenced by NOx 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 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-3 and 5.4 µg m-3 at Godow, although aerosol masses were not determined.

2.3 Instrumentation and analysis methods.

Chemicals for extraction and derivatization were obtained from Sigma-Aldrich Chemical Company. N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) used as the derivatizing agent included 1% trimethylchlorosilane as a catalyst. For the GC-MS analysis, filters were sonicated for 1 hour with methanol. Prior to extraction, 20 µg each of cis-ketopinic acid and d50-tetracosane were added as an internal standard (IS). The filter standards. Following sonication,
methanol extracts were then dried and then derivatized with 200 µL BSTFA and 100 µL pyridine, after which samples, Samples were then heated at 70 °C to complete the reaction (Jaoui et al., 2004). Smog chamber filters were The derivatized extracts were analyzed by GC-MS using a ThermoQuest (Austin, TX, USA) GC coupled with an ion trap mass spectrometer (ITMS). The injector, heated to 270 °C, was operated in splitless mode. Compounds were separated on a 60-m-long, 0.25-mm-i.d. RTx-5MS column (Restek, Inc., Bellefonte, PA, USA) with a 0.25-µm film thickness. The GC oven temperature program for the analysis started isothermally at 84 °C for 1 min, followed by a temperature ramp of 8 °C min⁻¹ to 200 °C, followed by a 2-min hold, then ramped at 10 °C min⁻¹ to 300 °C and a 15-min hold. The ion source, ion trap, and interface temperatures were 200, 200, and 300 °C, respectively. Mass spectra were collected in both the chemical ionization (CI) and electron ionization (EI) modes (Jaoui et al., 2004). A semi-continuous organic carbon/elemental carbon (OC/EC) instrument developed by a analyzer (Sunset Laboratories, Tigard, OR) measured total organic carbon of the aerosol. The aerosol sample is collected onto a quartz filter positioned within the oven housing. Prior to absence of elemental carbon in the quartz filter reaction system. Immediately upstream of the analyzer, a carbon-strip denuder was placed in line to remove gas-phase organic compounds in the air stream components which could interfere with the measurement. Analysis of the aerosol was measurements. The analysis for total OC were made using a thermal optical technique, and a description of this instrument have previously been discussed by Kleindienst et al. (2006) on a 15-min duty cycle.

2.2 Ambient aerosol samples
Ambient fine aerosol samples (PM$_{2.5}$) were collected on pre-baked quartz-fiber filters using a high-volume aerosol samplers (DH-80, Digtel) 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$_2$ emission was estimated at 0.6 µg/m$^2$ and OC value was 1.68 µg/m$^2$. The relative humidity level during sampling in Godow was 94%, SO$_2$ emission was estimated at 3.0 µg/m$^2$ (approximate value from the nearest sampling station — Zory) and OC value was 5.43 µg/m$^2$. Both locations were influenced by NOx emission — slightly in Zielonka at 1.3 µg/m$^2$ and 30.0 µg/m$^2$ in Godow (approximate value from the nearest sampling station — Zywiec).

2.3 Sample preparation and LC-MS analysis

For the LC/MS analysis, from each filter, two 1 cm$^2$ 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 preparation 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 phases. High-purity methanol (LC-MS ChromaSolv-Grade) used for extraction of SOA filters, reconstitution of aerosol extracts and preparation of the LC mobile phase was purchased from Sigma-Aldrich, Poland. 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.

From each filter, two 1 cm$^2$ punches were taken and extracted twice with 15 mL aliquots of methanol using a Multi-Orbital Shaker (PSU-20i, BioSan). Each extraction lasted 30 minutes. Two extracts were combined and concentrated using a rotary evaporator (Rotavapor® R215, Buchi) to approx. 1 mL volume, then filtered with disposable 0.2 µm PTFE syringe filters and taken to dryness under a gentle stream of nitrogen at ambient temperature. The residues were reconstituted with 180 µL of 1:1 high purity methanol / water mixture (v/v), shaken for 1 minute and analyzed with UPLC 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 with 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 ambient 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 minutes in length was applied. The concentration of chromatographic run commenced with 100% eluent B was 0 % for A over the first 3 min, eluent B increased to from 0-100 % from 3 to 8 min, was held constant at 100 % from 8 to 10 min, and then decreased back to 100-0 % from 10 to 13 min. The initial and final flow rate was 0.35 mL/min and while the flow from 3 to 10 min was 0.25 mL/min. The sample injection volume was of 0.5 μL was used. The Synapt G2-S spectrometer was equipped with an ESI source, which was operated in the negative ion mode. Optimal ESI source conditions were 3 kV capillary voltage, 20 V sampling cone and a FWHM mass resolving power. The high of 20,000. High resolution mass spectra were recorded from m/z 50 to -600 m/z 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 leucine enkephalin, directly into the ESI source.

3 Results and discussion

3.1 Chemical characterization

Table 1 shows the input and steady state conditions for all stages of the smog chamber experiments, including the values determined for carbon yield, Secondary Organic Carbon (SOC), organic mass to carbon mass ratio (OM/OC). The data indicate that with increasing RH, the formation of SOC and carbon yield was reduced, both under acidic and non-acidic conditions. The results obtained are consistent with those of Zhang et al. (2011). Secondary organic aerosol formed under non-acidic conditions was additionally analyzed for OM/OC and SOA yield. 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 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 smog chamber studies reported in the literature under the same nominal conditions in the presence of NOx (Edney et al., 2005; Kroll et al., 2006; Dommen et al., 2006; Surratt et al., 2007; Zhang et al., 2011).
Table 1. Initial and steady state conditions, yields and OM/OC data for smog-chamber experiments on isoprene photooxidation in the presence of acidic and non-acidic seed aerosol. The initial NOx was entirely nitric oxide. The non-acidic experiment was conducted at a low-concentration ammonium sulfate seed (~1 μg m⁻³). The acidic experiment was conducted with a higher concentration of inorganic seed (~30 μg m⁻³) generated from a nebulized solution for which half the sulfate mass was derived from sulfuric acid and the other half from ammonium sulfate (Lewandowski et al., 2015).

<table>
<thead>
<tr>
<th>Experiment ER662: Acidic seed aerosol (½ ammonium sulfate, ½ sulfuric acid by sulfate mass in precursor solution)</th>
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<tbody>
<tr>
<td>RH (%)</td>
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<tr>
<td>Temperature (C)</td>
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<tr>
<td>Initial Isoprene (ppmC)</td>
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<tr>
<td>Initial NO (ppm)</td>
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<td>Initial NO (ppm)</td>
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<td>Steady state conditions</td>
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<td>O₃ (ppm)</td>
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<tr>
<td>NO₂ (ppm)</td>
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<tr>
<td>ΔHC (μg m⁻³)</td>
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<tr>
<td>Carbon Yield</td>
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<tr>
<td>SOC (μgC m⁻³)</td>
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<tr>
<th>Experiment ER667: Non-acidic seed aerosol (ammonium sulfate)</th>
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<tr>
<td>RH (%)</td>
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<tr>
<td>Temperature (C)</td>
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<tr>
<td>Initial Isoprene (ppmC)</td>
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<tr>
<td>Initial NO (ppm)</td>
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<td>Initial NO (ppm)</td>
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<td>Steady state conditions</td>
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<tr>
<td>NO₂ (ppm)</td>
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<tr>
<td>ΔHC (μg m⁻³)</td>
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<tr>
<td>SOA yield</td>
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<tr>
<td>Carbon Yield</td>
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<tr>
<td>SOC (μgC m⁻³)</td>
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<td>OM/OC</td>
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The analysis of isoprene SOA from smog-chamber experiments and field samples was based on the interpretation of mass spectra of the derivatized (as silylated derivatives) and the undervatized ISOisoprene SOA products using...
GCMS by GC-MS (in EI and CI) and by LC-MS (in negative ion mode with electrospray ionization (ESI)) respectively. BSTFA react with each -COOH and -OH groups of the compounds to produce a [-Si(CH₃)₃] moiety for each reactive hydrogen atom. The common characteristic ions for all BSTFA derivatives are m/z 73, 75, 147, and 149. In CI mode, adduct ions from the derivatives included m/z: M⁺ + 73, M⁺ + 41, M⁺ + 29, and M⁺ + 1 while the fragment ions included m/z: M⁺ – 15, M⁺ – 73, M⁺ – 89, M⁺ – 117, M⁺ – 105, M⁺ – 133, and M⁺ – 207 (Jaoui et al., 2004). The LC-MS analyses were used to identify organosulfates, nitroxy- and nitrosoxy-organosulfates. The compounds were recognized by, are based on the deprotonated ions [M – H]⁻ and the corresponding fragmentation pathways evaluated by MS/MS analyses. Organosulfates were recognized by the loss of characteristic ions of m/z: 80 (SO₃⁻), 96 (SO₄⁻), and 97 (HSO₄⁻); (Darer et al., 2011; Szmigielski 2016). The nitroxy-organosulfates and nitrosoxy-organosulfates were recognized based on additional neutral losses of m/z 63 (HNO₃) and m/z 47 (HNO₂), respectively. Table 2 presents the list of compounds tentatively identified in the present study along with proposed structures, molecular weights (MWs) and main fragmentation ions (m/z). 2-Methylerythronic acid, 2-methylthreonic acid, and 2-methyltartaric acid are reported by our group further work is being conducted to be markers for ISO aging process recently (Jaoui et al., 2018). To our knowledge, organosulfate (MW 230), 2-methyltartaric acid organosulfate (MW 244), and 2-methyltartaric acid nitroxy-organosulfate (MW 275) were identified for the first time appear not to have been reported before. 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).

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

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>m/z BSTFA Derivative (methane-CI)</th>
<th>MW</th>
<th>Tentative Structure * and Chemical Name</th>
<th>Nomenclature References</th>
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<tbody>
<tr>
<td>C₅H₁₀O₂</td>
<td>247, 231, 157, 147, 73</td>
<td>102</td>
<td>3-methyl-3-butene-1,2-diol</td>
<td>Wang et al., 2005</td>
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<td></td>
<td></td>
<td>246</td>
<td>(C₅-diol-1)</td>
<td>Surratt et al., 2006</td>
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* and Chemical Name

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<tr>
<td>C₅H₁₀O₃</td>
<td>263, 247, 173, 83, 73</td>
<td>118 262</td>
<td>2-methyl-2,3-epoxy-but-1,4-diol (IEPOX-1)</td>
<td>Paulot et al., 2009&lt;br&gt;Surratt et al., 2010&lt;br&gt;Zhang et al., 2012</td>
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<td>C₅H₁₀O₃</td>
<td>263, 247, 173, 83, 73</td>
<td>118 262</td>
<td>2-methyl-3,4-epoxy-but-1,2-diol (IEPOX-2)</td>
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<tr>
<td>C₄H₈O₄</td>
<td>337, 321, 293, 219, 203</td>
<td>120 336</td>
<td>2-methylglyceric acid (2-MG)</td>
<td>Claeys et al., 2004a&lt;br&gt;Surratt et al., 2006&lt;br&gt;Edney et al., 2005&lt;br&gt;Szmigielski et al. 2007</td>
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**LC-MS**
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2-methylthreonic acid nitroxy-organosulfate

*In the table only one possible isomer is shown.
Figure 1. Extracted Ion Chromatograms (KPA: m/z 165; ketopinic acid (IS)); (IEPOX: m/z 173, 2 isomers), (mGA: 321; 2-methylglyceric acid), (mT: m/z 409; 2-methyltetrols, 4 isomers), (mTr: m/z 423; methylthreonic acids, 6 isomers), (mGAd: m/z 495; 2-methylglyceric acid dimer, 3 isomers), (mTA: m/z 437; 2-methyltartaric acid, 2 isomers) for non-acidic isoprene/NOx photooxidation experiments as a function of RH. Compounds detected as silylated derivatives. For clarity of the figure, not all isomers are shown.

Figure 1 presents GC-MS Extracted Ion Chromatograms (EIC) from the aerosol obtained for ER667 ISO during the non-acidic experiment (isoprene non-acidic seed aerosol from photooxidation experiments irradiation) at a wide range of relative humidities. According to attained chromatographic separations a number of acquired chromatograms shown in Figure 1, several isomers of analyzed associated with the compounds were analyzed can be distinguished, i.e. IEPOX-1 and IEPOX-2 or 4 isomers of 2-methyltetrols, however, only some of them are marked on the figure and their relative contributions to SOA masses at various relative humidity levels.

The formation of second generation compounds of ISO-SOA isoprene SOA products such as 2-methyltetrols (mT) and 2-methylglyceric acid (2-mGA) is well documented in the literature. These compounds are isoprene SOA markers and have been reported in many numerous field measurements and smog chamber studies under low- and high-NOx conditions (Claeys et al., 2004a; Edney et al., 2005; Kroll et al., 2006; Surratt et al., 2006, 2010). The formation mechanism under low-NOx conditions has been explained by the reactive uptake of isoprene epoxidiols (IEPOX) onto acidic aerosol seeds (Paulot et al., 2009; Surratt et al., 2010) and under high-NOx conditions by the further oxidation of methacryloylperoxynitrate (MPAN) (Chan et al., 2010; Surratt et al., 2010; Nguyen et al., 2015). Chemical mechanisms responsible for production of newly identified 2-methylerythronic acid, 2-methylthreonic acid and 2-methyltartaric acid are reported by Jaoui et al. 2018.

The LC-MS analyses focused mostly mainly on the formation of the variety of organosulfates, nitroxy- and nitrosoxy-organosulfates, although compounds identified by GC-MS analysis (e.g. 2-methylglyceric acid, 2-methylglyceric acid dimer, 2-methyltetrols, 2-methyltartaric acid and 2-methylthreonic acid) were also observed in LC-MS measurement (data not presented in this manuscript). 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 non-acidic photooxidation experiments with non-acidic aerosol seeds under various RH conditions. EightSix 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 smog 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.

Table 3. Estimated concentrations of reaction products (ng m⁻³) from ER667 the non-acidic photooxidation experiments (neutral seed [H⁺] = 54 nmol m⁻³ air: Lewandowski et al., 2015).

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* MW as BSTFA derivative
** Chromatographic responses of organosulfates [10^6]

![Graph showing concentration of various compounds at different RH percentages]
Figure 2. Concentrations of particle phase products from the non-acidic seed experiments (ER667non-acidic) estimated with GC-MS.
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-humid conditions of RH 9% (Figure 2). Among compounds detected with LC-MS, the most abundant were 2-methyltetrols, derived from 2-methyltetrols acid-catalysed multiphase chemistry of IEPOX (MW 216) and 2-methylglyceric acid MAE/HMML (MW 200) (Surrett et al., 2010; Lin et al., 2012, 2013; Nguyen et al., 2015). Other components were significantly less abundant. In most cases, increasing the RH resulted in decreased yields of the products detected. Only a few, although some compounds (2-methyltartaric acid, IEPOX-2, IEPOX-OS, 2-methylglyceric acid OS and 2-methylthreonic acid OS), deviated from the trend with the yields increased at medium and high concentrations at RH. Consequently, total SOC decreased with increased RH (Table 1). Generally, the influence of RH on the product yields was mild, with the exception of 2-methyltetrols, 2-methylglyceric acid dimer and 2-methylglyceric acid dimer which were produced in significantly larger amounts at RH 9% compared to RH 49%. This is generally consistent with Dommen et al. (2006) and Nguyen et al. (2011), who saw a negligible effect of relative humidity on SOA formation in photooxidation of isoprene in the absence of sulfate seeds aerosol.

Usually acidic seed aerosol. 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 presence of NOx 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-NOx.
organosulfates derived from isoprene photooxidation, 2-methyltetrols and SOA yield were enhanced under acidic conditions (Surratt et al., 2007a, 2007b, 2010; Gomez-Gonzalez et al., 2008; Jaoui et al., 2010; Zhang et al., 2011). However, 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 we detected could also occur via this mechanism.

3.2.2 Acidic seed aerosol

Table 4 and Figures 4-5 present the estimated amounts of polar oxygenated products detected using GC-MS and LC-MS techniques in samples from ER662 the acidic photooxidation experiments with acidic aerosol seeds under various RH conditions. We detected the same compounds as in the non-acidic seed experiments, with the same analytical limitations of the quantitation. 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.

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* MW as BSTFA derivative

** chromatographic responses of selected main organosulfates [10^4]

![Graph of concentration vs. RH (8%), RH (18%), RH (28%), RH (44%)]

- 2-methylglyceric acid
- 2-methyltetrols
- 2-methylglyceric acid dimer
- methylthreonic acids
Figure 4. Concentrations of particle phase products from the acidic seed experiments estimated with GC-MS.
Early smog 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., 2014a,b; Riedel et al., 2015). In our study, secondary organic carbon (SOC) produced in acidic-seed experiments was always higher than in nonacidic-non-acidic seed ones under the corresponding RH conditions, while the difference diminished with increasing RH to a negligible value of 0.3 µg C m⁻³ at RH 44 – 49% (Table 1 and Figure S1, supplementary information). However, the formation of the individual organic compounds detected did not follow the same pattern. As an example, Figure 6 compares shows a comparison of the results for concentrations of 2-methylglyceric acid combined under acidic and non-acidic condition as a function of relative humidity. Acidic seed aerosol has a greater effect of RH and H₂SO₄ was stronger than that of RH alone on 2-methylglyceric acid at lower relative humidity. Some of the compounds were 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, methylthreonic acid, 2-methylglyceric acid OS, 2-methylthreonic acid OS). Yields of the remaining compounds followed a mixed inconclusive pattern (supplementary information see Figs S1: Figures S1, and 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.
Figure 6. Influence of RH and seed acidity on the estimated concentration of 2-methylglyceric acid produced in chamber experiments with non-acidic seeds (red) and with acidic seeds (blue) (see similar figures). See Figure S3 for additional compounds in Fig. S3: supporting information.

3.3 Chromatographic comparison of smog-chamber experiments and field samples

We compared the results of smog-chamber experiments with authentic samples of ambient fine aerosol PM<sub>2.5</sub> collected at the two rural sites in Poland, Zielonka and Godow. To keep the experimental and ambient conditions as similar as possible, we selected the experiments carried under the highest RHs: ER662 at RH 44% (acidic seeds) and ER667 at RH 49% (non-acidic seeds). Figures 7–14 show the extracted ion chromatograms of selected components detected in the respective filter extracts. Several compounds occurred both in the smog chamber SOA and in the ambient samples: 2-methylglyceric acid OS (MW 200), furanetriol OS (MW 214), 2-methyltetrol OS (MW 216), 2-methylthreonic acid OS (MW 230), 2-methylthreonic acid NOS (MW 275). Tartaric acid and 2-methyltartaric acid OS (MW 244) was also found in ambient samples with only trace amounts in acidic seed aerosol (Fig. 11) while tartaric acid was only detected in smog chamber SOA (Fig. 12). The extracted ion chromatograms of 2-methyltetrol nitroxy-organosulfate (MW 261) were insufficient to provide reasonable fragmentation (Fig. 13). The comparison shows that the smog-chamber studies on the formation of isoprene SOA in the presence of acidic seed aerosol seeds and NO<sub>x</sub> provided a reasonable approximation of respective ambient processes at both sites even though only the Godow site could be strongly influenced by anthropogenic pollutants, mainly nitrogen oxides. Having only due to a nearby coal-fired power station. It appears that minor amounts of NO<sub>x</sub> in the intensity-based data, we refrain from–ambient atmosphere is sufficient to produce these compounds. These findings will require further quantitative speculations on the product occurrence confirmation.
Figure 7. Extracted Ion Chromatograms (EIC) of organosulfate with MW 200 from field studies and smog chamber experiments.

Figure 8. Extracted Ion Chromatograms (EIC) of organosulfate with MW 214 from field studies and smog chamber experiments.

Figure 9. Extracted Ion Chromatograms (EIC) of organosulfate with MW 216 from field studies and smog chamber experiments.

Figure 10. Extracted Ion Chromatograms (EIC) of organosulfate with MW 230 from field studies and smog chamber experiments.

Figure 11. Extracted Ion Chromatograms (EIC) of organosulfate with MW 244 from field studies and smog chamber experiments (not detected in ER667 sample).
Figure 7. Extracted Ion Chromatograms of 2-methylglyceric acid organosulfate with MW 200 from field studies and chamber experiments.

Figure 8. Extracted Ion Chromatograms of furanetriol organosulfate with MW 214 from field studies and chamber experiments.

Figure 9. Extracted Ion Chromatograms of 2-methyltartaric acid organosulfate with MW 244 from field studies and chamber experiments (not detected in non-acidic sample).

Figure 10. Extracted Ion Chromatograms (EIC) of nitrosoxy-organosulfate with MW 245 from chamber experiments (not detected in field samples).
3.4 Mass spectra and proposed fragmentation pathways of newly identified organosulfates, nitroxy- and nitrosoxy-organosulfates

All structures proposed below are tentative. Solely Based on the basis of high-resolution mass data and fragmentation spectra recorded for HPLC-resolved peaks, it is not possible difficult to distinguish between isomers of the same molecular structure. Moreover, some isomers. It has to be also considered that some HPLC of the peaks, even plotted for the selected m/z value (values in the extracted ion chromatograms), may correspond to more than one compound with the same molecular weight. Therefore, identifications for the structures proposed are tentative. This will result ambiguity results in the fragmentation spectra composed with having the fragment ions coming from different precursor ions with the same m/z.

Our proposals for the proposed structures offer the newly identified organosulfates, nitroxy- and nitrosoxy-organosulfates is based on the accurate mass measurements and the following assumptions:

a) all studied compounds have the same carbon backbone of 2-methylbutane;
b) the presence of the abundant m/z 97 peak corresponding to the HSO₄⁻ ion indicates that the hydrogen atom is present at the carbon atom next to anhydrosulfate O₂-SO₂-O- moiety (Attygalle et al., 2001). There can be, however, some exceptions as shown in Fig. 16Figures 11 and 1812; c) when the condition given in (b) is not fulfilled, elimination of sulfur trioxide molecule from the precursor ion can be observed detected (Szmigielski, 2013);
d) elimination of the HNO₂ and HNO₃ molecules from the precursor ion is a diagnostic for the presence of the nitrous (-ONO) and nitric (-ONO₂) esters, respectively. Similarly to assumption (a), a β-hydrogen must be present to enable the β-elimination.

**Figure 11.** (-)-Electrospray product ion mass spectrum of 2-methyltetrol nitrosoxy-organosulfate (MW 245) of the RT = 1.35 min peak (Figure 10) acquired for the acidic seed aerosol along with the proposed fragmentation pathway.
Figure 12. (-)Electrospray product ion mass spectrum of 2-methylthreonic acid organosulfate (MW 230) at RT = 0.63 min. (Figure S4) acquired for Zielonka PM$_2.5$ aerosol along with the proposed fragmentation pathway.

The 2-methyltetrox nitroxy-organosulfate detected at m/z 260 corresponds to the major early eluting compounds both for the smog chamber and ambient fine aerosol (Fig. 13). PM$_{2.5}$ as seen in Figure S4. The minor shifts in retention times of eluting compounds could be rationalized by are generally due to matrix effect effects (Spolnik et al., 2018). Two partially resolved peaks with identical mass spectrometric MS profiles can be noted indicating diastereoisomeric forms. This finding is consistent with earlier studies (Gomez-Gonzalez et al., 2008; Surratt et al., 2007a). A detailed interpretation of negative ion electrospray mass spectra led us to propose the proposed structure for 2-methyltetrox nitroxy-organosulfates bearing a nitroxy moiety at the primary hydroxyl group of 2-methyltetrox skeleton and sulfate group at the secondary hydroxyl group (Fig 15), which is, however, seen in a stark contrast to earlier proposals by Gomez-Gonzalez et al. and Surratt et al. Figure 13. The main fragmentation pathways correspond to a neutral loss of 63 u$_3$ (HNO$_3$) resulting in m/z
197 as a base peak and to bisulfate ion at \( m/z \) 97. Another diagnostic ion at \( m/z \) 184 could be attributed to a combined loss of NO\(_2\) and CH\(_2\)O, pointing to the presence of hydroxymethyl group in the molecule. The presence of \( m/z \) 213 and 183 ions supports the interpretation given above due to a characteristic neutral loss of a CH\(_2\)O fragment.

A revised structure for the MW 261 SOA component along with the proposed fragmentation scheme is given in Fig. 15 (Figure 13, where only the mass spectrum of another diastereoisomer is not shown).
Another second abundant smog-chamber-generated SOA component was detected at m/z 244. However, in contrast to 2-methyltetrol nitroxy-organosulfate, we failed to detect the MW 245 unknown in ambient fine aerosol that was not detected in PM$_{2.5}$, which would suggest the compound could play a relevant role as a reactive reaction intermediate in route to particle formation through isoprene photooxidation-SOA chains. Two base line-resolved peaks of identical electrospray product ion mass spectra could be attributed to diastereoisomers with an isoprene-retained backbone (Figure 12 and 16Figures 10). Surratt and co-workers observed the formation of the species this compound in the isoprene photooxidation experiment under high-NO$_x$ conditions and proposed the structure to 2-methylglyceric acid nitroxy-organosulfate (Surratt et al., 2007a). However, in the light of our mass spectral data we evidence the MW 245 unknown is the C$_3$ organosulfate, namely 2-methyltetrol nitrosoxy-organosulfates. The m/z 244 → m/z 226 transition in the product ion...
mass spectrum (Fig. 16Figure 11) points to the intact secondary hydroxyl moiety of the 2-methyltetrol skeleton. The lack of HNO₃ elimination from [M – H] \((m/z\ 244)\) precursor ion clearly excludes the presence of nitroxy group. However, an abundant \(m/z\ 197\) ion, which forms through the HNO₂ loss, could be associated with the existence of the -O-NO residue. The structure assigned to the abundant MW 245 component from ER662 (acidic seed aerosol) along with its proposed fragmentation scheme is presented in Fig. 16. The mass spectrum of another diastereoisomer is not given Figure 11.

**Figure 16.** (-)Electrospray product ion mass spectrum of 2-methyltetrol nitrosoxy-organosulfate (MW 245) of the RT = 1.35 min peak (Fig. 11) acquired for the ER662 acidic seed aerosol along with the proposed fragmentation pathway.

The two other additional abundant SOA organosulfates were determined at \(m/z\ 229\) and 243 and 229 for the smog chamber and ambient fine aerosol (Fig. 10PM₂.₅ as shown in Figures 12 and 14, respectively, which does not appear to our knowledge for the first time have previously been detected. The accurate mass data was recorded for the Godow fine
aerosol sample with the following characteristics: RT = 0.58 min. in Figure 9, C₇H₅O₉S: 242.98419816 Da, error +0.2 mDa (Figure 14) and RT = 0.63 min. in Figure S4, C₇H₅NO₈S: 229.00200011 Da, error +0.2 mDa (Figure 12) suggested a greater oxidation stage of pathways for these unknown organosulfates compared to that for the composition formation of sulfated-2-methyltetrols. Two partially resolved peaks of identical mass spectrometric signatures can be noted for these organosulfates indicating the presence of two chiral centres in their molecules (Fig. 9 and S4). In either case, first eluting diastereoisomers give rise to abundant peaks having high abundances, while the second one is of a more minor intensity suggesting the preference of the formation of less hindered compounds both in the troposphere and smog chamber experiments and PM₂.₅. A detailed interpretation of product ion mass spectra allowed to assign permitted assignment of structures of the MW 244 and MW 230 unknowns to 2-methyltartaric acid organosulfate and 2-methylthreonic acid organosulfate, respectively (Figures 14 and 18; with the mass spectrum of the minor diastereoisomer is not shown). Either spectrum displays abundant fragment ions at m/z 163 and 149, respectively, which could be explained by the SO₃ elimination from their precursor ions. Further fragmentations of m/z 163 ions, i.e., a neutral loss of water followed by decarboxylation, reveals the simultaneous presence of -O-SO₃H and –CO₂H residues in the MW 230 diastereoisomeric organosulfates. However, the absence of the bisulfate ion in the spectrum of the MW 244 organosulfate clearly indicates a lack of a proton adjacent to the sulfated group, and thus allows to propose suggests the sulfation of a secondary hydroxyl group. It is not the case of the MW 230 organosulfate and the presence of the bisulfate ion in the MS/MS spectrum does not necessarily reveal unambiguously reveals the sulfation at a primary hydroxyl group in the molecule. The proposed fragmentation schemes for the MW 244 and 230 novel organosulfates are depicted in Figures 14 and 18. Again, the mass spectra of related diastereoisomeric organosulfates are not presented.
**Figure 17.** (-)Electrospray product ion mass spectrum of 2-methyltartaric acid organosulfate (MW 244) recorded for the RT = 0.58 min peak (Fig. 11, Figure 9) from Godow fine aerosol along with the proposed fragmentation pathway.
Figure 18. A final(-)Electrospray product ion mass spectrum of 2-methylthreonic acid organosulfate (MW 230) at RT = 0.63 min. (Fig. 10) acquired for Zielonka PM$_2.5$ aerosol along with the proposed fragmentation pathway.

Another related organosulfate was detected at m/z 274 at abundant in substantial quantities in smog chamber-generated isoprene SOA from the chamber and rural PM$_2.5$ aerosol (Fig. 14), to Figure S4. To our knowledge for the first time, transition this compound has previously not been reported. The compound has transitions of m/z 274 → m/z 211 (a loss of HNO$_3$) and m/z 274 → m/z 97 (a loss of C$_5$H$_7$NO$_6$) provided by the product ion mass spectrum for Zielonka fine aerosol (Fig. 19) along with the high Zielonka PM$_2.5$ as seen in Figure 15. The high-resolution data (RT = 0.83 min., C$_5$H$_7$NO$_6$S: 273.9873 Da, error +0.4 mDa), which clearly points to isoprene-related nitroxy-organosulfate, from isoprene. A detailed explanation of other diagnostic ions led to propose the proposed structure of 2-methylthreonic acid nitroxy-organosulfate (Fig. 19). It could be assumed that due to a high oxidation stage (C/O = 0.5) the MW 275 organosulfate could serves as an identifying marker of highly processed isoprene aged aerosol. However, the further study is warranted to rationalize its formation mechanism and reactivity in the atmosphere.
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 Cregg, 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).
4. Summary

In this work, we have characterized several organic components of isoprene SOA particles, some of which have been reported in the literature. Methylthreonic acids (MW 150) and methyltartaric acid (MW 164), a highly oxygenate molecules, proposed recently as ISO aging SOA markers were also present in this study. However, several compounds were identified for the first time, including 2-methylthreonic acid (MW 150), 2-methyltartaric acid (MW 164), 2-methylthreonic acid organosulfate (MW 230), 2-methyltartaric acid organosulfate (MW 244) and 2-methyltartaric acid nitroxy-organosulfate (MW 275). Further research is warranted to rationalize the mechanisms of their formation in the atmosphere. The quantitation data revealed that the 2-methyltetros, 2-methylglyceric acid and 2-methyltrotol organosulfates are the most abundant components of isoprene SOA. Other molecular components contributing to SOA mass were epoxydiols, mono- and dicarboxylic acids, organosulfates as well as nitroxy- and nitrosoxy-organosulfates.

In addition, we showed that several organosulfates and nitroxy-organosulfates identified in smog chamber samples were also detected in samples of ambient aerosol collected at rural sites in Poland. Such consistency reinforces the relevance of the smog-chamber findings even though 2-methyltrotol nitroxy-organosulfate (MW 245) was found only in chamber experiments.

The effect of relative humidity on SOA formation was minor in the non-acidic seed experiments and robust under acidic seed aerosol. Total SOC decreased with increasing relative humidity (RH) but the individual components were influenced diversely. The yields of most compounds decreased, but 2-methyltartaric acid, increased levels of IEPOX-OS, 2-methylglyceric acid OS and 2-methylthreonic acid OS were produced at medium and high relative humidity values. The acidic seed experiments enhanced SOC production more than the non-acidic conditions under all RH conditions. However, at high humidity (44–49%), the difference was relatively small. Some of the individual SOA components followed the same pattern as the SOC while others were more abundant in non-acidic experiments or behaved in inconsistent manner. Further research is warranted to rationalize the mechanisms of their formation in the atmosphere.

The acidic seed experiments produced more SOC than the non-acidic ones, under all RH conditions. However, at high humidity (44–49%), the difference was rather small. Some individual SOA components followed the same pattern while others were more abundant in non-acidic experiments or behaved in a mixed way, depending on RH. Further experimental work on chemical mechanism and kinetics of reactions involved in formation of individual SOA components is required to explain the influence of acidity and liquid water content.

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References


