

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 #1

This manuscript describes the careful optimization of a method designed to thermally break down methylglyoxal oligomers and detect them as derivatized monomers. Such a method is a welcome addition to the experimental toolbox of aerosol chemists. Overall, the methods and data are clearly explained and the conclusions are reasoned out logically. While the optimization process and results are completely valid, the authors' ability to interpret their work is limited by the fact that standards for methylglyoxal oligomers do not exist. To be more precise, the authors have not demonstrated that the maximum amount of oligomers that they have been able to break down and detect is equal to the total amount of methylglyoxal oligomers in their samples. However, the manuscript seems to assert this questionable assumption many times. In fact, as the authors point out at the end, the 5 – 10-fold difference between methylglyoxal oligomers detected in this study and total oligomers detected by different methods in other studies of the same system suggests that many other oligomers are present, but don't either don't break down at all, or don't break down into monomers that were detectable using the present method. However, the lack of detection of any other carbonyl compounds mentioned in this study suggests to this reviewer that the undetected oligomers are most likely some type of methylglyoxal oligomer that is irreversibly formed. It may be that methylglyoxal acetal oligomers break down to monomers with heat (as is the case for glyoxal), but methylglyoxal aldol oligomers do not. Until there are methylglyoxal oligomer standards of each type to test, this question is not likely to be answered definitively.

1) To address this issue, the authors should qualify all of their statements (including even the title) about what they are detecting, perhaps by replacing “methylglyoxal oligomers” with a more exact phrase such as “reversibly-formed methylglyoxal oligomers.”

Author's comment

The authors agree with the reviewer. Nevertheless, it is not clear if the quantified oligomeric compounds are formed reversible. It is also possible to form oligomers for example due to aldol condensation, which is an irreversible oligomerisation reaction. Thus, the term “reversibly-formed methylglyoxal oligomers” cannot be easily applied.

In the present study it is assumed that the heating process decomposes methylglyoxal oligomers into monomers. Therefore, only those oligomeric compounds are detected which can be decomposed through the heat treatment which are now addressed as “heat-decomposable”.

Thus, the term “*(methylglyoxal) oligomers*” was changed to “*heat-decomposable (methylglyoxal) oligomers*” in the manuscript and the paragraph (Page 3, Line 72) “*Thus, the present study presents a fundamental approach for a reliable quantification of methylglyoxal oligomers in laboratory-generated SOA. The method is applicable for all oligomeric compounds, which can be decomposed into methylglyoxal monomers during the heating process at a temperature of 100 °C. As the oligomerisation mechanisms leading to the quantified oligomeric compounds are not known, it cannot be specified if the oligomers are reversibly or irreversibly formed. In addition, it cannot be excluded that there exist oligomers, which are not decomposable into their methylglyoxal monomers through the heating process. Thus, the quantified oligomers are termed as heat-decomposable methylglyoxal oligomers.*” was included in the manuscript.

This work will be of interest to those who study the chemistry of organic aerosol particles in the lab and in the field.

Specific Comments

2) Line 19: Some qualifying phrase seems to be missing here. Is this percentage the fraction of anthropogenic emissions, or of non-methane hydrocarbon emissions? Are aromatic emissions in China really 52% of the total of all biogenic and anthropogenic hydrocarbon emissions, including methane?

Author`s comment

The percentage is related to the emission of non-methane hydrocarbons measured at an industrial location. The emission is dominated by, e.g., textile, shoe and furniture manufactures. In the same study it is mentioned that at areas, which are not near to an industrial location, alkanes have the highest contribution to non-methane hydrocarbon emission in china.

The sentence (Page 2, Line 19) was changed to “[...] with up to 52% to the total non-methane hydrocarbon mass at an industrial dominated site in China (Liu et al., 2008).”

3) Line 92: It would be helpful to readers if a 1-sentence summary could be included here about how $O_3 + TME$ generates OH radicals and why this OH source was chosen.

Author`s comment

The ozonolysis of TME was chosen as OH-radical source because it generates OH radicals in the dark and under low NO_x conditions. It was found in previous experiments that the oxidation of 1,3,5-TMB at high NO_x levels, e.g., with HONO as OH-radical source leads to a negligible particle growth ($\Delta\text{HC} = 23 \text{ ppb}$; $\Delta\text{M} = 0 \text{ } \mu\text{g m}^{-3}$). Thus, the investigation of SOA formation and of particle-phase products like oligomers is not possible under these conditions. Additionally, the photolysis of H₂O₂ was used as OH-radical source (low NO_x) but the applied UV-C light ($\lambda = 254 \text{ nm}$) results in photolysis of the aromatic precursor compound. Thus, the photolysis of H₂O₂ is also not suitable as OH-radical source for the oxidation of 1,3,5-TMB. Consequently, SOA originated from 1,3,5-TMB oxidation has to be examined at low NO_x levels and without UV-C light. For that reason, the ozonolysis of TME was used, which is an OH-radical source under dark and low NO_x conditions.

The sentence (Page 3, Line 91) was changed to *“In order to investigate OH-radical oxidation of 1,3,5-TMB at low NO_x levels (< 1 ppb) and under dark conditions the ozonolysis of tetramethylethylene (TME) was used as OH-radical source (Berndt and Böge, 2006).”*

The paragraph (Page 3, Line 92) *“The cycloaddition of ozone to TME yields a primary ozonide, which reacts further and forms a stabilised Criegee Intermediate (sCI). The sCI decomposes via the hydroperoxide channel, leading to the formation of OH radicals (Gutbrod et al., 1996) with a yield of 0.92 ± 0.08 (Berndt and Böge, 2006).”* was added.

4) Line 96: Are the deliquescence and efflorescence RH values known for either seed particle material? Perhaps the phase of these particles is relevant to the results.

Author`s comment

In general and as an simplified approximation, atmospheric particles can be solid or liquid (Ziemann, 2010). The phase state can be changed due to deliquescence and efflorescence of the particles. The phase of the particles might have an influence on the partitioning between the gas and the particle phase, reactions in the particle phase, the mass transport of the reactants and oxidants into the particle phase, and the water uptake of the particles (Ziemann, 2010; Saukko et al., 2012).

For pure NH₄HSO₄ and (NH₄)₂SO₄ seed particles the deliquescence RH and efflorescence RH can be found in the literature. The deliquescence RH of (NH₄)₂SO₄ and NH₄HSO₄ seed particles were reported in the literature to be 79% and 39%, respectively (Cziczo et al., 1997). Thus, pure NH₄HSO₄ seed particles are liquid at the applied RH values of 50% and 75%. The efflorescence RH was measured in the literature as 33% for (NH₄)₂SO₄ seed particles and lower than 2% for

NH_4HSO_4 seed particles (Cziczo et al., 1997; Mikhailov et al., 2009). Thus, pure $(\text{NH}_4)_2\text{SO}_4$ seed particles might be solid over the whole RH range applied in the present study while pure NH_4HSO_4 particles are solid only at RH = 0%.

Nevertheless, for mixed particles including organic and inorganic compounds (as in the present study) the knowledge about the exact phase state is limited. The organic compounds change the deliquescence point (Andrews and Larson, 1993; Lightstone et al., 2000) as well as the hygroscopic behaviour of the particles (Lightstone et al., 2000; Prenni et al., 2003; Chen and Lee, 1999). This is strongly dependent on the type of the organic compounds and their properties. As the composition of the organic phase in the particles is not comprehensively elucidated, the phase state of the particles in the present study is not known.

However, Virtanen et al., 2010 postulated that particles are in an amorphous solid state if oligomeric compounds are present in the particles. Thus, it can be speculated that the particles in the present study containing a fraction of up to 8% of oligomeric compounds are also in an amorphous solid phase state changing with the fraction of oligomers and other organic compounds. Thus, the particles can have different phases, which might influence the product distribution in the particle phase and therefore the SOA yields.

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.”*

5) Line 99: Is the choice of organic aerosol density (1 g/mL) based on a literature measurement?

Author's comment

Different values can be found in the literature. Most of the studies assumed 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, which determined values between 1.35 g cm^{-3} and 1.40 g cm^{-3} . Kleindienst et al., 1999 used a density of 1 g cm^{-3} , which was used in the present study as well.

6) Line 102: What absorbent material were the denuders coated with?

Author's comment

The denuders are coated with XAD-4, which enables the trap of gas-phase compounds and avoid artefacts of gas-phase products on the PTFE-filters (Kahnt et al., 2011).

The sentence (Page 4, Line 100) was changed to “[...] experiments, 1.2 m³ 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 [...].”

7) Line 191: There is unclear logic here. If the incompletely derivatized methylglyoxal is able to reform oligomers once the temperature drops to 298 at t = 15 h, wouldn't the yellow bar in Figure 1b be even smaller than the black bar?

Author's comment

The authors agree with the reviewer and include a paragraph to clarify the results.

The authors assumed that the derivatisation as well as the oligomerisation proceeds during the 9 hours at room temperature (sample a). In comparison, sample b was directly measured after 15 hours heating thus, there is no further derivatisation and oligomerisation. Altogether, the derivatisation time of sample a (yellow bar) was longer than of sample b (black bar) leading to higher methylglyoxal concentrations even if oligomerisation occurs in sample a as well.

The sentence “*Despite the oligomerisation of methylglyoxal monomers during the 9 hours at room temperature, the derivatisation proceeds as well during this time leading to higher methylglyoxal concentrations in sample a than in sample b, which was directly measured after 15 hours heating (Fig. 1b).*” was added (Page 6, Line 195).

In addition, the sentence (Page 6; Line 185) is misleading and was changed to “*To probe this hypothesis a 6.25 μmol L⁻¹ methylglyoxal standard was heated for 15 hours and measured immediately (like sample b) or, alternatively, was allowed to stand at room temperature for 9 hours (like sample a).*”

8) Line 195: This paragraph is confusing. The authors suggest a possible explanation, then seem to eliminate it in the next sentence (assuming that “decomposition” and “loss” are the same process), without offering an alternative explanation.

Author's comment

The authors agree with the reviewer but this cannot be conclusively clarified. It can only be mentioned that no influence on the derivatisation reaction was found (Fig. 1b).

It can be suggested that there are additional reactions in the filter samples perhaps due to other particle-phase species, which do not exist in the standard sample. These further reactions might lead to lower concentrations in the filter samples after a heating time of 24 hours, which was not observed for the methylglyoxal standard solution.

The sentence (Page 6, Line 200) *“Thus, it can be speculated that the low methylglyoxal concentrations in the filter samples are a result of further reactions with particle-phase species, which do not exist in the standard samples.”* was included in the manuscript.

9) Line 215: The manuscript states here that Rodigast et al. 2015 found no influence of the pH on the PFBHA derivatisation reaction. However, in line 201 the same study is cited in support of an optimal pH value of 1 for the reaction. How can a factor with no influence be optimized?

Author’s comment

The authors agree with the reviewer. The sentence *“The pH during the heating process was investigated even if pH = 1 was found as an optimal pH for the PFBHA derivatisation (Rodigast et al., 2015).”* (Line 201) is misleading and was changed to *“The pH during the heating process was investigated as well.”*

10) Line 232: This is an important statement, but it leaves the reader wondering which other carbonyl compounds were being monitored in this work. It would be very helpful if the authors would list these compounds.

Author’s comment

In the present study, no other carbonyl compound was identified during the analysis with GC/MS after PFBHA derivatisation. However, 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). These compounds were not detected with the used analysis method and under the experimental conditions applied in the present study.

The sentence (Page 7, Line 230) 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.”*

11) Line 236: Confusing statement. According to Table 3, the method was developed using filters from experiments 2 and 3 from laboratory 1,3,5-TMB oxidation studies (plus methylglyoxal monomer standards). Now the method is applied to more of the samples from the same set of studies.

Author's comment

To clarify this the sentence will be changed.

The method was developed with filter samples from experiment #2 and #3 to use laboratory-generated SOA. After the method development the quantification method was applied to filter samples from further experiments (# 1, 4, 5, 6) to investigate the influence of seed particle acidity and relative humidity on the oligomer content.

Line 234: The sentence was changed to “[...] developed quantification method was afterwards applied to laboratory-generated SOA formed during further oxidation experiments of 1,3,5-TMB to investigate the influence of seed particle acidity and relative humidity on the oligomer content.”

12) Line 257: From the information given it is hard to see how these two studies “are in good agreement” with the present study, since the present study is measuring no acidity effect while the two literature studies compared seed / no seed conditions.

Author's comment

The authors agree with the reviewer and delete the sentence (Page 7, Line 255) “*This is in good agreement with the studies by Cocker et al. (2001) and Wyche et al. (2009) which observed no differences of SOA formation in the presence or absence of seed particles during the photooxidation of 1,3,5-TMB with NO_x.*”. The mentioned literature studies compared experiments with and without seed particles while in no-seed experiments SOA formation occurs due to nucleation forming organic particles. Organic particles might lead to a stronger partitioning of organic compounds and thus cannot be compared (Spittler et al., 2006; Pankow, 1994).

13) Line 289: The authors' measurements of the percentage methylglyoxal in 1,3,5-TMB SOA are right in line with other published values. Did Healy et al and Cocker et al. use seed particles? Can the authors comment on whether such percentages are consistent with partitioning theory and the vapor pressure of methylglyoxal?

Author's comment

Healy et al., 2008 used no seed particles while Cocker et al., 2001 used $(\text{NH}_4)_2\text{SO}_4$ seed particles.

To calculate the theoretically possible methylglyoxal mass in the particle phase (according to the partitioning theory and the vapor pressure), yields of methylglyoxal in the gas phase reported in the literature have to be assumed because the gas-phase yields of methylglyoxal were not measured in the present study. In the literature it is known that the oxidation of 1,3,5-TMB results in yields of 60 – 90% of methylglyoxal in the gas phase (Smith et al., 1999; Bandow and Washida, 1985; Tuazon et al., 1986). These gas-phase yields were taken as basis for the calculation of the theoretical possible methylglyoxal present in the particle phase:

Example: NH_4HSO_4 seed particle; RH = 50%: Calculation of the mass of methylglyoxal present in the particle phase in case of a gas phase yield of 60%:

Consumed 1,3,5-TMB: $\Delta\text{HC} = 55$ ppb

Methylglyoxal yield of 60% \rightarrow 33.0 ppb methylglyoxal = 8.12×10^{17} molecules m^{-3}

Calculation of methylglyoxal in per cent by volume with the Loschmidt constant

(2.46×10^{25} molecules m^{-3})

$$\frac{8.12 \times 10^{17} \text{ molecules } \text{m}^{-3}}{2.46 \times 10^{25} \text{ molecules } \text{m}^{-3}} = 3.30 \times 10^{-8} = 3.30 \times 10^{-6} \%$$

Calculation of the partial pressure (P) of methylglyoxal:

$$\frac{100 \%}{1 \text{ atm}} = \frac{3.30 \times 10^{-6} \%}{P}$$

$$P = 3.30 \times 10^{-8} \text{ atm}$$

Calculation of the concentration in the aqueous particle phase (c_L):

$$H = \frac{c_L}{P} \quad H \text{ (Henry constant)} = 3.7 \times 10^3 \text{ M atm}^{-1} \text{ (Betterton and Hoffmann, 1988)}$$

$$c_L = P \times H = 3.30 \times 10^{-8} \text{ atm} \times (3.7 \times 10^3 \text{ M atm}^{-1}) = 0.00012 \text{ mol L}^{-1}$$

Related to the liquid water content (LWC) of the particles (RH = 50%; NH_4HSO_4 seed particles, calculated with E-AIM model III):

$$\text{LWC} = 6.66 \mu\text{g } \text{m}^{-3} = 6.66 \times 10^{-9} \text{ kg in in } 1 \text{ m}^3 \text{ particles}$$

Calculation of the water volume:

$$V = \frac{m}{\rho} = \frac{6.66 \times 10^{-9} \text{ kg}}{1 \text{ kg m}^{-3}} = 6.66 \times 10^{-9} \text{ m}^3 = 6.66 \times 10^{-6} \text{ L}$$

m: mass of water

ρ : density of water

Calculation of methylglyoxal in mol (with $c_L = 0.00012 \text{ mol L}^{-1}$) in $6.66 \times 10^{-6} \text{ L}$ water:

$$\frac{0.00012 \text{ mol}}{1 \text{ L}} = \frac{x}{6.66 \times 10^{-6} \text{ L}}$$

$$x = 7.99 \times 10^{-10} \text{ mol} = 7.99 \times 10^{-4} \mu\text{mol}$$

Calculation of methylglyoxal in g with a molar mass of 72 g mol^{-1} :

$$7.99 \times 10^{-4} \mu\text{mol} = \underline{\underline{0.06 \mu\text{g}}}$$

Table 1: Calculation of the mass [μg] of methylglyoxal in the particle phase for RH = 50%.

Theoretical gas phase methylglyoxal yield	NH_4HSO_4		$(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$	
	Calculated	Measured	Calculated	Measured
60%	0.06 μg	0.14 μg	0.04 μg	0.09 μg
90%	0.09 μg		0.06 μg	

Table 2: Calculation of the mass [μg] of methylglyoxal in the particle phase for RH = 75%.

Theoretical gas phase methylglyoxal yield	NH_4HSO_4		$(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$	
	Calculated	Measured	Calculated	Measured
60%	0.11 μg	0.08 μg	0.11 μg	0.09 μg
90%	0.16 μg		0.16 μg	

As can be seen, at RH = 50% the calculated mass of methylglyoxal in the particle phase is lower than the measurements. In contrast, with RH = 75% the calculated mass is higher than the measured values. There are different reasons possible leading to the discrepancies. The theoretical calculations include no further reactions of methylglyoxal in the particle phase like oligomerisation, which might lead to a lower measured methylglyoxal mass. In addition, the equilibrium between the methylglyoxal monomers and oligomers can be influenced due to experimental conditions and the extraction of the filter samples with water, which is also not included in the calculations leading to lower or higher methylglyoxal masses in the particle phase.

14) Line 301: Do these literature studies suggest that either of the two explanations offered in the previous sentence are more likely than the other?

Author's comment

The literature studies were cited because they investigate the formation of methylglyoxal oligomeric compounds and was not related to studies investigating the effect of RH on oligomer formation.

The sentence (Page 9, Line 300) was changed to “*The formation of oligomeric compounds from methylglyoxal has been investigated [...]*”.

15) Line 315: The phrase “opposite trend” was unclear. What trend is this trend the opposite of?

Author's comment

The term “opposite trend” describes the dependency of the oligomer fractions in SOA on the relative humidity with different seed particles. It can be seen in Fig. 5b, with NH_4HSO_4 seed particles the fraction of the oligomeric compounds in SOA decreases with increasing RH while using $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles the oligomer fraction increases under elevated RH. Thus, there is an opposite trend of the contributions of oligomeric compounds to SOA between the different seed particles under various RH values.

Line 312: The sentence was changed to “[...] *opposite trend of the oligomer fractions with RH between NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles could be different oligomer formation mechanism caused by different seed particle acidity.*”

16) Line 334: Doesn't this logic also apply to the next two reactions that involve water loss? I am unsure why aldol reactions are enhanced and esterification and imidazole formation are decreased at high RH, when all involve water loss as part of the mechanism.

Author's comment

The water loss of aldol condensation (Figure 1) is an irreversible reaction while esterification, imidazole formation and acetal/hemiacetal formation is a reversible reaction (Figure 2).

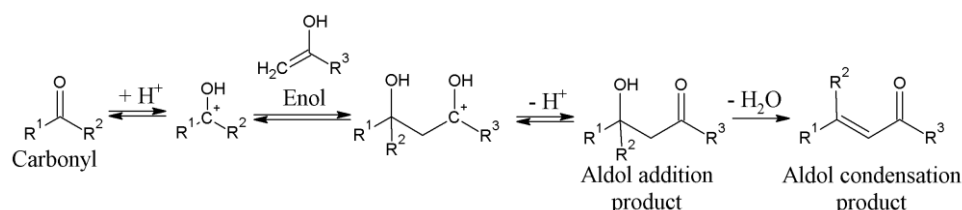


Fig. 1: Acid-catalyzed aldol-condensation (R: organic rest or H-atom).

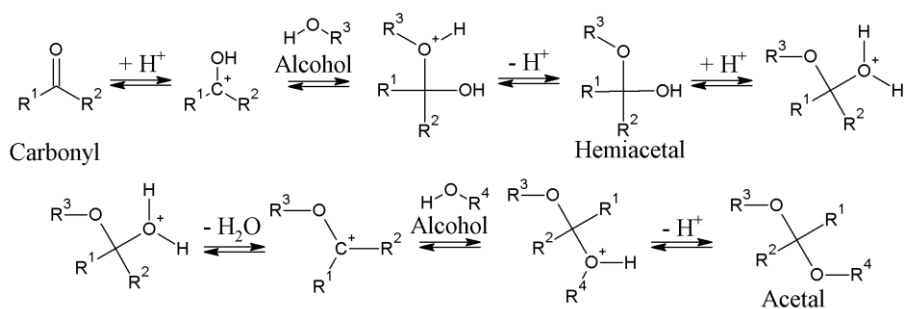


Fig. 2: Acid-catalysed acetal/hemiacetal formation (R: organic rest or H-atom).

The following sentences were changed to:

Page 9, Line 335 “[...] involves the reversible loss of water [...]”

Page 10, Line 336 “[...] decreases due to the shift of the equilibrium towards the monomers.”

Technical Corrections

Line 194: “might be” should be “are”. The authors know that H^+ and NH_4^+ ions are present in the samples and therefore the aqueous extracts.

Author’s comment

The sentence (Page 6, Line 195) was changed to “[...] these ions are present [...]”

Line 205: “PFTFE” should be “PTFE”

Author’s comment

The sentence (Page 6, Line 205) was changed to “[...] with PTFE filters,[...]”

Line 253: “condensate” should be “condense”

Author’s comment

The sentence (Page 7, Line 251) was changed to “[...] products condense on the pre-existing [...]”

Line 314: The period is missing after “conditions”

Author’s comment

The sentence (Page 9, Line 310) was changed to “[...] dry conditions ($\text{RH} = 0\%$).”

Line 343: “is” should be “it”

Author’s comment

The sentence (Page 10, Line 340) was changed to “[...] thus it does not provide [...]”

Line 352: “increases” should be “increase”

Author’s comment

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

Table 6 does not provide any additional information beyond Figure 5b, and could be eliminated.

Author’s comment

Table 6 was deleted from the manuscript.

The following changes were made to the manuscript

The term “*(methylglyoxal) oligomers*” was changed to “*heat-decomposable (methylglyoxal) oligomers*” in the manuscript and the figure caption of Figure 5.

Page 2, Line 19: “*Aromatic compounds represent a large fraction of the total emitted hydrocarbon mass contributing such as up to 52% to the hydrocarbon mass in China (Liu et al., 2008).*” was changed to “*Aromatic compounds represent a large fraction of the emitted hydrocarbons contributing with up to 52% to the total non-methane hydrocarbon mass at an industrial site in china (Liu et al., 2008).*”

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 73: The paragraph “*The method is applicable for all oligomeric compounds, which can be decomposed into methylglyoxal monomers during the heating process at a temperature of 100 °C. As the oligomerisation mechanisms leading to the quantified oligomeric compounds are not known, it cannot be specified if the oligomers are reversibly or irreversibly formed. In addition, it cannot be excluded that there exist oligomers, which are not decomposable into their methylglyoxal monomers through the heating process. Thus, the quantified oligomers are termed as heat-decomposable methylglyoxal oligomers.*” was included in the manuscript.

Page 3, Line 91: “*As OH-radical source the ozonolysis of tetramethylethylene (TME) was used (Berndt and Böge, 2006)*” was changed to “*In order to investigate OH-radical oxidation of 1,3,5-TMB at low NO_x levels (< 1 ppb) and under dark conditions the ozonolysis of tetramethylethylene (TME) was used as OH-radical source (Berndt and Böge, 2006).*”

Page 3, Line 92: The paragraph *“The cycloaddition of ozone to TME yields a primary ozonide, which reacts further and forms a stabilised Criegee Intermediate (sCI). The sCI decomposes via the hydroperoxide channel, leading to the formation of OH radicals (Gutbrod et al., 1996) with a yield of 0.92 ± 0.08 (Berndt and Böge, 2006).”* was added.

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 6; Line 185: *“To probe this hypothesis a $6.25 \mu\text{mol L}^{-1}$ methylglyoxal standard was heated for 15 hours and measured immediately (like sample a) or, alternatively, was allowed to stand at room temperature for 9 hours (like sample b).”* was changed to *“To probe this hypothesis a $6.25 \mu\text{mol L}^{-1}$ methylglyoxal standard was heated for 15 hours and measured immediately (like sample b) or, alternatively, was allowed to stand at room temperature for 9 hours (like sample a).”*

Page 6, Line 195: *“Naturally, both of these ions might be present in the aqueous filter extract.”* was changed to *“Naturally, both of these ions are present in the aqueous filter extract.”*

Page 6, Line 195: The sentence *“Despite the oligomerisation of methylglyoxal monomers during the 9 hours at room temperature, the derivatisation proceeds as well during this time leading to higher methylglyoxal concentrations in sample a than in sample b, which was directly measured after 15 hours heating (Fig. 1b).”* was added.

Page 6, Line 200: The sentence *“Thus, it can be speculated that the low methylglyoxal concentrations in the filter samples are a result of further reactions with particle-phase species, which do not exist in the standard samples.”* was included.

Page 6, Line 201: *“The pH during the heating process was investigated even if $\text{pH} = 1$ was found as an optimal pH for the PFBHA derivatisation (Rodigast et al., 2015)”* was changed to *“The pH during the heating process was investigated as well.”*

Page 6, Line 205: *“The effect of the pH was examined with PTFE filters, which were sampled after the OH-radical oxidation of 1,3,5-TMB at RH = 50% in the presence of NH₄HSO₄ particles (experiment #2).”* was changed to *“The effect of the pH was examined with PTFE filters, which were sampled after OH-radical oxidation of 1,3,5-TMB at RH = 50% in the presence of NH₄HSO₄ particles (experiment #2).”*

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 234: *“The developed method was afterwards applied to laboratory-generated SOA formed by the oxidation of 1,3,5-TMB.”* was changed to *“The developed quantification method was afterwards applied to laboratory-generated SOA formed during further oxidation experiments of 1,3,5-TMB to investigate the influence of seed particle acidity and relative humidity on the oligomer content.”*

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 7, Line 255: The sentence *“This is in good agreement with the studies by Cocker et al., 2001 and Wyche et al., 2009 which observed no differences of SOA formation in the presence or absence of seed particles during the photooxidation of 1,3,5-TMB with NO_x.”* was deleted.

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 9, Line 300: “*This has been investigated in a number of studies (e. g. 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).*” was changed to “*The formation of oligomeric compounds from methylglyoxal has been investigated in a number of studies (e. g. 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).*”

Page 9, Line 306: “*The concentrations were converted into the fraction of methylglyoxal oligomers of ΔM using the molar mass of methylglyoxal ($M_w = 72.06 \text{ g mol}^{-1}$; Table 6).*” was changed to “*The concentrations were converted into the fraction of methylglyoxal oligomers of ΔM using the molar mass of methylglyoxal ($M_w = 72.06 \text{ g mol}^{-1}$).*”

Page 9, Line 310: “*In the presence of NH_4HSO_4 seed particles the highest oligomer fraction ($8.2 \pm 0.7\%$) can be observed with $\text{RH} = 0\%$ whereas in the presence of $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles the oligomer fraction is the lowest ($2.1 \pm 0.4\%$) under dry conditions.*” was changed to “*In the presence of NH_4HSO_4 seed particles the highest oligomer fraction ($8.2 \pm 0.7\%$) can be observed with $\text{RH} = 0\%$ whereas in the presence of $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles the oligomer fraction is the lowest ($2.1 \pm 0.4\%$) under dry conditions ($\text{RH} = 0\%$).*”

Page 9, Line 312: “*A possible explanation for the opposite trend could be a different oligomer formation mechanism dependent on the different seed particles.*” was changed to “*A possible explanation for the opposite trend of the oligomer fractions with RH between NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles could be different oligomer formation mechanism caused by different seed particle acidity.*”

Page 9, Line 335: “*This equilibrium reaction involves the loss of water as it was reported for acetal/hemiacetal formation (Lim et al., 2010).*” was changed to “*This equilibrium reaction involves the reversible loss of water as it was reported for acetal/hemiacetal formation (Lim et al., 2010).*”

Page 10, Line 336: “*Thus, it can be expected that with higher LWCs the contribution of esterification reactions to oligomer formation decreases.*” was changed to “*Thus, it can be expected that with higher LWCs the contribution of esterification reactions to oligomer formation decreases due to the shift of the equilibrium towards the monomers.*”

Page 10, Line 340: “*However, imidazole formation involves also a loss of water, thus it does not provide a feasible explanation for the higher oligomer fraction at higher RH with $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles.*” was changed to “*However, imidazole formation involves also a reversible loss of water, thus it does not provide a feasible explanation for the higher oligomer fraction at higher RH with $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ seed particles.*”

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 increase, 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 12, Line 467: The reference Gutbrod et al., 1996 “Gutbrod, R., Schindler, R. N., Kraka, E., and Cremer, D.: Formation of OH radicals in the gas phase ozonolysis of alkenes: the unexpected role of carbonyl oxides, *Chemical Physics Letters*, 252, 221-229, 10.1016/0009-2614(96)00126-1, 1996.” was included in the manuscript.

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 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 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.

Page 19, Line 731: Table 6 was deleted.

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