Responses to Reviewers' Comments:

We thank the reviewers for their constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the reviewers are addressed as follows.

Referee #2

Overall Comment and Recommendation:

This study is primarily a method development study aimed at quantifying oligomers derived from multiphase chemistry of methylglyoxal by using GC/MS with prior derivatization. Many groups have shown that when you heat certain SOA types, such as IEPOX-derived SOA, you measure monomeric products (like 2-methyltetrols) in high quantities (Lopez-Hilfiker et al., 2016, ES&T). This is important since monomeric products like 2-methyltetrols are too volatile to exist in such large quantities to explain the observed SOA formation in lab or field studies. The present study utilized GC/MS with PFBHA derivatization to detect methylglyoxal monomers found in 1,3,5-TMB derived SOA. The authors systematically examined the influence of heating time, pH, and heating temperature on the decomposition of methylglyoxal oligomers. The authors found that the best result was likely achieved when heating the extracts for 24 hours at 100 degrees C and at pH of 1. The authors found that the oligomers accounted for up to 8% of the total SOA mass. The method the authors develop could be very useful in trying to provide mass closure of the oligomer fraction of methylglyoxal-derived oligomers. More importantly, this method could likely be adapted to determine oligomer mass fractions in other types of SOA. This is important since we currently lack appropriate authentic standards to quantify the oligomer content of the SOA. More often we have standards available to quantify the monomers, so this method would be of interest to many research groups working in this area. Before I can recommend final publication in ACP, I have many specific comments that need to be addressed by the authors. These specific comments are outlined below. Due to the nature of these comments, I must recommend to the Editor that this manuscript be accepted with major revisions noted. There are several method details missing that need to be clarified or added to the main text. In addition, in several sections of the manuscript, the English writing is at times quite poor. As a result, I encourage the authors to conduct further editing on the writing before resubmission.

Author`s comment

The manuscript was edited again.

Specific Comments:

1) Citations in main text:

The authors cite references through the manuscript using "Last name of first author et al., Year." As an example, please refer to Page 2, Line 52. The authors should change to Kalberer et al. (2004). The style in ACP is always "Author last name et al. (year)."

Author`s comment

The authors changed the style of the references cited in the manuscript.

2) Filter Extractions:

Have the authors tested extracting the filters in an organic solvent such as acetonitrile or methanol? I wonder how the extraction efficiencies of potentially large oligomers change with extraction solvent? This factor should at least be discussed in this manuscript and the likely uncertainties in obtaining exact oligomer concentrations from this method. What I'm getting at is the authors assume in the text that the filter extraction efficiency is likely 100% in water.

Author`s comment

The authors didn´t investigate the extraction of the oligomers from the PTFE filter samples with organic solvents like acetonitrile or methanol due to the following reasons:

i) Methylglyoxal was derivatised with PFBHA after extraction from the PTFE filters leading to the formation of oximes. The formed oximes were extracted with dichloromethane before injection in GC/MS, which was found as the best extracting reagent during optimisation of the PFBHA derivatisation method (Rodigast et al., 2015). Methanol and acetonitrile are miscible with dichloromethane, thus an extraction of the oximes would not be possible.

ii) The boiling points of methanol and acetonitrile are lower than for water. Thus, the samples could not be heated to a temperature of 100 °C which was found to be necessary for the decomposition of oligomers.

Due to the listed reasons it might be necessary to remove the organic solvents after extraction of the oligomers from the PTFE filters. To avoid a drying step, which might lead to a loss of compounds, water was used as extracting reagent for methylglyoxal and their oligomers.

Nevertheless, because the extraction efficiency was not investigated in the present study the following paragraph is included in the manuscript (Page 4, Line 115) *"Noticeably, the extraction efficiency was not investigated in the present study, thus it is not known. Water was used as extracting reagent, because organic solvents like methanol and acetonitrile have lower* *boiling points than water, thus lower heating temperatures can be applied for the decomposition of the oligomers. Besides this, organic solvents like methanol and acetonitrile are miscible with dichloromethane, thus an extraction of the derivatised methylglyoxal with dichloromethane prior the injection into GC/MS would not be possible."*

3) GC/MS operating details:

You should state here explicitly how long your GC/MS run is. Since it appears this is a long GC/MS run, did the authors check to see how the methylglyoxal standard calibration changes throughout the run? For example, did the authors consider rerunning the calibration at the end of the run? Did the response factor change/drift dramatically?

Author`s comment

The GC/MS method has a run time of 36 minutes including 10 minutes post run at 230 °C to remove remaining compound from the column. To mention this in the manuscript the sentence (Page 5, Line 146) was changed to *"The temperature of 230°C was held constant for 1 minute and ended with 320°C for 10 minutes, thus the method has a run time of 36 minutes."*

The 5-point calibration was measured three times before starting analysis of the samples from the aerosol chamber experiments. In addition, after six measurements of the chamber samples one calibration sample was measured again (Figure 3).

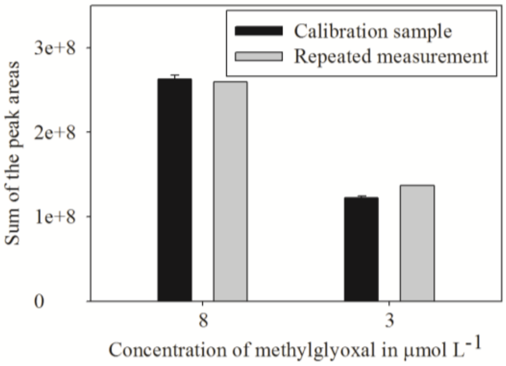

Figure 3: Comparison of the calibration at the beginning of the GC/MS measurements with a repeated measurement of the calibration after measuring samples from chamber experiment.

As it can be seen in Figure 3, the comparison between the calibration at the beginning of the measurements and after measuring filter samples showed good agreements. Thus, it can be concluded that the methylglyoxal calibration and their response factor had no significant changes during the analysis.

4) Method Development:

In the method development section when varying heating time, pH, and heating temperature, it seems that for the latter two the same experiment was used (i.e., experiment 2). In contrast, the heating time was explored with experiment 3. I think the authors would have been better to use the same type of aerosol generated under the exact same conditions when exploring these parameters of the method. I'm curious to know why this wasn't done or why it is justified to do this as is?

Author`s comment

To clarify this a sentence was included in the manuscript.

The heating time was investigated with filter samples from experiment #3 and the pH value as well as the heating temperature was investigated with samples from experiment #2.

For each measurement one filter half is needed. Due to the volume of the aerosol chamber (19 m^3) it was not possible to collect more than four filter samples (1.2 m^3 each) per experiment, which was not enough to investigate all method parameters.

For that reason, it was at least considered to use filter samples from the same experiment for the optimisation of the respective method parameters. Thus, the measurements within each method parameter are comparable and can be used for method optimisation.

The sentence (Page 4, Line 109) *"Filter samples from the same experiments were used for the optimisation of the respective method parameters."* was added.

5) SOA Yields:

Since the authors spend time in this study reporting SOA yields from 1,3,5-TMB oxidation, I have some questions about the differences in the amount of organic aerosol produced under the different RH conditions. Considering that you observe more SOA under dry conditions when compared to more humid conditions, I wonder what role your chamber walls are playing? Recent work from the Caltech (Seinfeld), CU-Boulder (Jimenez and Ziemann), and CMU (Donahue) groups suggest that the wall effect could be really important, especially if your goal is to report SOA yields in the literature. Thus, maybe you are losing more things to your wall under higher RH conditions? Have the authors considered how to correct SOA yields for this effect? If not, you should at least acknowledge the likely importance of wall losses of semivolatile and less volatile organic vapors.

Author`s comment

The wall loss can has an effect on the SOA yields as well as on the product distribution in the particle phase due to partitioning of the precursor compounds or products to the wall instead of into the particles (Matsunaga and Ziemann, 2010; Loza et al., 2010; Zhang et al., 2014; Grosjean, 1985; McMurry and Grosjean, 1985).

In the present study, the wall loss was not investigated but due to the higher surface of the aerosol chamber LEAK in comparison to the surface of the particles the wall loss might play an important role. It was calculated that LEAK has an about 3500 fold higher surface than the particles, thus the compounds are prone for deposition to the walls.

In previous experiments the wall loss of 1,3,5-TMB was measured at RH ≈ 0% resulting in an uptake coefficient $\gamma = 8.8 \times 10^{-8}$. Such uptake coefficients have to be measured for each oxidation product of 1,3,5-TMB in dependency on relative humidity to determine their wall loss and to estimate the effect of the wall loss on the SOA yield.

Even if the wall loss of methylglyoxal was not measured it is possible that the methylglyoxal concentration in the particle phase decreases due to partitioning of gas-phase methylglyoxal to the chamber walls. The lower particle-phase concentration of methylglyoxal results in lower fractions of methylglyoxal oligomers in SOA and thus to lower SOA yields. In addition, it could be assumed that the wall loss increases with increasing RH as it was measured for glyoxal by Loza et al., 2010.

Nevertheless, the wall loss was not considered during the investigation of the SOA yields of 1,3,5-TMB. Thus, it might be possible that the enhanced wall loss is a reason for the lower SOA yields under high RH values. To mention this in the manuscript the following sentence was included (Page 7, Line 246): *"Noticeably, the SOA yields of 1,3,5-TMB are not corrected for the wall loss to the surface of the aerosol chamber, which might have an influence on the reported SOA yields."*

6) Page 9, Lines 298-299:

Could it be that methylglyoxal's chamber wall losses are also changing with RH? Did the authors consider injecting methylgloxal in the gas phase of the chamber and investigate its wall losses with different RHs? That might provide more insights into the importance of your chamber wall.

Author`s comment

It might be possible that methylglyoxal has an increasing wall loss with increasing RH values. This was not investigated in the present study thus, the importance of the wall loss of methylglyoxal during the oxidation of 1,3,5-TMB cannot be estimated. The investigation of this effect would be an additional project and was not the focus of the study.

7) Page 9, Lines 329-332:

I wonder how the different seed aerosols you use might cause differences in aerosol phase separation/morphology? What role could this potentially have in explaining the differences in the oligomer fraction?

Author`s comment

NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles might have different phase states and thus different phase separations and morphologies under various RH values. The phase state is influenced due to deliquescence and efflorescence of the seed particles. The deliquescence and efflorescence RH of the pure inorganic particles can be found in the literature. The deliquescence RH of $(NH_4)_2SO_4$ particles was reported to be 79% while for NH_4HSO_4 particles a value of 39% was found (Cziczo et al., 1997). Thus, pure NH_4HSO_4 seed particles are liquid under the investigated RH range of 50% and 75% while $(NH_4)_2SO_4$ seed particles are solid.

As it was answered to comment 4 from reviewer #1, organic compounds in the particles influence the deliquescence point (Andrews and Larson, 1993; Lightstone et al., 2000) as well as the hygroscopicity of the particles (Lightstone et al., 2000; Prenni et al., 2003; Chen and Lee, 1999). In the present study mixed particles including inorganic and organic compounds exist, thus the phase separation/morphology of the particles in the oxidation experiments of 1,3,5-TMB may differ from the pure inorganic particles indicating the phase state of the particles during the oxidation experiments is not known.

In general, it is estimated that the phase of the particles can have an influence on the partitioning of the compounds from the gas into the particle phase or on further reactions in the particle phase (Ziemann, 2010; Saukko et al., 2012). In case of oligomerisation the oligomer fraction in the particles can be influenced due to the partitioning of methylglyoxal monomers into the particles or the direct formation of methylglyoxal in the particles as well as the further reaction of particulate methylglyoxal forming oligomers.

Virtanen et al., 2010 found an amorphous solid phase state of particles including oligomers. It was assumed, that the further reactions in the particle phase might be inhibited in solid particles (Saukko et al., 2012) thus, further oligomerisation reactions can be lowered after a certain fraction of oligomers exist in the particles. In addition, the partitioning of methylglyoxal monomers can be inhibited into solid particles (Saukko et al., 2012), which might also lead to lower oligomer fractions in SOA. It is not known if methylglyoxal is formed in the gas phase and partition into the particles or if it is formed directly in the particle phase. Under the assumption that particle-phase reactions are inhibited in solid particles it might also be possible that the formation of methylglyoxal in the particle phase is lowered in solid particles leading to lower oligomer fractions as well.

As the phase state of the particles in the present study is not known, the influence of the phase separation/morphology on the oligomerisation reactions is very speculative but it can be assumed that it has an influence.

The following paragraph was included in the manuscript (Page 8, Line 259): *"The RH value can have an influence on the phase state of the particles while the phase state has an effect on the partitioning of the compounds into the particles and the particle-phase reactions (Ziemann, 2010; Saukko et al., 2012). In the present study the particles are a mixture of inorganic and partitioned organic compounds, thus the phase state is not known but it might be possible that the phase state influences* ΔM *and the SOA yields."*

8) Oligomer Types:

It appears that the authors only consider the oligomer type resulting from methylglyoxal + methylglyoxal type reactions. However, considering the plethora of other monomers when oxidizing a VOC like 1,3,5-TMB, why did the authors not consider other types of oligomer reactions involving methylgloyxal + some other oxidized product? Was there no evidence for this in your GC/MS data? Related to this, why didn't the authors provide a TIC or EIC in the main text? In either the TIC or EIC, it would be helpful to provide peak labels and likely respective mass spectra to each chromatographic peak.

I mention this as recent work by Lin et al. (2014, ES&T) demonstrated the varying types of IEPOX-derived oligomers under different RH and seed aerosol conditions. It appeared from their LC/MS data that there was a very wide degree of types (e.g., light versus non-light absorbing) and lengths of oligomers present.

Author`s comment

The authors agree with the reviewer that other compounds than methylglyoxal can contribute to oligomer formation. But, in the present study only those oligomers are considered, which can be decomposed into methylglyoxal during the heating process. Notably, the applied GC/MS method is suitable for a variety of carbonyl compounds (Rodigast et al., 2015; Figure 4).

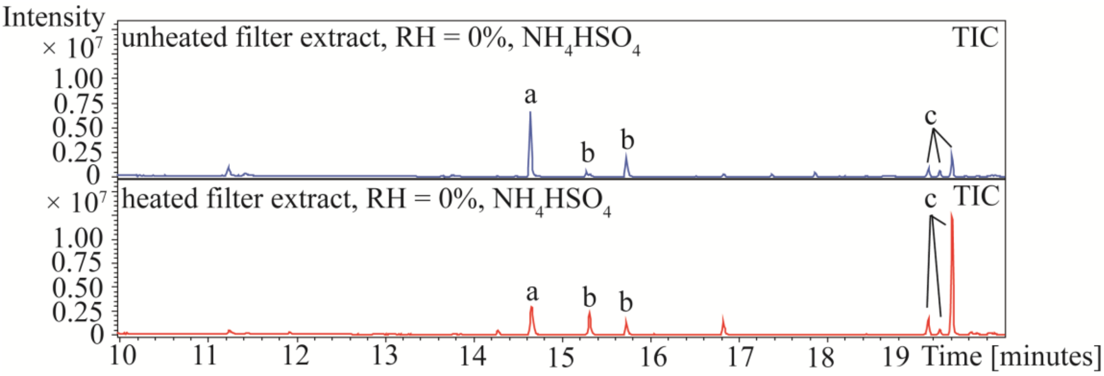

Figure 4: TIC of an unheated and heated filter extract; a: cyclohexanone-2,2,6,6,-d4, b: 2-trifluoronethyl)benzaldehyde, c: methylglyoxal.

The peaks labeled with “a” and “b” are the internal standards cyclohexanone-2,2,6,6,-d4 and 2-trifluoromethylbenzaldehyde. Methylglyoxal is labeled with “c” and it can be seen, that the peak intensity increases after heating due to decomposition of the methylglyoxal oligomers into methylglyoxal.

There are additional peaks, e.g., at a retention time of 16.8 minutes with a mass to charge ratio of 333 [$M^{\cdot +}$]. It was not possible to identify this compound during the GC/MS analysis.

To mention this in the manuscript the sentence (Page 7, Line 230) was changed to *“[…] no carbonyl compounds other than methylglyoxal were identified, which showed an increase after thermal decomposition.”*

Minor Comments:

1) Introduction, Lines 36-42: When generalizing the oligomeric mechanisms leading to SOA, why not include those derived from acid-catalyzed hydrolysis of epoxides (e.g.,Paulot et al., 2009, Science, Surratt et al., 2010, PNAS; Lin et al., 2014, ES&T)?

Author`s comment

The acid-catalysed hydrolysis of epoxides will also be included in the manuscript. Thus the sentence (Page 2, Line 36) was changed to: *“[…] imine formation (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), hydrolysis of epoxides (Paulot et al., 2009; Surratt et al., 2010) […]*”

2) Page 2, Line 46: You should probably define the ESI/MS/MS acronym being associated with tandem mass spectrometry interfaced to ESI.

Author`s comment

The sentence (Page 2, Line 43) was changed to: *“[…] electrospray ionisation mass spectrometry and electrospray ionisation tandem mass spectrometry (ESI/MS, ESI/MS/MS).”.*

3) Page 2, Line 50: Probably change "the effort for structure" to "past efforts for structural"

Author`s comment

The sentence (Page 2, Line 50) was changed to *“[…] the past effort for structure elucidation […]”.*

4) Page 3, Line 72: Do you mean to say "fundamental" here instead of "foundation"?

Author`s comment

The sentence (Page 3, Line 72) was changed to *“[…] presents a fundamental approach […]”.*

5) Page 3, Line 87: should this say instead: "was investigated in the Leipziger AerosolKammer (LEAK) chamber"?

Author`s comment

The sentence (Page 3, Line 87) was changed to *“[…] in the LEipziger AerosolKammer (LEAK).”.*

6.) Page 3, Line 90: Maybe change "ammonium hydrogensulfate" to "ammonium bisulfate?

Author`s comment

The sentence (Page 3, Line 89) was changed to *“[…] of ammonium bisulfate […]”.*

7) Page 3, Line 90: Maybe change "ammoniumsulfate" to "ammonium sulfate"?

Author`s comment

The sentence (Page 3, Line 89) was changed to *“[…] or ammonium sulfate […]”.*

8) Page 4, Line 98: Add vendor and model to "(PTR-TOF MS)"

Author`s comment

The sentence (Page 4, Line 96) was changed to *“[…] flight mass spectrometer (PTR-TOF MS; 8000; IONICON Analytik, Innsbruck, Germany) […]”.*

9) Page 4, Line 99: Add vendor and model to "(SMPS)"

Author`s comment

The sentence (Page 4, Line 98) was changed to *“[…] scanning mobility particle sizer (SMPS; 3010, TSI, USA) […]”.*

10) Page 4, Line 99: Why do the authors use 1 g cm^{-3} density? Are you using this based on a previous study? If so, please justify why you used this aerosol density.

Author´s comment

As it was mentioned in the answer to comment 5 from reviewer #1, the density of 1 g cm^{-3} is not based on previous measurements. Different values can be found in the literature while mostly a density of 1.4 g cm^{-3} (Sato et al., 2012; Praplan et al., 2014; Müller et al., 2012) based on the measurements by Alfarra et al., 2006 was used. In contrast, Kleindienst et al., 1999 used a density of 1 g cm^{-3}, which shows the discrepancies between the literature studies. In the present study a density of 1 g cm^{-3} was used, which was mentioned in the publication, thus a recalculation with other density values is possible.

11) Page 4, Line 100: Change "the particle phase" to "aerosol"

Author´s comment

The term “particle phase” was not changed to “aerosol” because only the particle phase is sampled on the PTFE filters and thus the term “aerosol” can be misleading.

12) Page 4, Line 100: Insert comma between "experiments" and "1.2"

Author`s comment

The sentence (Page 4, Line 100) was changed to *“[…] after the experiments, 1.2 m^3 of the chamber volume […]”.*

13) Page 4, Line 104: Did the authors determine what the break through could be on these filters during experiments? Were control tests done to know how well the denuder worked?

Author`s comment

In the present study the break through of the particle-phase products on the denuders was not investigated. This have to be investigated for each single product as it was done by Kahnt et al., 2011.

14) Page 7, Line 252: Change "condensate" to "condense"

Author`s comment

The sentence (Page 7, Line 251) was changed to *"[...] products condense on the [...]".*

15) Page 8, Lines 279-281: Citation is needed here. Are the authors arguing that particle-phase acidity might also be required for methylglyoxal oligomers to form? If so, is this why you think LWC matters? That is, the higher the LWC the more likely the aerosol pH is less acidic and thus affecting the amount of SOA due to oligomer formation? This is unclear to me in the current text.

Author`s comment

The structure of the oligomers is not clear, thus it is unknown, which reactions contribute to oligomer formation and if these are acid-catalysed or not. In the literature studies by Yasmeen et al., 2010; Sedehi et al., 2013 and Sareen et al., 2010 it is assumed that the pH value has an effect on the oligomerisation reactions. These findings were also used in the present study to explain the dependency of the oligomer fraction in SOA from the type of seed particle. Thus, due to the present study it was possible to support the findings by Yasmeen et al., 2010; Sedehi et al., 2013 and Sareen et al., 2010.

The LWC has an influence on the pH value as well as on the equilibrium of the oligomerisation reactions. Thus, it is not clear if the LWC effects the oligomer fraction of SOA due to changing the pH of the seed particles or the equilibrium state of the oligomerisation reaction.

To further verify this the structure of the oligomers and thus, the formation mechanism have to be elucidated, which was not the focus of the present study.

The sentence (Page 8, Line 279) is changed to *"Additionally, it can be speculated that the formation [...]".*

16) Page 9, Line 308: Do the authors mean to say "on average ~2%"?

Author`s comment

The sentence (Page 9, Line 308) was changed to: *"An average oligomer fraction of ≈ 2% up to ≈ 8% was observed.".*

17) Page 10, Line 350: Change "increases" to "increase"

Author`s comment

The sentence (Page 10, Line 348) was changed to *"[...] particle phase might increase, but [...]".*

The following changes were made to the manuscript

The style of the references are changed to *"Author last name et al. (year)"* in the manuscript.

Page 1, Line 2: *"Methylglyoxal is often described to form oligomeric compounds in the aqueous particle phase which might have a significant contribution to the formation of aqueous secondary organic aerosol (aqSOA)."* was changed to *"Methylglyoxal forms oligomeric compounds in the atmospheric aqueous particle phase, which could establish a significant contribution to the formation of aqueous secondary organic aerosol (aqSOA)."*

Page 1, Line 9: *"The method development was focused on the heating time (varied between 15 and 48 hours), pH during the heating process (pH = 1 - 7), and heating temperature (50°C, 100°C) and optimised values for these conditional parameters are presented."* was changed to *"The method development was focused on the heating time (varied between 15 and 48 hours), pH during the heating process (pH = 1 - 7), and heating temperature (50°C, 100°C). The optimised values of these method parameters are presented."*

Page 1, Line 12: *"The developed method was applied to quantify methylglyoxal oligomers formed during the OH-radical oxidation of 1,3,5-TMB in the Leipziger aerosol chamber (LEAK)."* was changed to *"The developed method was applied to quantify heat-decomposable methylglyoxal oligomers formed during the OH-radical oxidation of 1,3,5-trimethylbenzene (TMB) in the Leipziger aerosol chamber (LEAK)."*

Page 1, Line 14: *"A fraction of methylglyoxal oligomers of up to 8% of the produced organic particle mass was found, highlighting the importance of those oligomers formed solely by methylglyoxal for SOA formation."* was changed to *"A fraction of heat-decomposable methylglyoxal oligomers of up to 8% in the produced organic particle mass was found, highlighting the importance of those oligomers formed solely by methylglyoxal for SOA formation."*

Page 2, Line 20: *"One of these aromatic compounds is 1,3,5-trimethylbenzene (1,3,5-TMB), which was measured in the gas phase in concentrations ranging from 0.7 to 40.6 µg* m^{-3} *(Gee and Sollars, 1998; Khoder, 2007)."* was changed to "*One of these aromatic compounds is 1,3,5-trimethylbenzene (TMB), which was measured in the gas phase in concentrations ranging from 0.7 to 40.6 µg* m^{-3} *(Gee and Sollars, 1998; Khoder, 2007)."*

Page 2, Line 22: *"1,3,5-TMB can be oxidised in the gas phase leading to low-volatile oxidation products which partition into the particle phase and form secondary organic aerosol (SOA)."*

was changed to *"The gas-phase oxidation of 1,3,5-TMB leads to low-volatile oxidation products, which partition into the particle phase and form secondary organic aerosol (SOA)."*

Page 2, Line 24: *"Oxidation products of 1,3,5-TMB were investigated in a number of literature studies (e. g. Huang et al., 2015; Baltensperger et al., 2005; Kalberer et al., 2004; Kalberer et al., 2006; Paulsen et al., 2005; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Metzger et al., 2008; Wyche et al., 2009; Yu et al., 1997) and methylglyoxal was found as an oxidation product (Metzger et al., 2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005; Rickard et al., 2010; Kalberer et al., 2004; Yu et al., 1997; Kleindienst et al., 1999; Müller et al., 2012; Nishino et al., 2010; Hamilton et al., 2003; Tuazon et al., 1986; Bandow and Washida, 1985) with a fraction of the particle mass of up to 2% (Healy et al., 2008; Cocker et al., 2001)."* was changed to *"Oxidation products of 1,3,5-TMB were investigated in a number of literature studies (e. g. Huang et al., 2015; Baltensperger et al., 2005; Kalberer et al., 2004; Kalberer et al., 2006; Paulsen et al., 2005; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Metzger et al., 2008; Wyche et al., 2009; Yu et al., 1997). Methylglyoxal was found as one of the most important oxidation product (Metzger et al., 2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005; Rickard et al., 2010; Kalberer et al., 2004; Yu et al., 1997; Kleindienst et al., 1999; Müller et al., 2012; Nishino et al., 2010; Hamilton et al., 2003; Tuazon et al., 1986; Bandow and Washida, 1985; Lim and Turpin, 2015) contributing with a fraction of up to 2% to the particle mass (Healy et al., 2008; Cocker et al., 2001.)"*

Page 2, Line 31: *"Methylglyoxal has often been described to form oligomeric compounds in the aqueous particle phase (see, e. g. Herrmann et al., 2015 for an overview; De Haan et al., 2009; Kalberer et al., 2004; Loeffler et al., 2006; Zhao et al., 2006; Sareen et al., 2010; Altieri et al., 2008). These oligomers are supposed to play an important role in the formation of aqueous secondary organic aerosols (aqSOA; e. g. Kalberer et al., 2004)."* was changed to *"Methylglyoxal has often been described to form oligomeric compounds in the aqueous particle phase (see, e. g. Herrmann et al., 2015 for an overview; De Haan et al., 2009; Kalberer et al., 2004; Loeffler et al., 2006; Zhao et al., 2006; Sareen et al., 2010; Altieri et al., 2008), which are supposed to play an important role in the formation of aqueous secondary organic aerosols (aqSOA; e. g. Kalberer et al., 2004)."*

Page 2, Line 31: The reference Lim and Turpin, 2015 *"Lim, Y. B., and Turpin, B. J.: Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and* *implications for aqueous OH, Atmospheric Chemistry and Physics, 15, 12867-12877, 10.5194/acp-15-12867-2015, 2015."* was included.

Page 2, Line 36: *"In general, oligomeric compounds can be formed in the aqueous particle phase through aldol condensation (e. g. Tilgner and Herrmann, 2010; Sareen et al., 2010; Sedehi et al., 2013; Krizner et al., 2009; Barsanti and Pankow, 2005; De Haan et al., 2009; Yasmeen et al., 2010), acetal/hemiacetal formation (Kalberer et al., 2004 and Yasmeen et al., 2010), esterification (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), imine formation (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), polymerisation, and radical – radical reactions (Schaefer et al., 2015; Tan et al., 2012; Lim et al., 2013)."* was changed to *"In general, oligomeric compounds can be formed in the aqueous particle phase through aldol condensation (e. g. Tilgner and Herrmann, 2010; Sareen et al., 2010; Sedehi et al., 2013; Krizner et al., 2009; Barsanti and Pankow, 2005; De Haan et al., 2009; Yasmeen et al., 2010), acetal/hemiacetal formation (Kalberer et al., 2004 and Yasmeen et al., 2010), esterification (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), imine formation (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), hydrolysis of epoxides (Paulot et al., 2009; Surratt et al., 2010), polymerisation, and radical – radical reactions (Schaefer et al., 2015; Tan et al., 2012; Lim et al., 2013)."*

Page 2, Line 43: *"As it can be seen from Table 1, a number of mass spectrometric methods were used including (matrix assisted) laser desorption/ionisation mass spectrometry (MALDI-MS, LDI-MS), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), and electrospray ionisation mass spectrometry (ESI/MS, ESI/MS/MS)."* was changed to *"As it can be seen in Table 1, a number of mass spectrometric methods were used including (matrix assisted) laser desorption/ionisation mass spectrometry (MALDI-MS, LDI-MS), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), electrospray ionisation mass spectrometry and electrospray ionisation tandem mass spectrometry (ESI/MS, ESI/MS/MS)."*

Page 2, Line 50: *"Despite the effort for structure elucidation of oligomeric compounds a suitable quantification method is not available."* was changed to *"Despite the past effort for structure elucidation of oligomeric compounds a suitable quantification method is not available."*

Page 2, Line 51: *“Mostly, an overall contribution of oligomers to the particle mass was determined using e.g. a volatility tandem differential mobility analyser (VTDMA).”* was changed to *“Mostly, an overall contribution of oligomers to the particle mass was determined using, e.g., a volatility tandem differential mobility analyser (VTDMA).”*

Page 2, Line 57: *“Dommen et al., 2006 detected a contribution of oligomers increasing from 27% to 44% in the first 5 hours to organic particle mass formed in the photooxidation of isoprene.”* was changed to *“Dommen et al. (2006) detected a contribution of oligomers to the organic particle mass increasing from 27% to 44% in the first 5 hours of the photooxidation of isoprene.”*

Page 3, Line 62: *“De Haan et al., 2009 estimated the oligomer fraction formed by methylglyoxal in the aqueous phase concluding that 37% of methylglyoxal are dimers and oligomers with NMR.”* was changed to *“De Haan et al. (2009) estimated the oligomer fraction formed by methylglyoxal in the aqueous phase with NMR concluding 37% of methylglyoxal are dimers and oligomers.”*

Page 3, Line 70: *“In summary, a variety of methods exists which quantify the fraction of oligomeric compounds derived from methylglyoxal, but the results are contradicting due to the lack of a suitable method of quantification and second, due to different reaction conditions used in the studies.”* was changed to *“In summary, a variety of methods exists which quantify the fraction of oligomeric compounds derived from methylglyoxal, but the results are contradicting due to the lack of a suitable method for quantification and second, due to different reaction conditions used in the studies.”*

Page 3, Line 72: *“Thus, the present study presents a foundation approach for a reliable quantification of methylglyoxal oligomers in laboratory-generated SOA.”* was changed to *“Thus, the present study presents a fundamental approach for a reliable quantification of methylglyoxal oligomers in laboratory-generated SOA.”*

Page 3, Line 87: *“The OH-radical oxidation of 1,3,5-TMB was investigated in the aerosol chamber LEAK (Leipziger Aerosolkammer).”* was changed to *“The OH-radical oxidation of 1,3,5-TMB was investigated in the LEipziger AerosolKammer (LEAK).”*

Page 3, Line 89: *“The experiments were conducted in the presence of ammonium hydrogensulfate particles or ammoniumsulfate particles mixed with sulfuric acid to achieve different seed acidities.”* was changed to *“The experiments were conducted in the presence of* *ammonium bisulfate particles or ammonium sulfate particles mixed with sulfuric acid to achieve different seed acidities."*

Page 3, Line 92: "O_3 *was injected at the beginning of the experiments and ≈ 26 ppbv of TME was introduced into the aerosol chamber in steps of 15 minutes."* was changed to *"It was injected at the beginning of the experiments and ≈ 26 ppbv of TME was introduced into the aerosol chamber in steps of 15 minutes."*

Page 4, Line 96: *"The consumption of the precursor compound (ΔHC) was monitored over the reaction time of 90 minutes with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF MS)."* was changed to *"The consumption of the precursor compound (ΔHC) was monitored over a reaction time of 90 minutes with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF MS; 8000, IONICON Analytik, Innsbruck, Germany)."*

Page 4, Line 98: *"The volume size distribution of the seed particles was measured with a scanning mobility particle sizer (SMPS)."* was changed to *"The volume size distribution of the seed particles was measured with a scanning mobility particle sizer (SMPS; 3010, TSI, USA)."*

Page 4, Line 100: *"To collect the particle phase after the experiments 1.2* m^3 *of the chamber volume was sampled on a PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, USA) connected to a denuder (URG-2000-30B5, URG Corporation, Chapel Hill, NC, USA) (Kahnt et al., 2011) to avoid artefacts caused by adsorption of gas-phase organic compounds onto the filter."* was changed to *"To collect the particle phase after the experiments, 1.2* m^3 *of the chamber volume was sampled on a PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, USA) connected to a XAD-4 coated denuder (URG-2000-30B5, URG Corporation, Chapel Hill, NC, USA; Kahnt et al., 2011) to avoid artefacts caused by adsorption of gas-phase organic compounds onto the filter."*

Page 4, Line 109: The sentence *"Filter samples from the same experiments were used for the optimisation of the respective method parameters."* was added.

Page 4, Line 115: The paragraph *"Noticeably, the extraction efficiency was not investigated in the present study, thus it is not known. Water was used as extracting reagent, because organic solvents like methanol and acetonitrile have lower boiling points than water, thus lower heating temperatures can be applied for the decomposition of the oligomers. Besides this, organic solvents like methanol and acetonitrile are miscible with dichloromethane, thus an* *extraction of the derivatised methylglyoxal with dichloromethane prior the injection into GC/MS would not be possible."* was included in the manuscript.

Page 4, Line 126: "*After the derivatisation was completed the extracts were allowed to cool down to room temperature."* was changed to *"After the derivatisation was complete, the extracts were allowed to cool down to room temperature."*

Page 4, Line 135: *"1 µL of the organic phase was used for GC/MS analysis and the measurement was repeated for three times to ensure reliable GC/MS signals."* was changed to *"1 µL of the organic phase was injected into GC/MS for analysis. The measurements were repeated for three times to ensure reliable GC/MS signals."*

Page 5, Line 146: The sentence *"The temperature of 230°C was held constant for 1 minute and ended with 320°C for 10 minutes."* was changed to *"The temperature of 230°C was held constant for 1 minute and ended with 320°C for 10 minutes, thus the method has a run time of 36 minutes."*

Page 5. Line 161: *"The influence of the heating time was examined with PTFE filters which were sampled after the OH-radical oxidation of 1,3,5-TMB at RH = 75% in the presence of* NH_4HSO_4 *seed particles (experiment #3)."* was changed to *"The influence of the heating time was examined with PTFE filters which were sampled after OH-radical oxidation of 1,3,5-TMB at RH = 75% in the presence of* NH_4HSO_4 *seed particles (experiment #3)."*

Page 5, Line 162: *"To investigate the effect of the heating time on the cleavage of the oligomeric compounds, the aqueous filter extracts (extract 1) were acidified to pH = 1 and heated to 100°C for 15 – 48 hours."* was changed to *"To investigate the effect of the heating time on the decomposition of the heat-decomposable oligomeric compounds, the aqueous filter extracts (extract 1) were acidified to pH = 1 and heated to 100°C for 15 – 48 hours."*

Page 5, Line 164: *"The results were compared to the unheated aqueous filter extract (extract 2) to determine the increase of methylglyoxal concentration due to decomposition of the oligomer."* was changed to *"The results were compared to the unheated aqueous filter extracts (extract 2) to determine the increase of methylglyoxal concentration due to decomposition of the heat-decomposable oligomers."*

Page 5, Line 169: "*After 24 hours, methylglyoxal concentration was about six times higher* ($c = 1.82 \pm 0.14\ \mu mol\ L^{-1}$) *in comparison to the unheated filter extract* ($c = 0.29 \pm 0.01\ \mu mol\ L^{-1}$)*."* was changed to *"The methylglyoxal concentration was about six* *times higher ($c = 1.82 \pm 0.14$ µmol L^{-1}) in comparison to the unheated filter extract ($c = 0.29 \pm 0.01$ µmol L^{-1}).”*

Page 5, Line 173: *“A methylglyoxal concentration of $c = 5.32 \pm 0.05$ µmol L^{-1} was found which corresponds to a recovery of ≈ 85%.”* was changed to *“A methylglyoxal concentration of $c = 5.32 \pm 0.05$ µmol L^{-1} was found, which corresponds to a recovery of ≈ 85%.”*

Page 6, Line 182: *“Lower methylglyoxal concentration of sample b might be caused by an incomplete derivatisation due to the immediate measurement of the filter extract after 15 hours heating time.”* was changed to *“The lower methylglyoxal concentration of sample b might be caused by an incomplete derivatisation due to the immediate measurement of the filter extract after 15 hours heating time.”*

Page 6, Line 210: *“An increasing pH leads to a lower methylglyoxal concentration which can be observed for filter samples (Fig. 2a) as well as for methylglyoxal standard solution (Fig. 2b).”* was changed to *“An increasing pH leads to a lower methylglyoxal concentration, which can be observed for filter samples (Fig. 2a) as well as for the methylglyoxal standard solution (Fig. 2b).”*

Page 6, Line 213: *“As no influence of the pH on the PFBHA derivatisation reaction is reported by Rodigast et al., 2015, it can be concluded that the effect of the pH is connected to thermal decomposition of the oligomeric compounds.”* was changed to *“No influence of the pH on the PFBHA derivatisation reaction was reported by Rodigast et al. (2015) indicating the effect of the pH is connected to thermal decomposition of the heat-decomposable oligomeric compounds.”*

Page 7, Line 218: *“To examine the effect of the heating temperature, filter samples of experiment #2 were used.”* was changed to *“The effect of the heating temperature was examined with filter samples of experiment #2.”*

Page 7, Line 223: “*In comparison to the filter, which was neither acidified nor heated, the concentration was increased by a factor of two if the extract was heated to 100°C.”* was changed to *“In comparison to the filter, which was neither acidified nor heated, the concentration increased by a factor of two if the extract was heated to 100°C.”*

Page 7, Line 230: *“Noticeably, among the investigated filter samples no other carbonyl compounds showed an increase after thermal decomposition indicating that oligomers present in the particle phase of 1,3,5-TMB oxidation are solely methylglyoxal oligomers and/or oligomers of other carbonyl compounds need different conditions for decomposition.”* was changed to *"According to the literature studies other carbonyl compounds can be expected as particle-phase products, e.g., propionaldehyde (Cocker et al., 2001), glyoxal (Cocker et al., 2001; Huang et al., 2015), 2-methyl-4-oxo-2-pentenal (Healy et al., 2008; Huang et al., 2014), glycolaldehyde (Cocker et al., 2001) and 3,5-dimethylbenzaldehyde (Huang et al., 2014). Noticeably, no carbonyl compounds other than methylglyoxal were identified, which showed an increase after thermal decomposition."*

Page 7, Line 239: "*Healy et al., 2008 determined SOA yields (Y_{SOA}) of 1,3,5-TMB photooxidation in a range of 4.5 – 8.3%."* was changed to *"Healy et al. (2008) determined SOA yields (Y_{SOA}) of 1,3,5-TMB photooxidation ranging from 4.5 to 8.3%."*

Page 7, Line 240: *"Further studies determined Y_{SOA} between 0.29% and 15.6% (Table 4) under variation of the [HC]/[NO_x] ratio and concluded that SOA formation is enhanced at low NO_x mixing ratios (Sato et al., 2012; Kleindienst et al., 1999; Baltensperger et al., 2005; Wyche et al., 2009; Odum et al., 1997; Paulsen et al., 2005; Cocker et al., 2001)."* was changed to *"Further studies determined Y_{SOA} between 0.29% and 15.6% (Table 4) under variation of the [HC]/[NO_x] ratio concluding SOA formation is enhanced at low NO_x mixing ratios (Sato et al., 2012; Kleindienst et al., 1999; Baltensperger et al., 2005; Wyche et al., 2009; Odum et al., 1997; Paulsen et al., 2005; Cocker et al., 2001)."*

Page 7, Line 244: *"The SOA yields (Y_{SOA}) were also determined in the present study for all conducted experiments based on the ratio of ΔM to ΔHC (Table 2)."* was changed to *"The SOA yields were also determined in the present study for all conducted experiments based on the ratio of ΔM to ΔHC (Table 2)."*

Page 7, Line 246: The sentence *"Noticeably, the SOA yields of 1,3,5-TMB are not corrected for the wall loss to the surface of the aerosol chamber, which might have an influence on the reported SOA yields."* was included.

Page 7, Line 251: *"These products condensate on the pre-existing seed particles resulting in the immediate particle growth observed in Fig. 4a."* was changed to *"These products condense on the pre-existing seed particles resulting in the immediate particle growth observed in Fig. 4a."*

Page 8, Line 259: The paragraph *"The RH value can have an influence on the phase state of the particles while the phase state has an effect on the partitioning of the compounds into the particles and the particle-phase reactions (Ziemann, 2010; Saukko et al., 2012). In the present study the particles are a mixture of inorganic and partitioned organic compounds, thus the* *phase state is not known but it might be possible that the phase state influences ΔM and the SOA yields."* was added to the manuscript.

Page 8, Line 269: *"Higher RH resulted in lower* Y_{SOA} *between 4 and 5%."* was changed to *"Higher RH values resulted in lower* Y_{SOA} *between 4 and 5%."*

Page 8, Line 276: *"This is also supported by Saxena and Hildemann, 1996 which found an enhanced partitioning of organic compounds with several hydroxyl groups at higher LWCs of the particles."* was changed to *"This is also supported by Saxena and Hildemann (1996), which found an enhanced partitioning of organic compounds with several hydroxyl groups at higher LWCs of the particles."*

Page 8, Line 279: *"Additionally, the formation of oligomeric compounds can be enhanced at lower RH values resulting in higher* Y_{SOA} *due to the increasing conversion of the monomeric building blocks and their enhanced partitioning into the particle phase."* was changed to *"Additionally, it can be speculated that the formation of oligomeric compounds can be enhanced at lower RH values resulting in higher* Y_{SOA} *due to the increasing conversion of the monomeric building blocks and their enhanced partitioning into the particle phase."*

Page 9, Line 305: *"The method is based on the thermal decomposition of the methylglyoxal oligomers."* was changed to *" The method is based on the thermal decomposition of the heat-decomposable methylglyoxal oligomers into monomers."*

Page 9, Line 308: "*An oligomer fraction of ≈ 2 up to ≈ 8% was observed."* was changed to "*An average oligomer fraction of ≈ 2% up to ≈ 8% was observed."*

Page 9, Line 314: *"In Table 5 the pH of the seed particles were calculated with E-AIM."* was changed to *"In Table 5 the pH of the seed particles was calculated with E-AIM."*

Page 9, Line 321: *"Oligomerisation via acetal/hemiacetal formation occurs under water loss (Yasmeen et al., 2010)."* was changed to *"Oligomerisation via acetal/hemiacetal formation occurs under a reversible water loss (Yasmeen et al., 2010)."*

Page 9, Line 322: *"Higher RH in the aerosol chamber LEAK leads to higher LWCs in the seed particles (Table 5). With higher LWC in the particles the chemical equilibrium shifts towards the precursor compound resulting in a lower methylglyoxal oligomer fraction (Kalberer et al., 2004; Liggio et al., 2005)."* was changed to *"As higher RH values in the aerosol chamber LEAK leads to higher LWCs of the seed particles (Table 5) the chemical equilibrium of the* *reaction shifts towards the precursor compound resulting in a lower methylglyoxal oligomer fraction (Kalberer et al., 2004; Liggio et al., 2005).”*

Page 9, Line 325: *“The pH of NH_4HSO_4 particles decreases with decreasing RH (Table 5). Acetal/hemiacetal formation is an acid-catalysed reaction and thus oligomer formation might be enhanced under dry conditions due to a lower pH (Liggio et al., 2005).”* was changed to *“In addition, the pH of NH_4HSO_4 particles decreases with decreasing RH (Table 5) thus acid-catalysed acetal/hemiacetal formation might be enhanced under dry conditions due to a lower pH (Liggio et al., 2005).”*

Page 9, Line 329: *“As it was mentioned, aldol condensation can be assumed as the favored accretion reaction (Yasmeen et al., 2010).”* was changed to *“As it was mentioned, aldol condensation can be assumed as the favored accretion reaction under these conditions (Yasmeen et al., 2010).”*

Page 10, Line 348: *“Nevertheless, it can be expected, that with higher LWC of the seed particles and thus with a higher reaction volume, the absolute amount of methylglyoxal in the particle phase might increases, but not its particle-phase concentrations.”* was changed to *“Nevertheless, it can be expected, that with higher LWCs of the seed particles and thus with a higher reaction volume, the absolute amount of methylglyoxal in the particle phase might increase, but not its particle-phase concentration.”*

Page 10, Line 358: *“In summary, the present study provides a reliable quantification method of methylglyoxal oligomers formed by 1,3,5-TMB oxidation.”* was changed to *“In summary, the present study provides a reliable quantification method for heat-decomposable methylglyoxal oligomers formed by 1,3,5-TMB oxidation.”*

Page 13, Line 502: The reference Huang et al., 2014 *“Huang, M. Q., Hu, C. J., Guo, X. Y., Gu, X. J., Zhao, W. X., Wang, Z. Y., Fang, L., and Zhang, W. J.: Chemical composition of gas and particle-phase products of OH-initiated oxidation of 1,3,5-trimethylbenzene, Atmospheric Pollution Research, 5, 73-78, 10.5094/APR.2014.009, 2014.”* was included in the manuscript

Page 14, Line 549: The reference *“Lim, Y. B., and Turpin, B. J.: Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the aqueous phase and implications for aqueous OH, Atmospheric Chemistry and Physics, 15, 12867-12877, 10.5194/acp-15-12867-2015, 2015.”* was included.

Page 14, Line 559: The reference was changed to *“Müller, L., Reinnig, M. C., Warnke, J., and Hoffmann, T.: Unambiguous identification of esters as oligomers in secondary organic aerosol* *formed from cyclohexene and cyclohexene/alpha-pinene ozonolysis, Atmospheric Chemistry and Physics, 8, 1423-1433, 2008."*

Page 14, Line 562: The reference was changed to *"Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U.: Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments, Atmospheric Chemistry and Physics, 12, 829-843, 10.5194/acp-12-829-2012, 2012."*

Page 14, Line 590: The reference Paulot et al., 2009 *"Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733, 10.1126/science.1172910, 2009."* was included in the manuscript.

Page 15, Line 616: The reference Sauko et al., 2012 *"Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., Pedernera, D. A., Onasch, T. B., Laaksonen, A., Davidovits, P., Worsnop, D. R., and Virtanen, A.: Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors, Atmospheric Chemistry and Physics, 12, 7517-7529, 10.5194/acp-12-7517-2012, 2012."* was included in the manuscript.

Page 15, Line 654: The reference Surratt et al., 2010 *"Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, Proceedings of the National Academy of Sciences of the United States of America, 107, 6640-6645, 10.1073/pnas.0911114107, 2010."* was included in the manuscript.

Page 16, Line 692: The reference Ziemann, 2010 *"Ziemann, P. J.: Atmospheric chemistry Phase matters for aerosols, Nature, 467, 797-798, 2010."* was included in the manuscript.

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