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 methylgyloxal 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 ($\Delta HC = 23$ ppb; $\Delta M = 0\ \mu g\ m^{-3}$). Thus, the investigation of SOA formation and of particle-phase products like oligomers is not possible under these conditions. Additionally, the photolysis of H_2O_2 was used as OH-radical source (low NO_x) but the applied UV-C light ($\lambda = 254$ nm) results in photolysis of the aromatic precursor compound. Thus, the photolysis of H_2O_2 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 NH_4HSO_4 and $(NH_4)_2SO_4$ seed particles the deliquescence RH and efflorescence RH can be found in the literature. The deliquescence RH of $(NH_4)_2SO_4$ and NH_4HSO_4 seed particles were reported in the literature to be 79% and 39%, respectively (Cziczo et al., 1997). Thus, pure NH_4HSO_4 seed particles are liquid at the applied RH values of 50% and 75%. The efflorescence RH was measured in the literature as 33% for $(NH_4)_2SO_4$ seed particles and lower than 2% for NH_4HSO_4 seed particles (Cziczo et al., 1997; Mikhailov et al., 2009). Thus, pure $(NH_4)_2SO_4$ 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 derivisation 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 $(NH_4)_2SO_4$ 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: $\Delta HC = 55$ ppb

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

Calculation of methylglyoxal in per cent by volume with the Loschmidt constant (2.46×10^{25} molecules m^{-3})

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

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):

$$H = \frac{c_L}{P}$$

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

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

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

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

Calculation of the water volume:

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

m: mass of water

ρ: density of water

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

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

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

	NH_4HSO_4		$(NH_4)_2SO_4/H_2SO_4$	
Theoretical gas phase methylglyoxal yield	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%.

	NH_4HSO_4		$(NH_4)_2SO_4/H_2SO_4$	
Theoretical gas phase methylglyoxal yield	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 $(NH_4)_2SO_4/H_2SO_4$ 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 $(NH_4)_2SO_4/H_2SO_4$ 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).

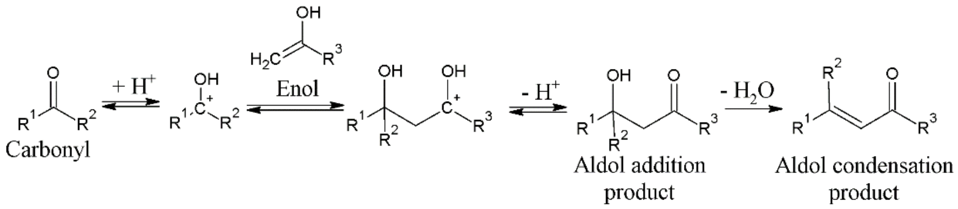

Fig. 1: Acid-catalysed aldol-condensation (R: organic rest or H-atom).

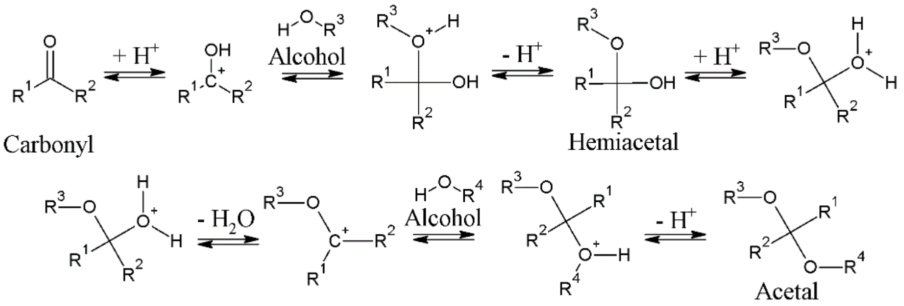

Fig. 2: Acid-catalysed acetal/hemiacetal formation (R: organic rest or H-atom).

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 (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 (Referee #1)

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 µmol 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 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)."*

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 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 PFTFE filters, which were sampled after the OH-radical oxidation of 1,3,5-TMB at RH = 50% in the presence of* NH_4HSO_4 *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* NH_4HSO_4 *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 (*$Mw = 72.06\ g\ mol^{-1}$*; Table 6)."* was changed to *"The concentrations were converted into the fraction of methylglyoxal oligomers of* ΔM *using the molar mass of methylglyoxal (*$Mw = 72.06\ g\ mol^{-1}$*)."*

Page 9, Line 310: *"In the presence of* NH_4HSO_4 *seed particles the highest oligomer fraction (8.2 ± 0.7%) can be observed with RH = 0% whereas in the presence of* $(NH_4)_2SO_4/H_2SO_4$ *seed particles the oligomer fraction is the lowest (2.1 ± 0.4%) under dry conditions."* was changed to *"In the presence of* NH_4HSO_4 *seed particles the highest oligomer fraction (8.2 ± 0.7%) can be observed with RH = 0% whereas in the presence of* $(NH_4)_2SO_4/H_2SO_4$ *seed particles the oligomer fraction is the lowest (2.1 ± 0.4%) under dry conditions (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* $(NH_4)_2SO_4/H_2SO_4$ *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 is does not provide a feasible explanation for the higher oligomer fraction at higher RH with* $(NH_4)_2SO_4/H_2SO_4$ *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* $(NH_4)_2SO_4/H_2SO_4$ *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 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 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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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).

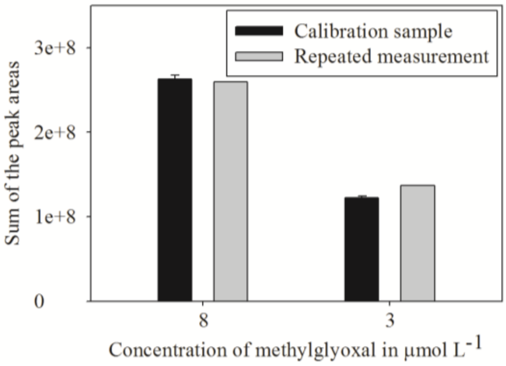

Figure 3: Comparison of the calibration at the beginning of the GC/MS measurements with a repeated measurement of the calibration after measuring samples from chamber experiment.

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 m³) it was not possible to collect more than four filter samples (1.2 m³ 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).

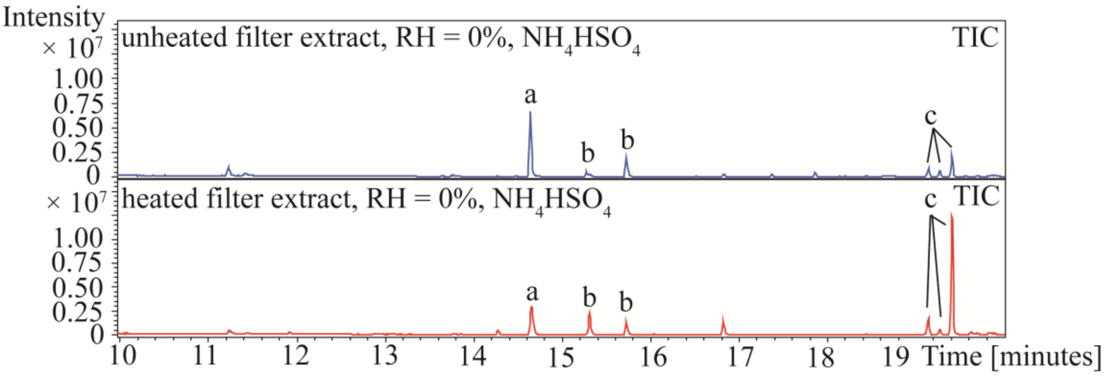

Figure 4: TIC of an unheated and heated filter extract; a: cyclohexanone-2,2,6,6,-d4, b: 2-trifluoronethyl)benzaldehyde, c: methylglyoxal.

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 (Referee #2)

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 ($c = 1.82 \pm 0.14\ \mu\text{mol}\ L^{-1}$) in comparison to the unheated filter extract ($c = 0.29 \pm 0.01\ \mu\text{mol}\ L^{-1}$).”*

Page 5, Line 173: *“A methylglyoxal concentration of $c = 5.32 \pm 0.05\ \mu\text{mol}\ L^{-1}$ was found which corresponds to a recovery of ≈ 85%.”* was changed to *“A methylglyoxal concentration of $c = 5.32 \pm 0.05\ \mu\text{mol}\ L^{-1}$ 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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A quantification method for heat-decomposable methylglyoxal oligomers and its application on 1,3,5-trimethylbenzene SOA

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Abstract

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). Thus-far, no suitable method for the quantification of methylglyoxal oligomers is available despite the great effort spent for structure elucidation. In the present study a simplified method was developed to quantify heat-decomposable methylglyoxal oligomers as a sum parameter. The method is based on the thermal decomposition of oligomers into methylglyoxal monomers. Formed methylglyoxal monomers were detected using PFBHA (o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride) derivatisation and gas chromatography/mass spectrometry (GC/MS) analysis. 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.
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). Oligomer formation was investigated as a function of seed particle acidity and relative humidity. 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. Overall, the present study provides a new and suitable method for quantification of heat-decomposable methylglyoxal oligomers in the aqueous particle phase.

1. Introduction

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 dominated site in China (Liu et al., 2008). 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). 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). 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). 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).

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). During the last decade, huge efforts were undertaken to detect and identify oligomeric compounds. 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). In addition, spectroscopic methods like UV/Vis (ultraviolet-visible spectroscopy), FTIR (Fourier transform infrared spectroscopy), and NMR (nuclear magnetic resonance spectroscopy) analysis were used for identification.

Despite the past effort for structure elucidation of oligomeric compounds a suitable quantification method is not available. Mostly, an overall contribution of oligomers to the particle mass was determined using, e.g., a volatility tandem differential mobility analyser (VTDMA). Kalberer et al. (2004) determined an oligomer contribution of 50% to the particle mass formed by the photooxidation of 1,3,5-TMB. In a further experiment, oligomer mass fractions of 80% and 90% were determined with a VTDMA-based approach for 1,3,5-TMB and α-pinene (Kalberer et al., 2006). Alfarra et al. (2006) investigated the photooxidation of 1,3,5-TMB and found an increase of the oligomer fraction of 3.1 and 3.7% $hour^{-1}$. A particulate oligomer fraction of 50% was reported for 1,3,5-TMB and α-pinene by Baltensperger et al. (2005). 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. Nguyen et al. (2011) investigated oligomers from isoprene photooxidation with ESI-MS and nano-DESI-MS (nanospray desorption electrospray ionisation) connected to a high resolution linear ion trap (LTQ-) orbitrap. They calculated an oligomer fraction of 80 – 90%.

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. In another approach it was estimated that after 4 days in aqueous particles containing amino acids, 15% of the carbonyl compounds are oligomers (Noziere et al., 2007). Contrary, with ammonium sulfate particles 30% of the carbonyl compounds are converted into oligomers (Noziere et al., 2007). These estimations are based on the rate constants for oligomer formation which were determined in the study by Noziere et al. (2007). Besides these estimations, quantification of oligomeric compounds was also conducted using surrogate compounds (Surratt et al., 2006, Zappoli et al., 1999, and Gao et al., 2004) or synthesised authentic standards (Birdsall et al., 2013).

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. 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.

2. Experimental

2.1 Chemicals and standards

1,3,5-TMB (≥ 99.8%), hydrochloric acid (37%), tetramethylethylene (99%), and sodium hydroxide (50 – 52%) were obtained from Sigma-Aldrich (Hamburg, Germany). *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (≥99%), methylglyoxal (40% in water), and ammonium hydrogensulfate (98%) were purchased from Fluka (Hamburg, Germany). Sulfuric acid (98%) was obtained from Merck KGaA (Darmstadt, Germany). Dichloromethane (Chromasolv 99.8%) was obtained from Riedel-de Haen (Seelze, Germany) and ammonium sulfate (99.5%) was purchased from Carl Roth (Karlsruhe, Germany). Ultrapure water was used to prepare the seed particle solutions, the authentic standards, and to extract the filter samples (Milli-Q gradient A 10, 18.2 MΩ cm, 3 ppb TOC, Millipore, USA).

2.2 Chamber experiments

The OH-radical oxidation of 1,3,5-TMB was investigated in the LEipziger AerosolKammer (LEAK). A detailed description of the aerosol chamber can be found elsewhere (Mutzel et al., 2016). The conditions of the experimental runs are summarised in Table 2. The experiments were conducted in the presence of ammonium bisulfate particles or ammonium sulfate particles mixed with sulfuric acid to achieve different seed acidities. 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 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). O_3 was produced by UV irradiation of O_2 with an O_2 flow rate of 5 L minute^{-1}. 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. 1,3,5-TMB (≈ 92 ppb) was injected into the aerosol chamber using a microliter-syringe. The oxidation of 1,3,5-TMB was studied at relative humidities (RH) between ≈ 0% and 75% adjusted by flushing the aerosol chamber with humid or dry air. 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). The volume size distribution of the seed particles was measured with a scanning mobility particle sizer (SMPS; 3010; TSI, USA). An average density of 1 g cm^{-3} was used to calculate the increase of the organic particle mass (ΔM). 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.

2.3 Sample preparation

For method development, PTFE filter samples from aerosol chamber experiments were used. The following method parameters were investigated: heating time, pH during the heating process, and heating temperature (Table 3). Filter samples from the same experiments were used for the optimisation of the respective method parameters.

2.3.1 Filter extraction

Two halves of the PTFE filters were cut into small pieces. Each filter half was extracted separately with 1 mL H_2O for 30 minutes using an orbital shaker (700 rpm, revolutions per minutes). They were shaken again separately with 1 mL H_2O for 30 minutes and flushed at the end of the procedure with 1 mL H_2O resulting in two 3 mL extracts. 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. The extract of one half of the filter was used for oligomer measurements (extract 1) and with the second one methylglyoxal monomers were quantified which were not a building block of oligomers (extract 2). A detailed description of the derivatisation procedure can be found in Rodigast et al. (2015).

2.3.2 Derivatisation procedure

Extract 1 – Heat-decomposable methylglyoxal oligomers

For quantification of heat-decomposable methylglyoxal oligomers the extract was acidified and heated to decompose the oligomeric bonds. The pH was adjusted with hydrochloric acid (37%) or sodium hydroxide (1 mol L^{-1}) to pH = 1, 3, 5, and 7 while heating temperatures of 50°C and 100°C were investigated. For the derivatisation of the formed monomeric methylglyoxal, 300 µL of *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 5 mg mL^{-1}) was added to the sample solution after 2 minutes of the heating process. Different heating times were tested varying between 15 hours and 48 hours. After the derivatisation was complete, the extracts were allowed to cool down to room temperature.

Extract 2 – Methylglyoxal monomer

The second half of the filters was used to quantify monomeric methylglyoxal. The filters were prepared according to the method described by Rodigast et al. (2015).

2.3.3 Extraction for GC/MS analysis

After derivatisation of both filter extracts (extract 1 and 2), derivatised methylglyoxal was extracted at pH = 1 for 30 minutes with 250 µL of dichloromethane using an orbital shaker (1500 rpm; Rodigast et al., 2015). 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.

For quantification, a 5-point calibration was performed at the beginning of each chromatographic run using a standard solution of methylglyoxal in a concentration range of 0.13 to 8 µmol L^{-1}.

2.4 Instrumentation

The samples were analysed using a GC System (6890 Series Agilent Technologies, Frankfurt, Germany) coupled with an electron ionisation quadrupole mass spectrometer in splitless mode with an inlet temperature of 250°C (Agilent 5973 Network mass selective detector, Frankfurt, Germany). The derivatives were separated with a HP-5MS UI column (Agilent J & W GC columns, 30 m × 0.25 mm × 0.25 µm) using the following temperature program: 50°C isothermal for 2 minutes and elevated to 230°C (10 °C $minute^{-1}$). 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.

3. Results

Hastings et al. (2005) investigated the influence of the temperature of the GC inlet on the detection of oligomeric compounds. These authors concluded that oligomers decompose into monomer building blocks at higher inlet temperatures (≥ 120°C) which caused problems for oligomer quantification. In the present study a quantification method is proposed to decompose heat-decomposable oligomers into methylglyoxal monomers due to heating, acidification and PFBHA derivatisation prior GC/MS injection.

(E) and (Z) isomers of methylglyoxal were formed during PFBHA derivatisation resulting in two peaks in the GC/MS chromatogram. For quantification, the sum of these peaks was used to avoid an over- or underestimation of methylglyoxal due to variations of the isomer peak ratio during the heating process.

3.1 Method development

Influence of heating time

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). 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. 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. Additionally, a 6.25 µmol L^{-1} standard solution of methylglyoxal was acidified and heated for different times to exclude an effect of the heating process on the derivatisation. The results are illustrated in Fig. 1a.

The highest methylglyoxal concentration can be found after a heating time of 24 hours. 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}). To exclude that the higher methylglyoxal concentrations were only a result of a better PFBHA derivatisation during heating, a methylglyoxal standard solution was also heated for 24 hours (Fig. 1b). A methylglyoxal concentration of $c = 5.32 \pm 0.05$ µmol L^{-1} was found, which corresponds to a recovery of ≈ 85%. Thus, an effect of the heating process on the derivatisation can be excluded indicating that the higher methylglyoxal concentration was caused by decomposition of heat-decomposable oligomers into monomers.

One filter extract was heated for 15 hours and allowed to stand at room temperature for 9 hours (sample a) to reach a total derivatisation time of 24 hours (as it was optimised for PFBHA derivatisation by Rodigast et al., 2015). To exclude reoligomerisation processes of methylglyoxal in sample a, one filter extract was heated for 15 hours and measured directly after the heating process (sample b). As it can be seen in Fig. 1a both filter samples (sample a and b) showed lower methylglyoxal concentrations than after heating for 24 hours. 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. In comparison, the lower concentration in sample a might be caused by reoligomerisation of methylglyoxal.

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). In Fig. 1b a lower methylglyoxal concentration can be observed for the immediately measured sample (3.11 ± 0.20 µmol L^{-1}) compared to the sample after 9 hours at room temperature (5.84 ± 0.27 µmol L^{-1}). Thus, it can be concluded that a derivatisation time of 24 hours is needed for a complete derivatisation despite the heating process. This supports the hypothesis that methylglyoxal monomers were not completely derivatised, if the filter sample was heated for 15 hours and directly measured (sample b). Based on the incomplete derivatisation after 15 hours heating time, methylglyoxal monomers are able to react again under oligomer formation during the 9 hours at room temperature. The rate constants are reported to be $k = 5 \times 10^{-6}$ M^{-1} $minutes^{-1}$ for ammonium ion catalysed and $k \leq 1 \times 10^{-3}$ M^{-1} $minutes^{-1}$ for H_3O^+ catalysed aldol reaction (Sareen et al., 2010). Naturally, both of these ions are present in the aqueous filter extract. 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).

Longer heating times than 24 hours (30 and 48 hours) led to lower methylglyoxal concentrations in the filter samples as well. A possible explanation might be the decomposition of the derivatised compound during the long heating process. As no decrease of the concentration was observed in the methylglyoxal standard solution (Fig. 1b) the loss of the derivatisation group is unlikely as a reason for the lower concentrations. 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. Based on the outlined results, a heating time of 24 hours was chosen.

The pH during the heating process was investigated as well..

Influence of pH

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 NH_4HSO_4 particles (experiment #2). The pH was varied between pH = 1 and pH = 7.

As it can be seen in Fig. 2a the highest methylglyoxal concentration can be found at pH = 1. The methylglyoxal concentration was about two times higher at pH = 1 ($c = 1.01 \pm 0.11$ µmol L^{-1}) compared to the filter extract, which was neither heated nor acidified ($c = 0.45 \pm 0.01$ µmol L^{-1}). 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). As this was observed for both types of samples it appears that the pH influences the derivatisation and/or the oligomer decomposition. 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. In summary, based on these results pH = 1 was used.

Influence of heating temperature

The effect of the heating temperature was examined with filter samples of experiment #2. The heating temperature was varied between 50°C and 100°C and the filter extracts were heated for 24 hours at pH = 1. A temperature above 100°C cannot be used to avoid evaporation of water and/or target compounds. Fig. 3a shows the influence of the temperature on the decomposition of the heat-decomposable methylglyoxal oligomers into monomers. Higher concentration of methylglyoxal can be detected with higher temperature. The results illustrated in Fig. 3a indicate that a higher temperature than 50°C is needed to decompose the oligomeric compounds. 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. Fig. 3b shows no significant influence of the temperature on the methylglyoxal standard solution. Thus, an influence of the heating temperature on the derivatisation procedure can be excluded.

Based on these results, the PTFE filter extracts from the aerosol chamber experiments were acidified to pH = 1 and heated for 24 hours to 100°C to decompose heat-decomposable oligomeric compounds into methylglyoxal. 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.

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.

3.2 SOA yield and growth curves of 1,3,5-TMB oxidation

SOA formation of 1,3,5-TMB was investigated in a number of literature studies mostly in the presence of NO_x and under variation of the hydrocarbon to NO_x ratio ($[HC]/[NO_x]$ ratio). Healy et al. (2008) determined SOA yields (Y_{SOA}) of 1,3,5-TMB photooxidation ranging from 4.5 to 8.3%. 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). Only Cao and Jang (2007) investigated SOA yields in the absence of NO_x and reported values between 7.1 and 13.8%. The SOA yields were also determined in the present study for all conducted experiments based on the ratio of ΔM to ΔHC (Table 2). 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. Y_{SOA} varied between 4 and 7% dependent on reaction conditions and is in good agreement to literature values.

For a further investigation of SOA-formation processes of 1,3,5-TMB, Fig. 4a illustrates the dependency between the consumption of 1,3,5-TMB (ΔHC) and the produced organic particle mass (ΔM). Particle growth started directly after the experiment was initialised indicating that the oxidation leads immediately to the formation of condensable products as first-generation oxidation products. These products condense on the pre-existing seed particles resulting in the immediate particle growth observed in Fig. 4a. Differences of the growth curves in dependence on the seed particles (NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$) were not observed concluding that the seed particle acidity (Table 5) has no influence on the SOA formation of 1,3,5-TMB. Cao and Jang (2007) found also only a small influence of seed particle acidity on SOA formation.

Fig. 4a showed great differences in the growth curves under variation of RH. 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. ΔM is the highest at RH = 0% (ΔM = 18.1 – 19.7 $\mu g\ m^{-3}$) whereas ΔM is the lowest under humid conditions (RH = 50% and 75%, ΔM = 11.3 – 11.7 $\mu g\ m^{-3}$ and 13.9 – 14.2 $\mu g\ m^{-3}$). Due to the variation of RH in the aerosol chamber the liquid water content (LWC) of the particles is changing (Table 5). The LWC was calculated using model II from the extended aerosol thermodynamic model (E-AIM; Clegg et al., 1998). With increasing RH the LWC of the seed particle increases as well. The LWC of the seed particles influences i) the partitioning of the compounds from the gas phase into the particle phase and ii) the formation and/or further reaction in the particle phase (Zuend et al., 2010; Cocker et al., 2001; Seinfeld et al., 2001; Fick et al., 2003). These two effects might influence the SOA formation under different relative humidities.

An effect can also be seen in Fig. 4b. The SOA formation is enhanced at RH = 0% leading to the highest SOA yields of $Y_{SOA} \approx 7\%$ for both seed particles. Higher RH values resulted in lower Y_{SOA} between 4 and 5%. These findings are in good agreement with the study by Cao and Jang (2007), which observed lower Y_{SOA} values at elevated RH.

The influence of RH on SOA formation is controversially discussed in the literature (Hennigan et al., 2008; Fick et al., 2003; Edney et al., 2000; Saxena and Hildemann, 1996; Baker et al., 2001; Hasson et al., 2001, Cocker et al., 2001). Edney et al. (2000) and Seinfeld et al. (2001) reported an enhanced SOA formation of hydrophilic compounds under humid conditions and a lowered SOA formation of hydrophobic compounds. 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. This might lead to the conclusion that the OH-radical oxidation of 1,3,5-TMB results in the formation of hydrophobic compounds which showed an enhanced partitioning under dry conditions. 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.

3.3 Particulate methylglyoxal

Methylglyoxal is reported in the literature as an important oxidation product of 1,3,5-TMB (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 yields in the particle phase between 0.7 and 2%.

The fraction of methylglyoxal in the particle phase in dependency on the reaction conditions is shown in Fig. 5a, with resulting fractions between ≈ 0.6% and ≈ 2.2%. With increasing RH the fraction decreases for both seed particles. Methylglyoxal has the highest fraction under dry conditions (1.73 ± 0.20% and 2.17 ± 0.20% for NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$) and with $(NH_4)_2SO_4/H_2SO_4$ seed particles.

Healy et al. (2008) measured a contribution of methylglyoxal to SOA mass of 2.06 ± 0.08% from the photooxidation of 1,3,5-TMB in the presence of NO_x at RH = 50%. In the present study a methylglyoxal fraction of 1.24 ± 0.04% for NH_4HSO_4 seed particles and 0.80 ± 0.08% for $(NH_4)_2SO_4/H_2SO_4$ seed particles was determined at RH = 50%. Thus, the contribution is slightly lower than measured by Healy et al. (2008). In comparison, Cocker et al. (2001) measured a particulate fraction of 0.72%.

The dependency of particulate methylglyoxal on RH could be a result of the influence of RH on the partitioning from the gas- into the particle phase or on further reactions in the particle phase forming oligomers. 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).

3.4 Heat-decomposable methylglyoxal oligomers

A method was developed to determine the contribution of heat-decomposable methylglyoxal oligomers to the produced organic particle mass ΔM. The method is based on the thermal decomposition of the heat-decomposable methylglyoxal oligomers into monomers. Thus, the concentration of monomeric methylglyoxal was determined prior and after thermal decomposition. The concentrations were converted into the fraction of methylglyoxal oligomers of ΔM using the molar mass of methylglyoxal (Mw = 72.06 g mol^{-1}). An average oligomer fraction of ≈ 2% up to ≈ 8% was observed.

Fig. 5b shows the dependency of the detected heat-decomposable methylglyoxal oligomers on the relative humidity with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles. In the presence of NH_4HSO_4 seed particles the highest oligomer fraction (8.2 ± 0.7%) can be observed with RH = 0% whereas in the presence of $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction is the lowest (2.1 ± 0.4%) under dry conditions (RH = 0%). A possible explanation for the opposite trend of the oligomer fractions with RH between NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles could be different oligomer formation mechanism caused by different seed particle acidity. The type of accretion reaction might change with pH (Yasmeen et al., 2010). In Table 5 the pH of the seed particles was calculated with E-AIM. NH_4HSO_4 particles have pH = 0.1 and 1.2 at RH = 50% and 75%. In comparison $(NH_4)_2SO_4/H_2SO_4$ seed particle are less acidic (pH = 4.0 at RH = 50% and pH = 4.2 at RH = 75%).

It was postulated by Yasmeen et al. (2010) that a lower pH (pH < 3.5) favor acetal/hemiacetal formation whereas at high pH (pH = 4 - 5) aldol condensation are more relevant. This has been supported by Sedehi et al. (2013) and Sareen et al. (2010).

Thus, in the presence of strong acidic NH_4HSO_4 seed particles acetal/hemiacetal formation might be the favored oligomer formation mechanism. Oligomerisation via acetal/hemiacetal formation occurs under a reversible water loss (Yasmeen et al., 2010). 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). 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).

In the presence of $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction increases with increasing RH (Fig. 5b). As it was mentioned, aldol condensation can be assumed as the favored accretion reaction under these conditions (Yasmeen et al., 2010). Aldol condensation includes as a first step aldol addition followed by a loss of water. The loss of water is irreversible, thus the aldol condensation will not be inhibited with higher LWC of the seed particles.

Other accretion reactions can contribute to the formation of heat-decomposable methylglyoxal oligomers with $(NH_4)_2SO_4/H_2SO_4$ seed particles as well. Altieri et al. (2008) detected products formed through acid-catalysed esterification at pH ≈ 4. This equilibrium reaction involves the reversible loss of water as it was reported for acetal/hemiacetal formation (Lim et al., 2010). 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.

Imidazole formation was also postulated as possible oligomer-formation mechanism for methylglyoxal (Sedehi et al., 2013; De Haan et al., 2011). It was found that imidazole formation is of minor importance compared to aldol condensation (Sedehi et al., 2013). 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 $(NH_4)_2SO_4/H_2SO_4$ seed particles.

Radical – radical reactions are also postulated as a possible reaction pathway to form oligomers (Schaefer et al., 2015; Lim et al., 2013; Rincon et al., 2009; Lim et al., 2010; Sun et al., 2010). Radical-radical reactions of methylglyoxal might occur following the H - atom abstraction of methylglyoxal with OH radicals and a subsequent recombination of the resulting alkyl radicals (as discussed for glyoxal in Schaefer et al., 2015). The contribution of radical – radical reactions to oligomer formation is not well understood as obviously, the reaction of alkyl radicals with oxygen tends to suppress this pathway. 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 concentrations. For aerosol particle systems, ionic strength effects (Herrmann et al., 2015) are able to influence the uptake of methylglyoxal into the particle phase as well. Waxman et al. (2015) observed a salting-out effect for methylglyoxal for all investigated seed particles at higher ionic strengths.

Low pH combined with high solute concentrations as calculated for the present aerosol particles, can trigger isomerisation (or switching) reactions as discussed by Herrmann et al. (2015). Overall, a clear discussion on how radical-radical reaction might be affected by increasing LWC (through increasing RH) and by pH is difficult at the current level of knowledge.

In summary, the present study provides a reliable quantification method for heat-decomposable methylglyoxal oligomers formed by 1,3,5-TMB oxidation. The fraction of oligomeric substances formed solely by methylglyoxal oligomerisation varied dependent on RH and seed particle acidity between 2 – 8%, which is lower than the determined values by Kalberer et al. (2004) and Baltensperger et al. (2005) (varying between 50 and 80%). In the present study only heat-decomposable methylglyoxal oligomers were quantified, thus there might be oligomers originating from other monomers than methylglyoxal, which were not determined in the present study leading to lower oligomer fractions of ΔM compared to the literature studies. The obtained data are not fully conclusive and literature studies are often contradicting. Thus, more experiments are necessary to get a clearer picture about the influence of RH and particle phase acidity on oligomer formation and to explain the non-linear relation between the oligomer fraction and RH.

4. Summary

In the present study a method was developed to quantify oligomers formed from methylglyoxal. The method is based on the thermal decomposition of heat-decomposable methylglyoxal oligomers into monomers. The formed methylglyoxal monomers were detected with PFBHA derivatisation and GC/MS analysis. The influence of heating time, pH and heating temperature on the decomposition of heat-decomposable methylglyoxal oligomers was systematically investigated. The best result was achieved with a heating time of 24 hours at 100°C and pH = 1. The method was applied to heat-decomposable methylglyoxal oligomers formed during the oxidation of 1,3,5-TMB resulting in an oligomer fraction of up to ≈ 8%. A contradicting dependency of the oligomer fraction under varying RH with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles was found, which might be caused by different oligomer formation mechanisms.

Overall, the present method provides an important step revealing the amount of oligomers present in the particle phase, their tentative formation mechanism and their importance for aqSOA formation.

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Table 1: Overview of methods for structure elucidation of oligomeric compounds (after Hallquist et al., 2009).

Method	Reference
(Matrix assisted) laser desorption/ionisation mass spectrometry (MALDI-MS, LDI-MS)	Dommen et al., 2006; Kalberer et al., 2004; Kalberer et al., 2006; Reinhardt et al., 2007; Holmes and Petrucci, 2006; Surratt et al., 2006; Denkenberger et al., 2007
Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)	Kundu et al., 2012; Altieri et al., 2008; Tolocka et al., 2004; Hall and Johnston, 2012; Denkenberger et al., 2007; Tan et al., 2012
On-line atmospheric pressure chemical ionisation tandem mass spectrometry (APCI tandem MS)	Müller et al., 2008
Aerosol mass spectrometry (AMS)	Sareen et al., 2010; Schwier et al., 2010; Bahreini et al., 2005; Heaton et al., 2007
Electrospray ionisation mass spectrometry (ESI/MS, ESI/MS/MS)	Altieri et al., 2008; Hall and Johnston, 2012; Surratt et al., 2006; Yasmeen et al., 2010; Hastings et al., 2005; Bones et al., 2010; Surratt et al., 2007; Hamilton et al., 2006; Sadezky et al., 2006; Sato et al., 2012; Noziere et al., 2010; Tolocka et al., 2004; Iinuma et al., 2004; Nguyen et al., 2011; Bahreini et al., 2005
Aerosol time of flight mass spectrometry (ALTOFMS)	Huang et al., 2015
Gas chromatography mass spectrometry (GC/MS)	Hastings et al., 2005; Surratt et al., 2006; Szmigielski et al., 2007; Angove et al., 2006
Ion trap mass spectrometry (IT-MS)	Surratt et al., 2006; Gao et al., 2004
Photoelectron resonance capture ionisation-aerosol mass spectrometry (PERCI-MS)	Zahardis et al., 2005
Ultraviolet-visible spectroscopy (UV/Vis)	Nemet et al., 2004; Noziere and Esteve, 2005; Bones et al., 2010; Song et al., 2013; Casale et al., 2007; Alfarra et al., 2006; Drozd and McNeill, 2014; Noziere and Cordova, 2008
Fourier transform infrared spectroscopy (FTIR)	Loeffler et al., 2006; Bones et al., 2010; Jang et al., 2003; Jang and Kamens, 2001; Holmes and Petrucci, 2006
nuclear magnetic resonance spectroscopy (NMR)	Nemet et al., 2004; Bones et al., 2010; Angove et al., 2006; Garland et al., 2006; Kua et al., 2013; De Haan et al., 2011

Table 2: Experiments in the aerosol chamber LEAK for the OH radical oxidation of 1,3,5-TMB. All experiments were conducted at 293 K and with 91.9 ppb 1,3,5-TMB.

Experiment number	seed	RH [%]	O_{3ini} [ppb]	ΔHC [ppb]	ΔM [µg m^{-3}]	SOA yield Y_{SOA} [%]
#1	78 mmol L^{-1} NH_4HSO_4	≈ 0	≈ 137	57.2	19.7	7.00
#2	78 mmol L^{-1} NH_4HSO_4	50	≈ 133	55.2	11.3	4.12
#3	78 mmol L^{-1} NH_4HSO_4	75	≈ 134	56.2	14.2	5.14
#4	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	≈ 0	≈ 132	56.2	18.1	6.55
#5	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	50	≈ 135	56.5	11.7	4.21
#6	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	75	≈ 144	57.2	13.9	4.94

1,3,5-TMB: 1,3,5-Trimethylbenzene; RH: Relative humidity

Table 3: Investigated method parameters and used PTFE filters from 1,3,5-TMB oxidation for method development.

Parameter	Range	Filter of experiment
Heating time	15, **24**, 30, 48 hours	#3
pH	**1**, 3, 5, 7	#2
Heating temperature	50, **100** °C	#2

Selected parameters given in **bold**.

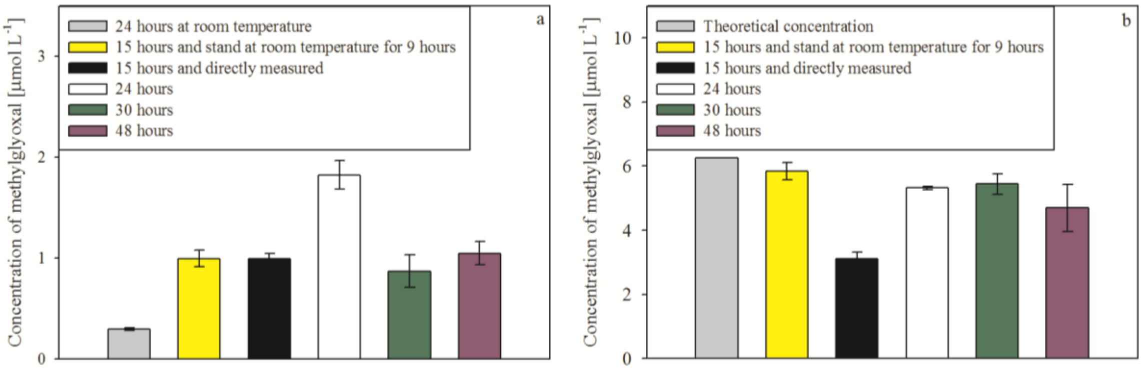

Figure 1: Influence of the heating time on the detected methylglyoxal concentrations in filter samples (a) and the methylglyoxal standard solution (b).

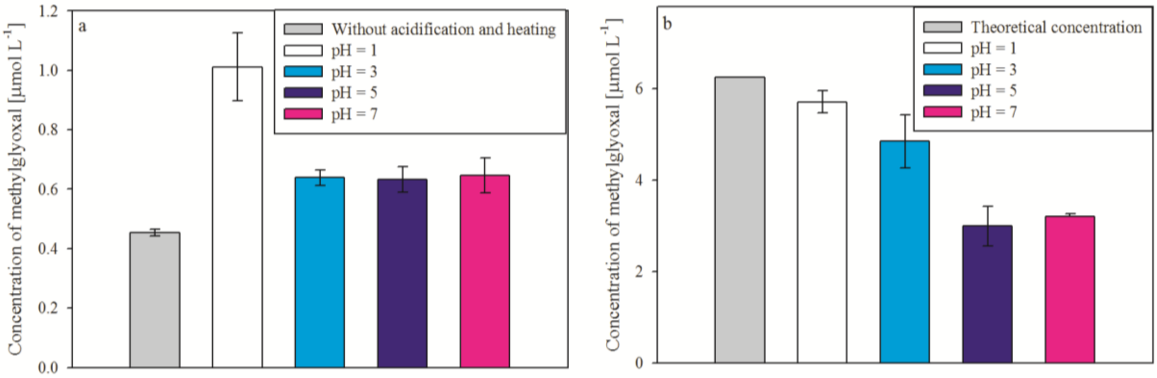

Figure 2: Influence of pH on the detected methylglyoxal concentration in filter samples (a) and the methylglyoxal standard solution (b).

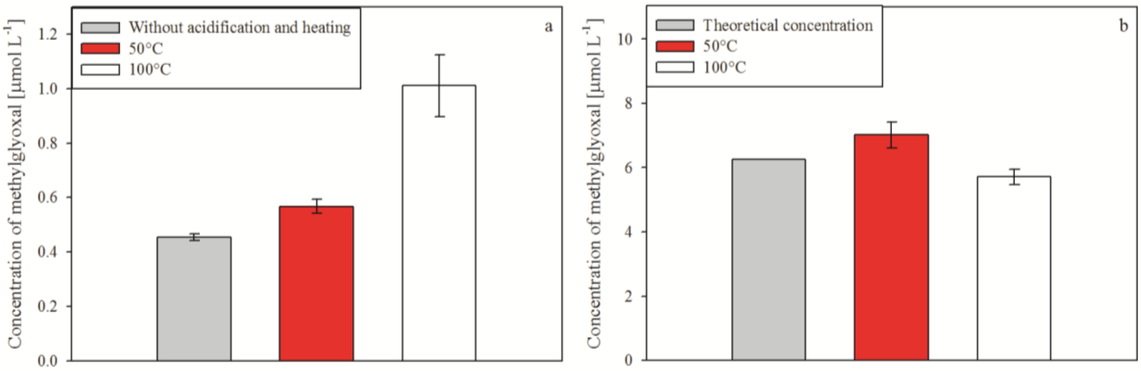

Figure 3: Influence of the heating temperature on the detected methylglyoxal concentration in filter samples (a) and the standard solution (b).

Table 4: SOA yields (Y_{SOA}) of 1,3,5-TMB reported in the literature.

SOA yield Y_{SOA} [%]	**Reference**
2.81 - 7.91	Cocker et al., 2001
4.5 – 8.34	Healy et al., 2008
2.5 ± 0.1 – 15.6 ± 1.0	Sato et al., 2012
3.1	Odum et al., 1997
0.41 ± 0.1	Kleindienst et al., 1999
0.29 – 6.36	Wyche et al., 2009
4.7 ± 0.7	Paulsen et al., 2005
7.1 ± 0.3 – 13.8 ± 0.6	Cao and Jang, 2007

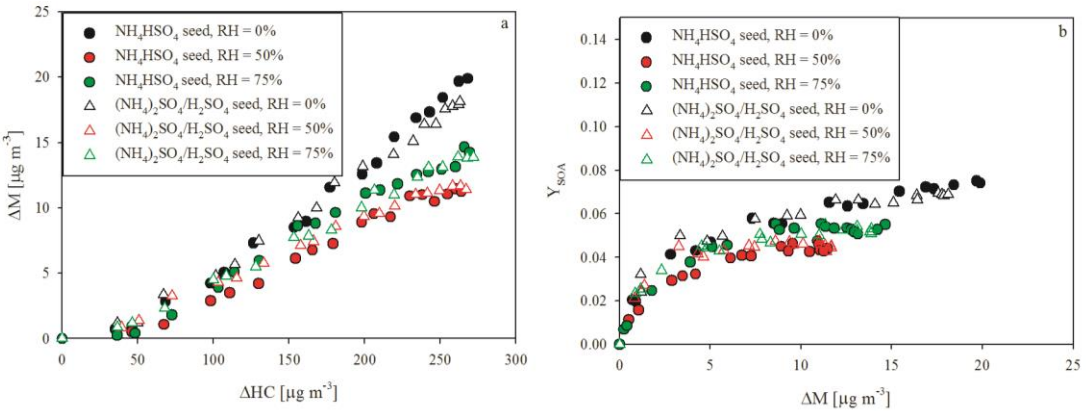

Figure 4: SOA growth curve (a) and yield curve (b) of the OH radical oxidation of 1,3,5-TMB in the presence of NH_4HSO_4 or $(NH_4)_2SO_4/H_2SO_4$ seed under variation of RH.

Table 5: LWC and pH of the seed particles calculated with E-AIM.

seed	RH [%]	pH$_{seed}$[a]	LWC [g m^{-3}][a]
78 mmol L^{-1} NH_4HSO_4	≈ 0	-[b]	-[b]
78 mmol L^{-1} NH_4HSO_4	50	0.1	6.66×10^{-6}
78 mmol L^{-1} NH_4HSO_4	75	1.2	12.29×10^{-6}
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	≈ 0	-[b]	-[b]
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	50	4.0	4.25×10^{-6}
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	75	4.2	11.56×10^{-6}

LWC: Liquid water content; [a] pH and LWC of the seed particles were calculated for different RH using model II from the extended aerosol thermodynamic model (E-AIM; Clegg et al., 1998); [b] calculation of the pH and LWC was not possible due to the low relative humidity of RH ≈ 0%. A RH = 10% is set as lower limit in E-AIM.

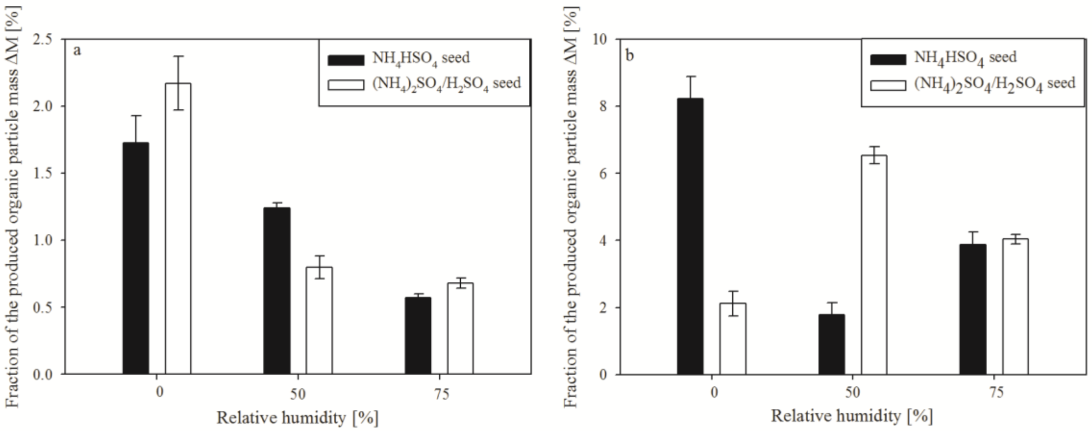

Figure 5: Contribution of methylglyoxal (a) and their heat-decomposable oligomers (b) to the produced organic particle mass (ΔM) with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles under variation of the relative humidity.