A quantification method for heat-decomposable methylglyoxal oligomers and its application on 1,3,5-trimethylbenzene SOA

Maria Rodigast, Anke Mutzel, and Hartmut Herrmann*

Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Dept. (ACD), Permoserstr. 15, D-04318 Leipzig, Germany

*Corresponding author. Tel: +49-341-2717-7024; fax: +49-341-271799-7024.

E-mail address: herrmann@tropos.de

1 **Abstract**

2 Methylglyoxal forms oligomeric compounds in the atmospheric aqueous particle phase, which could establish
3 a significant contribution to the formation of aqueous secondary organic aerosol (aqSOA). Thus-far, no
4 suitable method for the quantification of methylglyoxal oligomers is available despite the great effort spent for
5 structure elucidation. In the present study a simplified method was developed to quantify heat-decomposable
6 methylglyoxal oligomers as a sum parameter. The method is based on the thermal decomposition of oligomers
7 into methylglyoxal monomers. Formed methylglyoxal monomers were detected using PFBHA (o-(2,3,4,5,6-
8 pentafluorobenzyl)hydroxylamine hydrochloride) derivatisation and gas chromatography/mass spectrometry
9 (GC/MS) analysis. The method development was focused on the heating time (varied between 15 and 48
10 hours), pH during the heating process (pH = 1 - 7), and heating temperature (50°C, 100°C). The optimised
11 values of these method parameters are presented.
12 The developed method was applied to quantify heat-decomposable methylglyoxal oligomers formed during
13 the OH-radical oxidation of 1,3,5-trimethylbenzene (TMB) in the Leipziger aerosol chamber (LEAK).
14 Oligomer formation was investigated as a function of seed particle acidity and relative humidity. A fraction of
15 heat-decomposable methylglyoxal oligomers of up to 8% in the produced organic particle mass was found,
16 highlighting the importance of those oligomers formed solely by methylglyoxal for SOA formation. Overall,
17 the present study provides a new and suitable method for quantification of heat-decomposable methylglyoxal
18 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

59   a contribution of oligomers to the organic particle mass increasing from 27% to 44% in the first 5 hours of the

60   photooxidation of isoprene. Nguyen et al. (2011) investigated oligomers from isoprene photooxidation with

61   ESI-MS and nano-DESI-MS (nanospray desorption electrospray ionisation) connected to a high resolution

62   linear ion trap (LTQ-) orbitrap. They calculated an oligomer fraction of 80 – 90%.

63   De Haan et al. (2009) estimated the oligomer fraction formed by methylglyoxal in the aqueous phase

64   with NMR concluding 37% of methylglyoxal are dimers and oligomers. In another approach it was estimated

65   that after 4 days in aqueous particles containing amino acids, 15% of the carbonyl compounds are oligomers

66   (Noziere et al., 2007). Contrary, with ammonium sulfate particles 30% of the carbonyl compounds are

67   converted into oligomers (Noziere et al., 2007). These estimations are based on the rate constants for oligomer

68   formation which were determined in the study by Noziere et al. (2007). Besides these estimations,

69   quantification of oligomeric compounds was also conducted using surrogate compounds (Surratt et al., 2006,

70   Zappoli et al., 1999, and Gao et al., 2004) or synthesised authentic standards (Birdsall et al., 2013).

71   In summary, a variety of methods exists which quantify the fraction of oligomeric compounds derived

72   from methylglyoxal, but the results are contradicting due to the lack of a suitable method for quantification

73   and second, due to different reaction conditions used in the studies. Thus, the present study presents a

74   fundamental approach for a reliable quantification of methylglyoxal oligomers in laboratory-generated SOA.

75   The method is applicable for all oligomeric compounds, which can be decomposed into methylglyoxal

76   monomers during the heating process at a temperature of 100 °C. As the oligomerisation mechanisms leading

77   to the quantified oligomeric compounds are not known, it cannot be specified if the oligomers are reversibly

78   or irreversibly formed. In addition, it cannot be excluded that there exist oligomers, which are not

79   decomposable into their methylglyoxal monomers through the heating process. Thus, the quantified oligomers

80   are termed as heat-decomposable methylglyoxal oligomers.

81

82   **2. Experimental**

83   2.1 Chemicals and standards

84   1,3,5-TMB ($\geq$ 99.8%), hydrochloric acid (37%), tetramethylethylene (99%), and sodium hydroxide

85   (50 – 52%) were obtained from Sigma-Aldrich (Hamburg, Germany). O-(2,3,4,5,6-pentafluorobenzyl)-

86   hydroxylamine hydrochloride ($\geq$99%), methylglyoxal (40% in water), and ammonium hydrogensulfate (98%)

87   were purchased from Fluka (Hamburg, Germany). Sulfuric acid (98%) was obtained from Merck KGaA

88   (Darmstadt, Germany). Dichloromethane (Chromasolv 99.8%) was obtained from Riedel-de Haen (Seelze,

89   Germany) and ammonium sulfate (99.5%) was purchased from Carl Roth (Karlsruhe, Germany). Ultrapure

90   water was used to prepare the seed particle solutions, the authentic standards, and to extract the filter samples

91   (Milli-Q gradient A 10, 18.2 MΩ cm, 3 ppb TOC, Millipore, USA).

92

93   2.2 Chamber experiments

94   The OH-radical oxidation of 1,3,5-TMB was investigated in the LEipziger AerosolKammer (LEAK). A

95   detailed description of the aerosol chamber can be found elsewhere (Mutzel et al., 2016). The conditions of

96   the experimental runs are summarised in Table 2. The experiments were conducted in the presence of

97   ammonium bisulfate particles or ammonium sulfate particles mixed with sulfuric acid to achieve different seed

98   acidities. In order to investigate OH-radical oxidation of 1,3,5-TMB at low NO$_x$ levels (< 1 ppb) and under

99   dark conditions the ozonolysis of tetramethylethylene (TME) was used as OH-radical source (Berndt and

100 Böge, 2006). The cycloaddition of ozone to TME yields a primary ozonide, which reacts further and forms a

101 stabilised Criegee Intermediate (sCI). The sCI decomposes via the hydroperoxide channel, leading to the

102 formation of OH radicals (Gutbrod et al., 1996) with a yield of 0.92 ± 0.08 (Berndt and Böge, 2006). O_3 was

103 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

104 experiments and ≈ 26 ppbv of TME was introduced into the aerosol chamber in steps of 15 minutes. 1,3,5-

105 TMB (≈ 92 ppb) was injected into the aerosol chamber using a microliter-syringe. The oxidation of 1,3,5-TMB

106 was studied at relative humidities (RH) between $\approx 0\%$ and 75% adjusted by flushing the aerosol chamber with

107 humid or dry air. The consumption of the precursor compound (ΔHC) was monitored over a reaction time of

108 90 minutes with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF MS; 8000, IONICON

109 Analytik, Innsbruck, Germany). The volume size distribution of the seed particles was measured with a

110 scanning mobility particle sizer (SMPS; 3010; TSI, USA). An average density of 1 g cm^{-3} was used to calculate

111 the increase of the organic particle mass (ΔM). To collect the particle phase after the experiments, 1.2 m^3 of

112 the chamber volume was sampled on a PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, 47

113 mm in diameter, PALLFLEX T60A20, PALL, NY, USA) connected to a XAD-4 coated denuder (URG-2000-

114 30B5, URG Corporation, Chapel Hill, NC, USA) (Kahnt et al., 2011) to avoid artefacts caused by adsorption

115 of gas-phase organic compounds onto the filter.

116

117 2.3 Sample preparation

118 For method development, PTFE filter samples from aerosol chamber experiments were used. The following

119 method parameters were investigated: heating time, pH during the heating process, and heating temperature

120 (Table 3). Filter samples from the same experiments were used for the optimisation of the respective method

121 parameters.

122

123 2.3.1 Filter extraction

124 Two halves of the PTFE filters were cut into small pieces. Each filter half was extracted separately with 1 mL

125 H_2O for 30 minutes using an orbital shaker (700 rpm, revolutions per minutes). They were shaken again

126 separately with 1 mL H_2O for 30 minutes and flushed at the end of the procedure with 1 mL H_2O resulting in

127 two 3 mL extracts. Noticeably, the extraction efficiency was not investigated in the present study, thus it is not

128 known. Water was used as extracting reagent, because organic solvents like methanol and acetonitrile have

129 lower boiling points than water, thus lower heating temperatures can be applied for the decomposition of the

130 oligomers. Besides this, organic solvents like methanol and acetonitrile are miscible with dichloromethane,

131 thus an extraction of the derivatised methylglyoxal with dichloromethane prior the injection into GC/MS would

132 not be possible. The extract of one half of the filter was used for oligomer measurements (extract 1) and with

133 the second one methylglyoxal monomers were quantified which were not a building block of oligomers

134 (extract 2). A detailed description of the derivatisation procedure can be found in Rodigast et al. (2015).

135

136 2.3.2 Derivatisation procedure

137 *Extract 1 – Heat-decomposable methylglyoxal oligomers*

138 For quantification of heat-decomposable methylglyoxal oligomers the extract was acidified and heated to

139 decompose the oligomeric bonds. The pH was adjusted with hydrochloric acid (37%) or sodium hydroxide

140 (1 mol L^{-1}) to pH = 1, 3, 5, and 7 while heating temperatures of 50°C and 100°C were investigated. For the

141 derivatisation of the formed monomeric methylglyoxal, 300 µL of *o*-(2,3,4,5,6-

142 pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 5 mg mL^{-1}) was added to the sample solution after

143 2 minutes of the heating process. Different heating times were tested varying between 15 hours and 48 hours.

144 After the derivatisation was complete, the extracts were allowed to cool down to room temperature.

145

146 *Extract 2 – Methylglyoxal monomer*

147 The second half of the filters was used to quantify monomeric methylglyoxal. The filters were prepared

148 according to the method described by Rodigast et al. (2015).

149

150 2.3.3 Extraction for GC/MS analysis

151 After derivatisation of both filter extracts (extract 1 and 2), derivatised methylglyoxal was extracted at pH = 1

152 for 30 minutes with 250 µL of dichloromethane using an orbital shaker (1500 rpm; Rodigast et al., 2015). 1 µL

153 of the organic phase was injected into GC/MS for analysis. The measurements were repeated for three times

154 to ensure reliable GC/MS signals.

155 For quantification, a 5-point calibration was performed at the beginning of each chromatographic run using a

156 standard solution of methylglyoxal in a concentration range of 0.13 to 8 µmol L^{-1}.

157

158 2.4 Instrumentation

159 The samples were analysed using a GC System (6890 Series Agilent Technologies, Frankfurt, Germany)

160 coupled with an electron ionisation quadrupole mass spectrometer in splitless mode with an inlet temperature

161 of 250°C (Agilent 5973 Network mass selective detector, Frankfurt, Germany). The derivatives were separated

162 with a HP-5MS UI column (Agilent J & W GC columns, 30 m × 0.25 mm × 0.25 µm) using the following

163 temperature program: 50°C isothermal for 2 minutes and elevated to 230°C (10 °C minute^{-1}). The temperature

164 of 230°C was held constant for 1 minute and ended with 320°C for 10 minutes, thus the method has a run time

165 of 36 minutes.

166

167 **3. Results**

168 Hastings et al. (2005) investigated the influence of the temperature of the GC inlet on the detection of

169 oligomeric compounds. These authors concluded that oligomers decompose into monomer building blocks at

170 higher inlet temperatures ($\geq$ 120°C) which caused problems for oligomer quantification. In the present study a

171 quantification method is proposed to decompose heat-decomposable oligomers into methylglyoxal monomers

172 due to heating, acidification and PFBHA derivatisation prior GC/MS injection.

173 (E) and (Z) isomers of methylglyoxal were formed during PFBHA derivatisation resulting in two peaks in the

174 GC/MS chromatogram. For quantification, the sum of these peaks was used to avoid an over- or

175 underestimation of methylglyoxal due to variations of the isomer peak ratio during the heating process.

176

177 **3.1 Method development**

178 *Influence of heating time*

179 The influence of the heating time was examined with PTFE filters which were sampled after OH-radical

180 oxidation of 1,3,5-TMB at $RH = 75\%$ in the presence of NH_4HSO_4 seed particles (experiment #3). To

181 investigate the effect of the heating time on the decomposition of the heat-decomposable oligomeric

182 compounds, the aqueous filter extracts (extract 1) were acidified to $pH = 1$ and heated to $100°C$ for

183 $15 - 48$ hours. The results were compared to the unheated aqueous filter extracts (extract 2) to determine the

184 increase of methylglyoxal concentration due to decomposition of the heat-decomposable oligomers.

185 Additionally, a $6.25\ \mu mol\ L^{-1}$ standard solution of methylglyoxal was acidified and heated for different times

186 to exclude an effect of the heating process on the derivatisation. The results are illustrated in Fig. 1a.

187 The highest methylglyoxal concentration can be found after a heating time of 24 hours. The methylglyoxal

188 concentration was about six times higher ($c = 1.82 \pm 0.14\ \mu mol\ L^{-1}$) in comparison to the unheated filter extract

189 ($c = 0.29 \pm 0.01\ \mu mol\ L^{-1}$). To exclude that the higher methylglyoxal concentrations were only a result of a

190 better PFBHA derivatisation during heating, a methylglyoxal standard solution was also heated for 24 hours

191 (Fig. 1b). A methylglyoxal concentration of $c = 5.32 \pm 0.05\ \mu mol\ L^{-1}$ was found, which corresponds to a

192 recovery of $\approx 85\%$. Thus, an effect of the heating process on the derivatisation can be excluded indicating that

193 the higher methylglyoxal concentration was caused by decomposition of heat-decomposable oligomers into

194 monomers.

195 One filter extract was heated for 15 hours and allowed to stand at room temperature for 9 hours

196 (sample a) to reach a total derivatisation time of 24 hours (as it was optimised for PFBHA derivatisation by

197 Rodigast et al., 2015). To exclude reoligomerisation processes of methylglyoxal in sample a, one filter extract

198 was heated for 15 hours and measured directly after the heating process (sample b). As it can be seen in Fig. 1a

199 both filter samples (sample a and b) showed lower methylglyoxal concentrations than after heating for 24

200 hours. The lower methylglyoxal concentration of sample b might be caused by an incomplete derivatisation

201 due to the immediate measurement of the filter extract after 15 hours heating time. In comparison, the lower

202 concentration in sample a might be caused by reoligomerisation of methylglyoxal.

203 To probe this hypothesis a $6.25\ \mu mol\ L^{-1}$ methylglyoxal standard was heated for 15 hours and

204 measured immediately (like sample b) or, alternatively, was allowed to stand at room temperature for 9 hours

205 (like sample a). In Fig. 1b a lower methylglyoxal concentration can be observed for the immediately measured

206 sample ($3.11 \pm 0.20\ \mu mol\ L^{-1}$) compared to the sample after 9 hours at room temperature

207 ($5.84 \pm 0.27\ \mu mol\ L^{-1}$). Thus, it can be concluded that a derivatisation time of 24 hours is needed for a complete

208 derivatisation despite the heating process. This supports the hypothesis that methylglyoxal monomers were not

209 completely derivatised, if the filter sample was heated for 15 hours and directly measured (sample b). Based

210 on the incomplete derivatisation after 15 hours heating time, methylglyoxal monomers are able to react again

211 under oligomer formation during the 9 hours at room temperature. The rate constants are reported to be

212 $k = 5 \times 10^{-6}\ M^{-1}\ minutes^{-1}$ for ammonium ion catalysed and $k \leq 1 \times 10^{-3}\ M^{-1}\ minutes^{-1}$ for H_3O^+ catalysed aldol

213 reaction (Sareen et al., 2010). Naturally, both of these ions are present in the aqueous filter extract. Despite the

214 oligomerisation of methylglyoxal monomers during the 9 hours at room temperature, the derivatisation

215 proceeds as well during this time leading to higher methylglyoxal concentrations in sample a than in sample

216 b, which was directly measured after 15 hours heating (Fig. 1b).

217   Longer heating times than 24 hours (30 and 48 hours) led to lower methylglyoxal concentrations in
218   the filter samples as well. A possible explanation might be the decomposition of the derivatised compound
219   during the long heating process. As no decrease of the concentration was observed in the methylglyoxal
220   standard solution (Fig. 1b) the loss of the derivatisation group is unlikely as a reason for the lower
221   concentrations. Thus, it can be speculated that the low methylglyoxal concentrations in the filter samples are
222   a result of further reactions with particle-phase species, which do not exist in the standard samples. Based on
223   the outlined results, a heating time of 24 hours was chosen.
224   The pH during the heating process was investigated as well..
225

226   *Influence of pH*
227   The effect of the pH was examined with PTFE filters, which were sampled after OH-radical oxidation of 1,3,5-
228   TMB at RH = 50% in the presence of NH_4HSO_4 particles (experiment #2). The pH was varied between pH =
229   1 and pH = 7.
230   As it can be seen in Fig. 2a the highest methylglyoxal concentration can be found at pH = 1. The methylglyoxal
231   concentration was about two times higher at pH = 1 (c = 1.01 ± 0.11 µmol L^{-1}) compared to the filter extract,
232   which was neither heated nor acidified (c = 0.45 ± 0.01 µmol L^{-1}). An increasing pH leads to a lower
233   methylglyoxal concentration, which can be observed for filter samples (Fig. 2a) as well as for the
234   methylglyoxal standard solution (Fig. 2b). As this was observed for both types of samples it appears that the
235   pH influences the derivatisation and/or the oligomer decomposition. No influence of the pH on the PFBHA
236   derivatisation reaction was reported by Rodigast et al. (2015) indicating the effect of the pH is connected to
237   thermal decomposition of the heat-decomposable oligomeric compounds. In summary, based on these results
238   pH = 1 was used.
239

240   *Influence of heating temperature*
241   The effect of the heating temperature was examined with filter samples of experiment #2. The heating
242   temperature was varied between 50°C and 100°C and the filter extracts were heated for 24 hours at pH = 1. A
243   temperature above 100°C cannot be used to avoid evaporation of water and/or target compounds. Fig. 3a shows
244   the influence of the temperature on the decomposition of the heat-decomposable methylglyoxal oligomers into
245   monomers. Higher concentration of methylglyoxal can be detected with higher temperature. The results
246   illustrated in Fig. 3a indicate that a higher temperature than 50°C is needed to decompose the oligomeric
247   compounds. In comparison to the filter, which was neither acidified nor heated, the concentration increased by
248   a factor of two if the extract was heated to 100°C. Fig. 3b shows no significant influence of the temperature
249   on the methylglyoxal standard solution. Thus, an influence of the heating temperature on the derivatisation
250   procedure can be excluded.
251   Based on these results, the PTFE filter extracts from the aerosol chamber experiments were acidified
252   to pH = 1 and heated for 24 hours to 100°C to decompose heat-decomposable oligomeric compounds into
253   methylglyoxal. According to the literature studies other carbonyl compounds can be expected as particle-phase
254   products, e.g., propionaldehyde (Cocker et al., 2001), glyoxal (Cocker et al., 2001; Huang et al., 2015), 2-
255   methyl-4-oxo-2-pentenal (Healy et al., 2008; Huang et al., 2014), glycolaldehyde (Cocker et al., 2001) and

256 3,5-dimethylbenzaldehyde (Huang et al., 2014). Noticeably, no carbonyl compounds other than methylglyoxal

257 were identified, which showed an increase after thermal decomposition.

258   The developed quantification method was afterwards applied to laboratory-generated SOA formed

259 during further oxidation experiments of 1,3,5-TMB to investigate the influence of seed particle acidity and

260 relative humidity on the oligomer content.

261

262 **3.2 SOA yield and growth curves of 1,3,5-TMB oxidation**

263 SOA formation of 1,3,5-TMB was investigated in a number of literature studies mostly in the presence of NO_x

264 and under variation of the hydrocarbon to NO_x ratio ([HC]/[NO_x] ratio). Healy et al. (2008) determined SOA

265 yields (Y_{SOA}) of 1,3,5-TMB photooxidation ranging from 4.5 to 8.3%. Further studies determined Y_{SOA}

266 between 0.29% and 15.6% (Table 4) under variation of the [HC]/[NO_x] ratio concluding SOA formation is

267 enhanced at low NO_x mixing ratios (Sato et al., 2012; Kleindienst et al., 1999; Baltensperger et al., 2005;

268 Wyche et al., 2009; Odum et al., 1997; Paulsen et al., 2005; Cocker et al., 2001). Only Cao and Jang (2007)

269 investigated SOA yields in the absence of NO_x and reported values between 7.1 and 13.8%. The SOA yields

270 were also determined in the present study for all conducted experiments based on the ratio of ΔM to ΔHC

271 (Table 2). Noticeably, the SOA yields of 1,3,5-TMB are not corrected for the wall loss to the surface of the

272 aerosol chamber, which might have an influence on the reported SOA yields. Y_{SOA} varied between 4 and 7%

273 dependent on reaction conditions and is in good agreement to literature values.

274   For a further investigation of SOA-formation processes of 1,3,5-TMB, Fig. 4a illustrates the

275 dependency between the consumption of 1,3,5-TMB (ΔHC) and the produced organic particle mass (ΔM).

276 Particle growth started directly after the experiment was initialised indicating that the oxidation leads

277 immediately to the formation of condensable products as first-generation oxidation products. These products

278 condense on the pre-existing seed particles resulting in the immediate particle growth observed in Fig. 4a.

279 Differences of the growth curves in dependence on the seed particles (NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$) were

280 not observed concluding that the seed particle acidity (Table 5) has no influence on the SOA formation of

281 1,3,5-TMB. Cao and Jang (2007) found also only a small influence of seed particle acidity on SOA formation.

282   Fig. 4a showed great differences in the growth curves under variation of RH. The RH value can have

283 an influence on the phase state of the particles while the phase state has an effect on the partitioning of the

284 compounds into the particles and the particle-phase reactions (Ziemann, 2010; Saukko et al., 2012). In the

285 present study the particles are a mixture of inorganic and partitioned organic compounds, thus the phase state

286 is not known but it might be possible that the phase state influences ΔM and the SOA yields. ΔM is the highest

287 at RH = 0% (ΔM = 18.1 – 19.7 µg m^{-3}) whereas ΔM is the lowest under humid conditions (RH = 50% and

288 75%, ΔM = 11.3 – 11.7 µg m^{-3} and 13.9 – 14.2 µg m^{-3}). Due to the variation of RH in the aerosol chamber the

289 liquid water content (LWC) of the particles is changing (Table 5). The LWC was calculated using model II

290 from the extended aerosol thermodynamic model (E-AIM; Clegg et al., 1998). With increasing RH the LWC

291 of the seed particle increases as well. The LWC of the seed particles influences i) the partitioning of the

292 compounds from the gas phase into the particle phase and ii) the formation and/or further reaction in the particle

293 phase (Zuend et al., 2010; Cocker et al., 2001; Seinfeld et al., 2001; Fick et al., 2003). These two effects might

294 influence the SOA formation under different relative humidities.

295   An effect can also be seen in Fig. 4b. The SOA formation is enhanced at RH = 0% leading to the

296   highest SOA yields of $Y_{SOA} \approx 7\%$ for both seed particles. Higher RH values resulted in lower Y_{SOA} between 4

297   and 5%. These findings are in good agreement with the study by Cao and Jang (2007), which observed lower

298   Y_{SOA} values at elevated RH.

299   The influence of RH on SOA formation is controversially discussed in the literature (Hennigan et al.,

300   2008; Fick et al., 2003; Edney et al., 2000; Saxena and Hildemann, 1996; Baker et al., 2001; Hasson et al.,

301   2001, Cocker et al., 2001). Edney et al. (2000) and Seinfeld et al. (2001) reported an enhanced SOA formation

302   of hydrophilic compounds under humid conditions and a lowered SOA formation of hydrophobic compounds.

303   This is also supported by Saxena and Hildemann (1996), which found an enhanced partitioning of organic

304   compounds with several hydroxyl groups at higher LWCs of the particles. This might lead to the conclusion

305   that the OH-radical oxidation of 1,3,5-TMB results in the formation of hydrophobic compounds which showed

306   an enhanced partitioning under dry conditions. Additionally, it can be speculated that the formation of

307   oligomeric compounds can be enhanced at lower RH values resulting in higher Y_{SOA} due to the increasing

308   conversion of the monomeric building blocks and their enhanced partitioning into the particle phase.

309

310 3.3 Particulate methylglyoxal

311 Methylglyoxal is reported in the literature as an important oxidation product of 1,3,5-TMB (Metzger et al.,

312 2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005;

313 Rickard et al., 2010; Kalberer et al., 2004; Yu et al., 1997; Kleindienst et al., 1999; Müller et al., 2012; Nishino

314 et al., 2010; Hamilton et al., 2003; Tuazon et al., 1986; Bandow and Washida, 1985) with yields in the particle

315 phase between 0.7 and 2%.

316   The fraction of methylglyoxal in the particle phase in dependency on the reaction conditions is shown

317 in Fig. 5a, with resulting fractions between $\approx 0.6\%$ and $\approx 2.2\%$. With increasing RH the fraction decreases for

318 both seed particles. Methylglyoxal has the highest fraction under dry conditions (1.73 ± 0.20% and

319 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.

320   Healy et al. (2008) measured a contribution of methylglyoxal to SOA mass of 2.06 ± 0.08% from the

321 photooxidation of 1,3,5-TMB in the presence of NO_x at RH = 50%. In the present study a methylglyoxal

322 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

323 was determined at RH = 50%. Thus, the contribution is slightly lower than measured by Healy et al. (2008).

324 In comparison, Cocker et al. (2001) measured a particulate fraction of 0.72%.

325   The dependency of particulate methylglyoxal on RH could be a result of the influence of RH on the

326 partitioning from the gas- into the particle phase or on further reactions in the particle phase forming oligomers.

327 The formation of oligomeric compounds from methylglyoxal has been investigated in a number of studies

328 (e. g. De Haan et al., 2009; Kalberer et al., 2004; Loeffler et al., 2006; Zhao et al., 2006; Sareen et al., 2010;

329 Altieri et al., 2008).

330

331 3.4 Heat-decomposable methylglyoxal oligomers

332 A method was developed to determine the contribution of heat-decomposable methylglyoxal oligomers to the

333 produced organic particle mass ΔM. The method is based on the thermal decomposition of the heat-

334 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 $\approx 2\%$ up to $\approx 8\%$ 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.

374   Radical – radical reactions are also postulated as a possible reaction pathway to form oligomers

375 (Schaefer et al., 2015; Lim et al., 2013; Rincon et al., 2009; Lim et al., 2010; Sun et al., 2010). Radical-radical

376 reactions of methylglyoxal might occur following the H - atom abstraction of methylglyoxal with OH radicals

377 and a subsequent recombination of the resulting alkyl radicals (as discussed for glyoxal in Schaefer et al.,

378 2015). The contribution of radical – radical reactions to oligomer formation is not well understood as

379 obviously, the reaction of alkyl radicals with oxygen tends to suppress this pathway. Nevertheless, it can be

380 expected, that with higher LWCs of the seed particles and thus with a higher reaction volume, the absolute

381 amount of methylglyoxal in the particle phase might increase, but not its particle-phase concentrations. For

382 aerosol particle systems, ionic strength effects (Herrmann et al., 2015) are able to influence the uptake of

383 methylglyoxal into the particle phase as well. Waxman et al. (2015) observed a salting-out effect for

384 methylglyoxal for all investigated seed particles at higher ionic strengths.

385   Low pH combined with high solute concentrations as calculated for the present aerosol particles, can

386 trigger isomerisation (or switching) reactions as discussed by Herrmann et al. (2015). Overall, a clear

387 discussion on how radical-radical reaction might be affected by increasing LWC (through increasing RH) and

388 by pH is difficult at the current level of knowledge.

389   In summary, the present study provides a reliable quantification method for heat-decomposable

390 methylglyoxal oligomers formed by 1,3,5-TMB oxidation. The fraction of oligomeric substances formed solely

391 by methylglyoxal oligomerisation varied dependent on RH and seed particle acidity between $2 - 8\%$, which is

392 lower than the determined values by Kalberer et al. (2004) and Baltensperger et al. (2005) (varying between

393 50 and 80%). In the present study only heat-decomposable methylglyoxal oligomers were quantified, thus

394 there might be oligomers originating from other monomers than methylglyoxal, which were not determined in

395 the present study leading to lower oligomer fractions of ΔM compared to the literature studies. The obtained

396 data are not fully conclusive and literature studies are often contradicting. Thus, more experiments are

397 necessary to get a clearer picture about the influence of RH and particle phase acidity on oligomer formation

398 and to explain the non-linear relation between the oligomer fraction and RH.

399

400 **4. Summary**

401 In the present study a method was developed to quantify oligomers formed from methylglyoxal. The method

402 is based on the thermal decomposition of heat-decomposable methylglyoxal oligomers into monomers. The

403 formed methylglyoxal monomers were detected with PFBHA derivatisation and GC/MS analysis. The

404 influence of heating time, pH and heating temperature on the decomposition of heat-decomposable

405 methylglyoxal oligomers was systematically investigated. The best result was achieved with a heating time of

406 24 hours at 100°C and pH = 1. The method was applied to heat-decomposable methylglyoxal oligomers

407 formed during the oxidation of 1,3,5-TMB resulting in an oligomer fraction of up to $\approx 8\%$. A contradicting

408 dependency of the oligomer fraction under varying RH with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles

409 was found, which might be caused by different oligomer formation mechanisms.

410 Overall, the present method provides an important step revealing the amount of oligomers present in the

411 particle phase, their tentative formation mechanism and their importance for aqSOA formation.

412

413 **5. Acknowledgements**

References

418 Alfarra, M. R., Paulsen, D., Gysel, M., Garforth, A. A., Dommen, J., Prevot, A. S. H., Worsnop, D. R.,
419   Baltensperger, U., and Coe, H.: A mass spectrometric study of secondary organic aerosols formed from the
420   photooxidation of anthropogenic and biogenic precursors in a reaction chamber, Atmospheric Chemistry and
421   Physics, 6, 5279-5293, 10.5194/acp-6-5279-2006, 2006.
422 Altieri, K. E., Seitzinger, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers
423   formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms
424   investigated by ultra-high resolution FT-ICR mass spectrometry, Atmospheric Environment, 42, 1476-1490,
425   10.1016/j.atmosenv.2007.11.015, 2008.
426 Angove, D. E., Fookes, C. J. R., Hynes, R. G., Walters, C. K., and Azzi, M.: The characterisation of secondary
427   organic aerosol formed during the photodecomposition of 1,3-butadiene in air containing nitric oxide,
428   Atmospheric Environment, 40, 4597-4607, 10.1016/j.atmosenv.2006.03.046, 2006.
429 Bahreini, R., Keywood, M. D., Ng, N. L., Varutbangkul, V., Gao, S., Flagan, R. C., Seinfeld, J. H., Worsnop,
430   D. R., and Jimenez, J. L.: Measurements of secondary organic aerosol from oxidation of cycloalkenes,
431   terpenes, and m-xylene using an Aerodyne aerosol mass spectrometer, Environmental Science &
432   Technology, 39, 5674-5688, 10.1021/es048061a, 2005.
433 Baker, J., Aschmann, S. M., Arey, J., and Atkinson, R.: Reactions of stabilized Criegee intermediates from the
434   gas-phase reactions of O-3 with selected alkenes, International Journal of Chemical Kinetics, 34, 73-85,
435   2001.
436 Baltensperger, U., Kalberer, M., Dommen, J., Paulsen, D., Alfarra, M. R., Coe, H., Fisseha, R., Gascho, A.,
437   Gysel, M., Nyeki, S., Sax, M., Steinbacher, M., Prevot, A. S. H., Sjogren, S., Weingartner, E., and Zenobi,
438   R.: Secondary organic aerosols from anthropogenic and biogenic precursors, Faraday Discussions, 130, 265-
439   278, 10.1039/b417367h, 2005.
440 Bandow, H., and Washida, N.: Ring-cleavage reactions of aromatic hydrocarbons studied by FT-IR
441   spectroscopy .III. Photooxidation of 1,2,3-,1,2,4-, and 1,3,5-trimethylbenzene in the NOx-air system,
442   Bulletin of the Chemical Society of Japan, 58, 2549-2555, 10.1246/bcsj.58.2549, 1985.
443 Barsanti, K. C., and Pankow, J. F.: Thermodynamics of the formation of atmospheric organic particulate matter
444   by accretion reactions - 2. Dialdehydes, methylglyoxal, and diketones, Atmospheric Environment, 39, 6597-
445   6607, 10.1016/j.atmosenv.2005.07.056, 2005.
446 Berndt, T., and Böge, O.: Formation of phenol and carbonyls from the atmospheric reaction of OH radicals
447   with benzene, Physical Chemistry Chemical Physics, 8, 1205-1214, 10.1039/b514148f, 2006.
448 Birdsall, A. W., Zentner, C. A., and Elrod, M. J.: Study of the kinetics and equilibria of the oligomerization
449   reactions of 2-methylglyceric acid, Atmospheric Chemistry and Physics, 13, 3097-3109, 10.5194/acp-13-
450   3097-2013, 2013.
451 Bones, D. L., Henricksen, D. K., Mang, S. A., Gonsior, M., Bateman, A. P., Nguyen, T. B., Cooper, W. J., and
452   Nizkorodov, S. A.: Appearance of strong absorbers and fluorophores in limonene-O-3 secondary organic
453   aerosol due to NH4+-mediated chemical aging over long time scales, Journal of Geophysical Research-
454   Atmospheres, 115, 14, 10.1029/2009jd012864, 2010.
455 Cao, G., and Jang, M.: Effects of particle acidity and UV light on secondary organic aerosol formation from
456   oxidation of aromatics in the absence of NOx, Atmospheric Environment, 41, 7603-7613,
457   10.1016/j.atmosenv.2007.05.034, 2007.
458 Casale, M. T., Richman, A. R., Elrod, M. J., Garland, R. M., Beaver, M. R., and Tolbert, M. A.: Kinetics of
459   acid-catalyzed aldol condensation reactions of aliphatic aldehydes, Atmospheric Environment, 41, 6212-
460   6224, 10.1016/j.atmosenv.2007.04.002, 2007.
461 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system H+−NH4+−SO42-
462   −NO3−H2O at tropospheric temperatures, Journal of physical Chemistry A, 102, 2137-2154,
463   10.1021/jp973042r, 1998.
464 Cocker, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas-particle
465   partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems,
466   Atmospheric Environment, 35, 6073-6085, 10.1016/s1352-2310(01)00405-8, 2001.
467 De Haan, D. O., Corrigan, A. L., Tolbert, M. A., Jimenez, J. L., Wood, S. E., and Turley, J. J.: Secondary
468   organic aerosol formation by self-reactions of methylglyoxal and glyoxal in evaporating droplets,
469   Environmental Science & Technology, 43, 8184-8190, 10.1021/es902152t, 2009.

470 De Haan, D. O., Hawkins, L. N., Kononenko, J. A., Turley, J. J., Corrigan, A. L., Tolbert, M. A., and Jimenez,
471   J. L.: Formation of Nitrogen-Containing Oligomers by Methylglyoxal and Amines in Simulated Evaporating
472   Cloud Droplets, Environmental Science & Technology, 45, 984-991, 10.1021/es102933x, 2011.
473 Denkenberger, K. A., Moffet, R. C., Holecek, J. C., Rebotier, T. P., and Prather, K. A.: Real-time, single-
474   particle measurements of oligomers in aged ambient aerosol particles, Environmental Science & Technology,
475   41, 5439-5446, 10.1021/es070329l, 2007.
476 Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M. R., Gascho, A., Weingartner, E., Prevot, A.
477   S. H., Verheggen, B., and Baltensperger, U.: Laboratory observation of oligomers in the aerosol from
478   isoprene/NOx photooxidation, Geophysical Research Letters, 33, 1-5, 10.1029/2006GL026523, 2006.
479 Drozd, G. T., and McNeill, V. F.: Organic matrix effects on the formation of light-absorbing compounds from
480   alpha-dicarbonyls in aqueous salt solution, Environmental Science-Processes & Impacts, 16, 741-747,
481   10.1039/c3em00579h, 2014.
482 Edney, E. O., Driscoll, D. J., Speer, R. E., Weathers, W. S., Kleindienst, T. E., Li, W., and Smith, D. F.: Impact
483   of aerosol liquid water on secondary organic aerosol yields of irradiated toluene/propylene/NOx/(NH4)(2)
484   SO4/air mixtures, Atmospheric Environment, 34, 3907-3919, 10.1016/s1352-2310(00)00174-6, 2000.
485 Fick, J., Pommer, L., Nilsson, C., and Andersson, B.: Effect of OH radicals, relative humidity, and time on the
486   composition of the products formed in the ozonolysis of alpha-pinene, Atmospheric Environment, 37, 4087-
487   4096, 10.1016/s1352-2310(03)00522-3, 2003.
488 Gao, S., Keywood, M., Ng, N. L., Surratt, J., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J.
489   H.: Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of
490   cycloalkenes and alpha-pinene, Journal of Physical Chemistry A, 108, 10147-10164, 10.1021/jp047466e,
491   2004.
492 Garland, R. M., Elrod, M. J., Kincaid, K., Beaver, M. R., Jimenez, J. L., and Tolbert, M. A.: Acid-catalyzed
493   reactions of hexanal on sulfuric acid particles: Identification of reaction products, Atmospheric Environment,
494   40, 6863-6878, 10.1016/j.atmosenv.2006.07.009, 2006.
495 Gee, I. L., and Sollars, C. J.: Ambient air levels of volatile organic compounds in Latin American and Asian
496   cities, Chemosphere, 36, 2497-2506, 10.1016/S0045-6535(97)10217-X, 1998.
497 Gutbrod, R., Schindler, R. N., Kraka, E., and Cremer, D.: Formation of OH radicals in the gas phase ozonolysis
498   of alkenes: the unexpected role of carbonyl oxides, Chemical Physics Letters, 252, 221-229, 10.1016/0009-
499   2614(96)00126-1, 1996.
500 Hall, W. A., and Johnston, M. V.: Oligomer Formation Pathways in Secondary Organic Aerosol from MS and
501   MS/MS Measurements with High Mass Accuracy and Resolving Power, Journal of the American Society
502   for Mass Spectrometry, 23, 1097-1108, 10.1007/s13361-012-0362-6, 2012.
503 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue,
504   N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M.,
505   Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A.,
506   Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and
507   impact of secondary organic aerosol: current and emerging issues, Atmospheric Chemistry and Physics, 9,
508   5155-5236, 10.5194/acp-9-5155-2009, 2009.
509 Hamilton, J. F., Lewis, A. C., Bloss, C., Wagner, V., Henderson, A. P., Golding, B. T., Wirtz, K., Martin-
510   Reviejo, M., and Pilling, M. J.: Measurements of photo-oxidation products from the reaction of a series of
511   alkyl-benzenes with hydroxyl radicals during EXACT using comprehensive gas chromatography,
512   Atmospheric Chemistry and Physics, 3, 1999-2014, 10.5194/acp-3-1999-2003, 2003.
513 Hamilton, J. F., Lewis, A. C., Reynolds, J. C., Carpenter, L. J., and Lubben, A.: Investigating the composition
514   of organic aerosol resulting from cyclohexene ozonolysis: low molecular weight and heterogeneous reaction
515   products, Atmospheric Chemistry and Physics, 6, 4973-4984, 2006.
516 Hasson, A. S., Orzechowska, G., and Paulson, S. E.: Production of stabilized Criegee intermediates and
517   peroxides in the gas phase ozonolysis of alkenes 1. Ethene, trans-2-butene, and 2,3-dimethyl-2-butene,
518   Journal of Geophysical Research-Atmospheres, 106, 34131-34142, 10.1029/2001jd000597, 2001.
519 Hastings, W. P., Koehler, C. A., Bailey, E. L., and De Haan, D. O.: Secondary organic aerosol formation by
520   glyoxal hydration and oligomer formation: Humidity effects and equilibrium shifts during analysis,
521   Environmental Science & Technology, 39, 8728-8735, 10.1021/es050446l, 2005.
522 Healy, R. M., Wenger, J. C., Metzger, A., Duplissy, J., Kalberer, M., and Dommen, J.: Gas/particle partitioning
523   of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene, Atmospheric Chemistry and
524   Physics, 8, 3215-3230, 10.5194/acp-8-3215-2008, 2008.
525 Heaton, K. J., Dreyfus, M. A., Wang, S., and Johnston, M. V.: Oligomers in the early stage of biogenic
526   secondary organic aerosol formation and growth, Environmental Science & Technology, 41, 6129-6136,
527   10.1021/es070314n, 2007.
528 Hennigan, C. J., Bergin, M. H., Dibb, J. E., and Weber, R. J.: Enhanced secondary organic aerosol formation
529   due to water uptake by fine particles, Geophysical Research Letters, 35, 5, 10.1029/2008gl035046, 2008.

530 Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric
531   aqueous-phase chemistry: Kinetics, mechanisms, and its coupling to a changing gas phase, Chemical
532   Reviews, 115, 4259-4334, 10.1021/cr500447k, 2015.
533 Holmes, B. J., and Petrucci, G. A.: Water-soluble oligomer formation from acid-catalyzed reactions of
534   levoglucosan in proxies of atmospheric aqueous aerosols, Environmental Science & Technology, 40, 4983-
535   4989, 10.1021/es060646c, 2006.
536 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
537   composition of gas and particle-phase products of OH-initiated oxidation of 1,3,5-trimethylbenzene,
538   Atmospheric Pollution Research, 5, 73-78, 10.5094/APR.2014.009, 2014.
539 Huang, M. Q., Lin, Y. H., Huang, X. Y., Liu, X. Q., Guo, X. Y., Hu, C. J., Zhao, W. X., Gu, X. J., Fang, L.,
540   and Zhang, W. J.: Experimental study of particulate products for aging of 1,3,5-trimethylbenzene secondary
541   organic aerosol, Atmospheric Pollution Research, 6, 209-219, 10.5094/APR.2015.025, 2015.
542 Iinuma, Y., Böge, O., Gnauk, T., and Herrmann, H.: Aerosol-chamber study of the a-pinene/O3 reaction:
543   influence of particle acidity on aerosol yields and products, Atmospheric Environment, 38, 761-773,
544   10.1016/j.atmosenv.2003.10.015, 2004.
545 Jang, M., Lee, S., and Kamens, R. M.: Organic aerosol growth by acid-catalyzed heterogeneous reactions of
546   octanal in a flow reactor, Atmospheric Environment, 37, 2125-2138, 10.1016/s1352-2310(03)00077-3, 2003.
547 Jang, M. S., and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous reactions of
548   aldehydes in the presence of a sulfuric acid aerosol catalyst, Environmental Science & Technology, 35, 4758-
549   4766, 10.1021/es010790s, 2001.
550 Kahnt, A., Iinuma, Y., Böge, O., Mutzel, A., and Herrmann, H.: Denuder sampling techniques for the
551   determination of gas-phase carbonyl compounds: A comparison and characterisation of in situ and ex situ
552   derivatisation methods, Journal of Chromatography B, 879, 1402-1411, 10.1016/j.jchromb.2011.02.028,
553   2011.
554 Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner,
555   E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of polymers as major components of
556   atmospheric organic aerosols, Science, 303, 1659-1662, 10.1126/science.1092185, 2004.
557 Kalberer, M., Sax, M., and Samburova, V.: Molecular size evolution of oligomers in organic aerosols collected
558   in urban atmospheres and generated in a smog chamber, Environmental Science & Technology, 40, 5917-
559   5922, 10.1021/es0525760, 2006.
560 Khoder, M. I.: Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo, Atmospheric
561   Environment, 41, 554-566, 10.1016/j.atmosenv.2006.08.051, 2007.
562 Kleindienst, T. E., Smith, D. F., Li, W., Edney, E. O., Driscoll, D. J., Speer, R. E., and Weathers, W. S.:
563   Secondary organic aerosol formation from the oxidation of aromatic hydrocarbons in the presence of dry
564   submicron ammonium sulfate aerosol, Atmospheric Environment, 33, 3669-3681, 10.1016/S1352-
565   2310(99)00121-1, 1999.
566 Krizner, H. E., De Haan, D. O., and Kua, J.: Thermodynamics and Kinetics of Methylglyoxal Dimer
567   Formation: A Computational Study, Journal of Physical Chemistry A, 113, 6994-7001, 10.1021/jp903213k,
568   2009.
569 Kua, J., Galloway, M. M., Millage, K. D., Avila, J. E., and De Haan, D. O.: Glycolaldehyde Monomer and
570   Oligomer Equilibria in Aqueous Solution: Comparing Computational Chemistry and NMR Data, Journal of
571   Physical Chemistry A, 117, 2997-3008, 10.1021/jp312202j, 2013.
572 Kundu, S., Fisseha, R., Putman, A. L., Rahn, T. A., and Mazzoleni, L. R.: High molecular weight SOA
573   formation during limonene ozonolysis: insights from ultrahigh-resolution FT-ICR mass spectrometry
574   characterization, Atmospheric Chemistry and Physics, 12, 5523-5536, 10.5194/acp-12-5523-2012, 2012.
575 Liggio, J., Li, S. M., and McLaren, R.: Heterogeneous reactions of glyoxal on particulate matter: Identification
576   of acetals and sulfate esters, Environmental Science & Technology, 39, 1532-1541, 10.1021/es048375y,
577   2005.
578 Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in
579   secondary organic aerosol (SOA) formation, Atmospheric Chemistry and Physics, 10, 10521-10539,
580   10.5194/acp-10-10521-2010, 2010.
581 Lim, Y. B., Tan, Y., and Turpin, B. J.: Chemical insights, explicit chemistry, and yields of secondary organic
582   aerosol from OH radical oxidation of methylglyoxal and glyoxal in the aqueous phase, Atmospheric
583   Chemistry and Physics, 13, 8651-8667, 10.5194/acp-13-8651-2013, 2013.
584 Lim, Y. B., and Turpin, B. J.: Laboratory evidence of organic peroxide and peroxyhemiacetal formation in the
585   aqueous phase and implications for aqueous OH, Atmospheric Chemistry and Physics, 15, 12867-12877,
586   10.5194/acp-15-12867-2015, 2015.
587 Liu, Y., Shao, M., Lu, S. H., Liao, C. C., Wang, J. L., and Chen, G.: Volatile organic compound (VOC)
588   measurements in the pearl river delta (PRD) region, China, Atmospheric Chemistry and Physics, 8, 1531-
589   1545, 2008.

590   Loeffler, K. W., Koehler, C. A., Paul, N. M., and De Haan, D. O.: Oligomer formation in evaporating aqueous
591   glyoxal and methyl glyoxal solutions, Environmental Science & Technology, 40, 6318-6323,
592   10.1021/es060810w, 2006.
593   Metzger, A., Dommen, J., Gaeggeler, K., Duplissy, J., Prevot, A. S. H., Kleffmann, J., Elshorbany, Y.,
594   Wisthaler, A., and Baltensperger, U.: Evaluation of 1,3,5 trimethylbenzene degradation in the detailed
595   tropospheric chemistry mechanism, MCMv3.1, using environmental chamber data, Atmospheric Chemistry
596   and Physics, 8, 6453-6468, 10.5194/acp-8-6453-2008, 2008.
597   Müller, L., Reinnig, M. C., Warnke, J., and Hoffmann, T.: Unambiguous identification of esters as oligomers
598   in secondary organic aerosol formed from cyclohexene and cyclohexene/alpha-pinene ozonolysis,
599   Atmospheric Chemistry and Physics, 8, 1423-1433, 2008.
600   Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U.: Analysis
601   of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber
602   experiments, Atmospheric Chemistry and Physics, 12, 829-843, 10.5194/acp-12-829-2012, 2012.
603   Mutzel, A., Rodigast, M., Iinuma, Y., Boge, O., and Herrmann, H.: Monoterpene SOA - Contribution of first-
604   generation oxidation products to formation and chemical composition, Atmospheric Environment, 130, 136-
605   144, 10.1016/j.atmosenv.2015.10.080, 2016.
606   Nemet, I., Vikic-Topic, D., and Varga-Defterdarovic, L.: Spectroscopic studies of methylglyoxal in water and
607   dimethylsulfoxide, Bioorganic Chemistry, 32, 560-570, 10.1016/j.bioorg.2004.05.008, 2004.
608   Nguyen, T. B., Roach, P. J., Laskin, J., Laskin, A., and Nizkorodov, S. A.: Effect of humidity on the
609   composition of isoprene photooxidation secondary organic aerosol, Atmospheric Chemistry and Physics, 11,
610   6931-6944, 10.5194/acp-11-6931-2011, 2011.
611   Nishino, N., Arey, J., and Atkinson, R.: Formation yields of glyoxal and methylglyoxal from the gas-phase
612   OH radical-initiated reactions of toluene, xylenes, and trimethylbenzenes as a function of NO_2 concentration,
613   Journal of Physical Chemistry A, 114, 10140-10147, 10.1021/jp105112h, 2010.
614   Noziere, B., and Esteve, W.: Organic reactions increasing the absorption index of atmospheric sulfuric acid
615   aerosols, Geophysical Research Letters, 32, 5, 10.1029/2004gl021942, 2005.
616   Noziere, B., Dziedzic, P., and Cordova, A.: Formation of secondary light-absorbing "fulvic-like" oligomers:
617   A common process in aqueous and ionic atmospheric particles?, Geophysical Research Letters, 34, 1-5,
618   10.1029/2007GL031300, 2007.
619   Noziere, B., and Cordova, A.: A kinetic and mechanistic study of the amino acid catalyzed aldol condensation
620   of acetaldehyde in aqueous and salt solutions, Journal of Physical Chemistry A, 112, 2827-2837,
621   10.1021/jp7096845, 2008.
622   Noziere, B., Dziedzic, P., and Cordova, A.: Inorganic ammonium salts and carbonate salts are efficient
623   catalysts for aldol condensation in atmospheric aerosols, Physical Chemistry Chemical Physics, 12, 3864-
624   3872, 10.1039/B924443C, 2010.
625   Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Aromatics,
626   reformulated gasoline, and atmospheric organic aerosol formation, Environmental Science & Technology,
627   31, 1890-1897, 10.1021/es9605351, 1997.
628   Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.:
629   Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733,
630   10.1126/science.1172910, 2009.
631   Paulsen, D., Dommen, J., Kalberer, M., Prevot, A. S. H., Richter, R., Sax, M., Steinbacher, M., Weingartner,
632   E., and Baltensperger, U.: Secondary organic aerosol formation by irradiation of 1,3,5-trimethylbenzene-
633   NOx-H2O in a new reaction chamber for atmospheric chemistry and physics, Environmental Science &
634   Technology, 39, 2668-2678, 10.1021/es0489137, 2005.
635   Reinhardt, A., Emmenegger, C., Gerrits, B., Panse, C., Dommen, J., Baltensperger, U., Zenobi, R., and
636   Kalberer, M.: Ultrahigh mass resolution and accurate mass measurements as a tool to characterize oligomers
637   in secondary organic aerosols, Analytical Chemistry, 79, 4074-4082, 10.1021/ac062425v, 2007.
638   Rickard, A. R., Wyche, K. P., Metzger, A., Monks, P. S., Ellis, A. M., Dommen, J., Baltensperger, U., Jenkin,
639   M. E., and Pilling, M. J.: Gas phase precursors to anthropogenic secondary organic aerosol: Using the Master
640   Chemical Mechanism to probe detailed observations of 1,3,5-trimethylbenzene photo-oxidation,
641   Atmospheric Environment, 44, 5423-5433, 10.1016/j.atmosenv.2009.09.043, 2010.
642   Rincon, A. G., Guzman, M. I., Hoffmann, M. R., and Colussi, A. J.: Optical absorptivity versus molecular
643   composition of model organic aerosol matter, Journal of Physical Chemistry A, 113, 10512-10520,
644   10.1021/jp904644n, 2009.
645   Rodigast, M., Mutzel, A., Iinuma, Y., Haferkorn, S., and Herrmann, H.: Characterisation and optimisation of
646   a sample preparation method for the detection and quantification of atmospherically relevant carbonyl
647   compounds in aqueous medium, Atmospheric Measurement Techniques, 8, 2409-2416, 10.5194/amt-8-
648   2409-2015, 2015.

649   Sadezky, A., Chaimbault, P., Mellouki, A., Rompp, A., Winterhalter, R., Le Bras, G., and Moortgat, G. K.:
650   Formation of secondary organic aerosol and oligomers from the ozonolysis of enol ethers, Atmospheric
651   Chemistry and Physics, 6, 5009-5024, 2006.
652   Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed
653   by methylglyoxal in aqueous aerosol mimics, Atmospheric Chemistry and Physics, 10, 997-1016, 2010.
654   Sato, K., Takami, A., Kato, Y., Seta, T., Fujitani, Y., Hikida, T., Shimono, A., and Imamura, T.: AMS and
655   LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of
656   NOx: effects of chemical structure on SOA aging, Atmospheric Chemistry and Physics, 12, 4667-4682,
657   10.5194/acp-12-4667-2012, 2012.
658   Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., Pedernera, D. A., Onasch, T.
659   B., Laaksonen, A., Davidovits, P., Worsnop, D. R., and Virtanen, A.: Humidity-dependent phase state of
660   SOA particles from biogenic and anthropogenic precursors, Atmospheric Chemistry and Physics, 12, 7517-
661   7529, 10.5194/acp-12-7517-2012, 2012.
662   Saxena, P., and Hildemann, L. M.: Water-soluble organics in atmospheric particles: A critical review of the
663   literature and application of thermodynamics to identify candidate compounds, Journal of Atmospheric
664   Chemistry, 24, 57-109, 10.1007/bf00053823, 1996.
665   Schaefer, T., van Pinxteren, D., and Herrmann, H.: Multiphase chemistry of glyoxal: Revised kinetics of the
666   alkyl radical reaction with molecular oxygen and the reaction of Glyoxal with OH, NO3, and SO4- in aqueous
667   solution, Environmental Science & Technology, 49, 343-350, 10.1021/es505860s, 2015.
668   Schwier, A. N., Sareen, N., Mitroo, D., Shapiro, E. L., and McNeill, V. F.: Glyoxal-Methylglyoxal Cross-
669   Reactions in Secondary Organic Aerosol Formation, Environmental Science & Technology, 44, 6174-6182,
670   10.1021/es101225q, 2010.
671   Sedehi, N., Takano, H., Blasic, V. A., Sullivan, K. A., and De Haan, D. O.: Temperature- and pH-dependent
672   aqueous-phase kinetics of the reactions of glyoxal and methylglyoxal with atmospheric amines and
673   ammonium sulfate, Atmospheric Environment, 77, 656-663, 10.1016/j.atmosenv.2013.05.070, 2013.
674   Seinfeld, J. H., Erdakos, G. B., Asher, W. E., and Pankow, J. F.: Modeling the formation of secondary organic
675   aerosol (SOA). 2. The predicted effects of relative humidity on aerosol formation in the a-pinene-, b-pinene-,
676   sabinene-, D3-carene-, and cyclohexene-ozone systems (vol 35, pg 1806, 2001), Environmental Science &
677   Technology, 35, 1806-1817, 10.1021/es011025g, 2001.
678   Smith, D. F., Kleindienst, T. E., and McIver, C. D.: Primary product distributions from the reaction of OH with
679   m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene, Journal of Atmospheric Chemistry, 34, 339-364,
680   10.1023/A:1006277328628, 1999.
681   Song, C., Gyawali, M., Zaveri, R. A., Shilling, J. E., and Arnott, W. P.: Light absorption by secondary organic
682   aerosol from alpha-pinene: Effects of oxidants, seed aerosol acidity, and relative humidity, Journal of
683   Geophysical Research-Atmospheres, 118, 9, 10.1002/jgrd.50767, 2013.
684   Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-
685   phase reactions of phenolic compounds based on high resolution mass spectrometry, Atmospheric Chemistry
686   and Physics, 10, 4809-4822, 10.5194/acp-10-4809-2010, 2010.
687   Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R.,
688   Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of
689   secondary organic aerosol formed from the photooxidation of isoprene, Journal of Physical Chemistry A,
690   110, 9665-9690, 10.1021/jp061734m, 2006.
691   Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg,
692   J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in
693   secondary organic aerosol, Environmental Science & Technology, 41, 517-527, 10.1021/es062081q, 2007.
694   Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan,
695   R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol
696   formation from isoprene, Proceedings of the National Academy of Sciences of the United States of America,
697   107, 6640-6645, 10.1073/pnas.0911114107, 2010.
698   Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M.,
699   Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in
700   secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas
701   chromatography/ion trap mass spectrometry, Journal of Mass Spectrometry, 42, 101-116, 10.1002/jms.1146,
702   2007.
703   Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: SOA from methylglyoxal in clouds and wet
704   aerosols: Measurement and prediction of key products, Atmospheric Environment, 44, 5218-5226,
705   10.1016/j.atmosenv.2010.08.045, 2010.
706   Tan, Y., Lim, Y. B., Altieri, K. E., Seitzinger, S. P., and Turpin, B. J.: Mechanisms leading to oligomers and
707   SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal,
708   Atmospheric Chemistry and Physics, 12, 801-813, 10.5194/acp-12-801-2012, 2012.

709 Tilgner, A., and Herrmann, H.: Radical-driven carbonyl-to-acid conversion and acid degradation in
710   tropospheric aqueous systems studied by CAPRAM, Atmospheric Environment, 44, 5415-5422,
711   10.1016/j.atmosenv.2010.07.050, 2010.
712 Tolocka, M. P., Jang, M., Ginter, J. M., Cox, F. J., Kamens, R. M., and Johnston, M. V.: Formation of
713   oligomers in secondary organic aerosol, Environmental Science & Technology, 38, 1428-1434,
714   10.1021/es035030r, 2004.
715 Tuazon, E. C., MacLeod, H., Atkinson, R., and Carter, W. P. L.: .alpha.-dicarbonyl yields from the NOx-air
716   photooxidations of a series of aromatic hydrocarbons in air, Environmental Science & Technology, 20, 383-
717   387, 10.1021/es00146a010, 1986.
718 Waxman, E. M., Elm, J., Kurten, T., Mikkelsen, K. V., Ziemann, P. J., and Vokamer, R.: Glyoxal and
719   Methylglyoxal Setschenow Salting Constants in Sulfate, Nitrate, and Chloride Solutions: Measurements and
720   Gibbs Energies, Environmental Science & Technology, 49, 11500-11508, 10.1021/acs.est.5b02782, 2015.
721 Wyche, K. P., Monks, P. S., Ellis, A. M., Cordell, R. L., Parker, A. E., Whyte, C., Metzger, A., Dommen, J.,
722   Duplissy, J., Prevot, A. S. H., Baltensperger, U., Rickard, A. R., and Wulfert, F.: Gas phase precursors to
723   anthropogenic secondary organic aerosol: detailed observations of 1,3,5-trimethylbenzene photooxidation,
724   Atmospheric Chemistry and Physics, 9, 635-665, 10.5194/acp-9-635/2009/, 2009.
725 Yasmeen, F., Sauret, N., Gal, J. F., Maria, P. C., Massi, L., Maenhaut, W., and Claeys, M.: Characterization
726   of oligomers from methylglyoxal under dark conditions: a pathway to produce secondary organic aerosol
727   through cloud processing during nighttime, Atmospheric Chemistry and Physics, 10, 3803-3812,
728   10.5194/acp-10-3803-2010, 2010.
729 Yu, J. Z., Jeffries, H. E., and Sexton, K. G.: Atmospheric photooxidation of alkylbenzenes -I. Carbonyl product
730   analyses, Atmospheric Environment, 31, 2261-2280, 10.1016/S1352-2310(97)00011-3, 1997.
731 Zahardis, J., LaFranchi, B. W., and Petrucci, G. A.: Photoelectron resonance capture ionization-aerosol mass
732   spectrometry of the ozonolysis products of oleic acid particles: Direct measure of higher molecular weight
733   oxygenates, Journal of Geophysical Research-Atmospheres, 110, 10, 10.1029/2004jd005336, 2005.
734 Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M. C., Gelencser, A., Kiss, G., Krivacsy, Z., Molnar, A.,
735   Meszaros, E., Hansson, H. C., Rosman, K., and Zebuhr, Y.: Inorganic, organic and macromolecular
736   components of fine aerosol in different areas of Europe in relation to their water solubility, Atmospheric
737   Environment, 33, 2733-2743, 10.1016/s1352-2310(98)00362-8, 1999.
738 Zhao, J., Levitt, N. P., Zhang, R. Y., and Chen, J. M.: Heterogeneous reactions of methylglyoxal in acidic
739   media: Implications for secondary organic aerosol formation, Environmental Science & Technology, 40,
740   7682-7687, 10.1021/es060610k, 2006.
741 Ziemann, P. J.: Atmpsheric chmeistry Phase matters for aerosols, Nature, 467, 797-798, 2010.
742 Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and phase
743   stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols,
744   Atmospheric Chemistry and Physics, 10, 7795-7820, 10.5194/acp-10-7795-2010, 2010.

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$_4$HSO$_4$	≈ 0	≈ 137	57.2	19.7	7.00
#2	78 mmol L^{-1} NH$_4$HSO$_4$	50	≈ 133	55.2	11.3	4.12
#3	78 mmol L^{-1} NH$_4$HSO$_4$	75	≈ 134	56.2	14.2	5.14
#4	60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/ 0.4 mmol L^{-1} H$_2$SO$_4$	≈ 0	≈ 132	56.2	18.1	6.55
#5	60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/ 0.4 mmol L^{-1} H$_2$SO$_4$	50	≈ 135	56.5	11.7	4.21
#6	60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/ 0.4 mmol L^{-1} H$_2$SO$_4$	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.

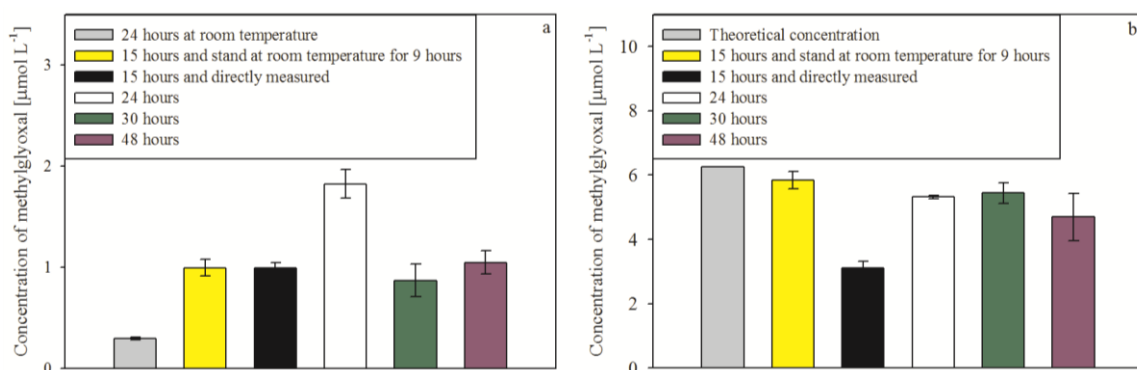| Parameter	Range	Filter of experiment
Heating time	15, **24**, 30, 48 hours	#3
pH	**1**, 3, 5, 7	#2
Heating temperature	50, **100** °C	#2

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).
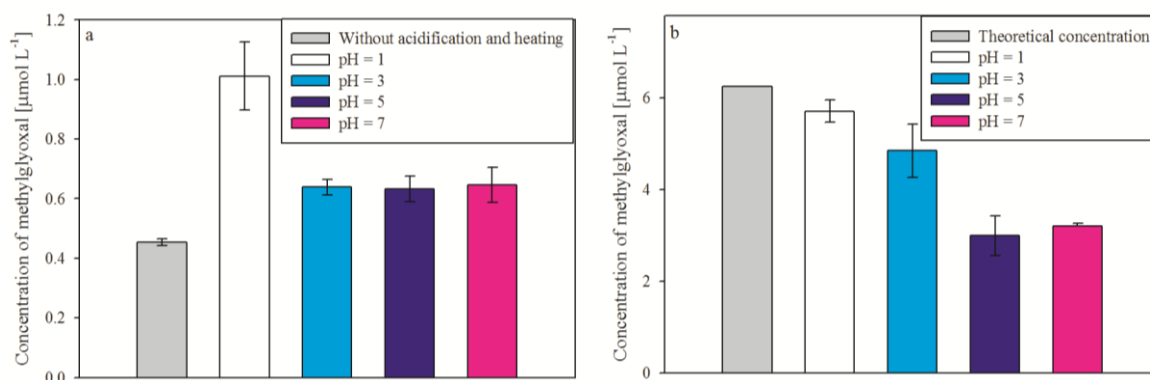

Figure 2: Influence of pH on the detected methylglyoxal concentration in filter samples (a) and the methylglyoxal standard solution (b).
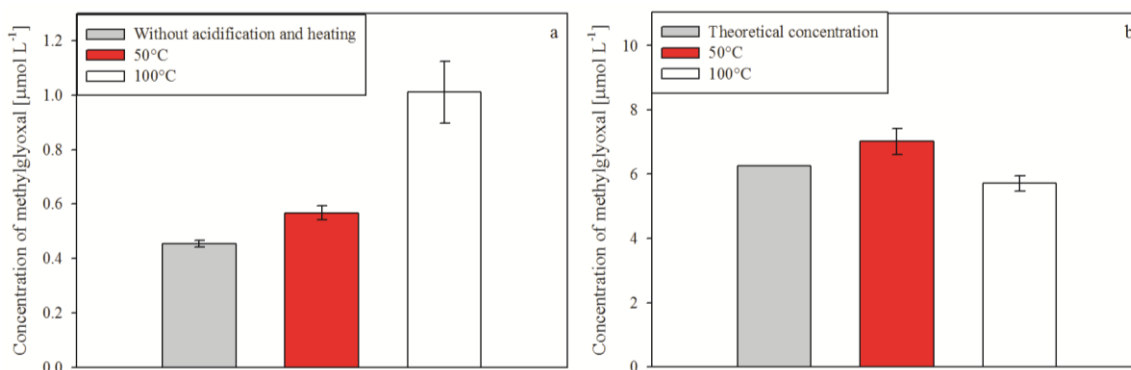

Figure 3: Influence of the heating temperature on the detected methylglyoxal concentration in filter samples (a) and the standard solution (b).

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

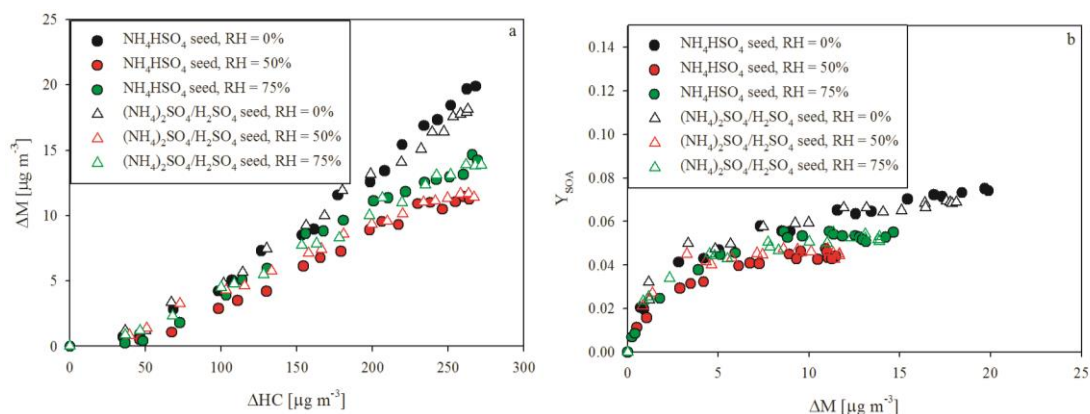| SOA yield Y_{SOA} [%]	Reference
2.81 - 7.91	Cocker et al., 2001
4.5 – 8.34	Healy et al., 2008
$2.5 \pm 0.1 - 15.6 \pm 1.0$	Sato et al., 2012
3.1	Odum et al., 1997
0.41 ± 0.1	Kleindienst et al., 1999
0.29 – 6.36	Wyche et al., 2009
4.7 ± 0.7	Paulsen et al., 2005
$7.1 \pm 0.3 - 13.8 \pm 0.6$	Cao and Jang, 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$_4$HSO$_4$	≈ 0	-[b]	-[b]
78 mmol L^{-1} NH$_4$HSO$_4$	50	0.1	6.66×10^{-6}
78 mmol L^{-1} NH$_4$HSO$_4$	75	1.2	12.29×10^{-6}
60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/0.4 mmol L^{-1} H$_2$SO$_4$	≈ 0	-[b]	-[b]
60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/0.4 mmol L^{-1} H$_2$SO$_4$	50	4.0	4.25×10^{-6}
60 mmol L^{-1} (NH$_4$)$_2$SO$_4$/0.4 mmol L^{-1} H$_2$SO$_4$	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.
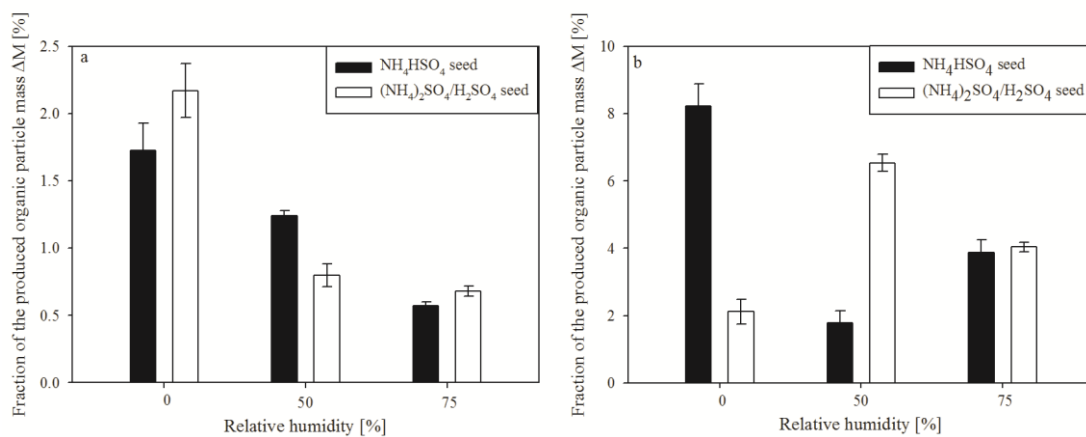

Figure 5: Contribution of methylglyoxal (a) and their heat-decomposable oligomers (b) to the produced organic particle mass (ΔM) with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles under variation of the relative humidity.