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

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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 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-volatility 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 any 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 m³ 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. Notably, 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 including also singly and doubly

148   hydrated methylglyoxal, which can be hydrolysed at room temperature into monomers. The filters were

149   prepared according to the method described by Rodigast et al. (2015), thus 300 µL of an aqueous PFBHA

150   solution (5 mg mL^{-1}) was added to the filter extracts. After a derivatisation time of 24 hours at room

151   temperature the derivatised methylglyoxal monomers were extracted.

152

153   2.3.3 Extraction for GC/MS analysis

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

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

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

157   to ensure reliable GC/MS signals.

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

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

160

161   2.4 Instrumentation

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

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

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

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

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

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

168   of 36 minutes.

169

170   **3. Results**

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

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

173   higher inlet temperatures (≥ 120°C) which caused problems for oligomer quantification. In the present study a

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

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

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

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

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

179

180 **3.1 Method development**

181 *Influence of heating time*

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

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

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

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

186 15 – 48 hours. The results were compared to the unheated aqueous filter extracts (extract 2) to determine the

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

188 Additionally, a 6.25 µmol L^{-1} standard solution of methylglyoxal was acidified and heated for different times

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

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

191 concentration was about six times higher (c = 1.82 ± 0.14 µmol L^{-1}) in comparison to the unheated filter extract

192 (c = 0.29 ± 0.01 µmol L^{-1}). To exclude that the higher methylglyoxal concentrations were only a result of a

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

194 (Fig. 1b). A methylglyoxal concentration of c = 5.32 ± 0.05 µmol L^{-1} was found, which corresponds to a

195 recovery of ≈ 85%. Thus, an effect of the heating process on the derivatisation can be excluded indicating that

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

197 monomers.

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

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

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

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

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

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

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

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

206 To probe this hypothesis a 6.25 µmol L^{-1} methylglyoxal standard was heated for 15 hours and

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

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

209 sample (3.11 ± 0.20 µmol L^{-1}) compared to the sample after 9 hours at room temperature

210 (5.84 ± 0.27 µmol L^{-1}). Thus, it can be concluded that a derivatisation time of 24 hours is needed for a complete

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

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

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

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

215 k = 5 × 10^{-6} M^{-1} minutes^{-1} for ammonium ion catalysed and k ≤ 1 × 10^{-3} M^{-1} minutes^{-1} for H_3O^+ catalysed aldol

216 reaction (Sareen et al., 2010). Naturally, both of these ions are present in the aqueous filter extract. Despite the
217 oligomerisation of methylglyoxal monomers during the 9 hours at room temperature, the derivatisation
218 proceeds as well during this time leading to higher methylglyoxal concentrations in sample b than in sample
219 a, which was directly measured after 15 hours heating (Fig. 1a).

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

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

228

229 *Influence of pH*

230 The effect of the pH was examined with PTFE filters, which were sampled after OH-radical oxidation of 1,3,5-
231 TMB at RH = 50% in the presence of NH_4HSO_4 particles (experiment #2). The pH was varied between pH =
232 1 and pH = 7.

233 As it can be seen in Fig. 2a the highest methylglyoxal concentration can be found at pH = 1. The methylglyoxal
234 concentration was about two times higher at pH = 1 (c = 1.01 ± 0.11 µmol L^{-1}) compared to the filter extract,
235 which was neither heated nor acidified (c = 0.45 ± 0.01 µmol L^{-1}). An increasing pH leads to a lower
236 methylglyoxal concentration, which can be observed for filter samples (Fig. 2a) as well as for the
237 methylglyoxal standard solution (Fig. 2b). As this was observed for both types of samples it appears that the
238 pH influences the derivatisation and/or the oligomer decomposition. No influence of the pH on the PFBHA
239 derivatisation reaction was reported by Rodigast et al. (2015) indicating the effect of the pH is connected to
240 thermal decomposition of the heat-decomposable oligomeric compounds. In summary, based on these results
241 pH = 1 was used.

242

243 *Influence of heating temperature*

244 The effect of the heating temperature was examined with filter samples of experiment #2. The heating
245 temperature was varied between 50°C and 100°C and the filter extracts were heated for 24 hours at pH = 1. A
246 temperature above 100°C cannot be used to avoid evaporation of water and/or target compounds. Fig. 3a shows
247 the influence of the temperature on the decomposition of the heat-decomposable methylglyoxal oligomers into
248 monomers. Higher concentration of methylglyoxal can be detected with higher temperature. The results
249 illustrated in Fig. 3a indicate that a higher temperature than 50°C is needed to decompose the oligomeric
250 compounds. In comparison to the filter, which was neither acidified nor heated, the concentration increased by
251 a factor of two if the extract was heated to 100°C. Fig. 3b shows no significant influence of the temperature
252 on the methylglyoxal standard solution. Thus, an influence of the heating temperature on the derivatisation
253 procedure can be excluded.

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

256 methylglyoxal. According to the literature studies other carbonyl compounds can be expected as particle-phase

257 products, e.g., propionaldehyde (Cocker et al., 2001), glyoxal (Cocker et al., 2001; Huang et al., 2015), 2-

258 methyl-4-oxo-2-pentenal (Healy et al., 2008; Huang et al., 2014), glycolaldehyde (Cocker et al., 2001) and

259 3,5-dimethylbenzaldehyde (Huang et al., 2014). Noticeably, no carbonyl compounds other than methylglyoxal

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

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

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

263 relative humidity on the oligomer content.

264

265 **3.2 SOA yield and growth curves of 1,3,5-TMB oxidation**

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

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

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

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

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

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

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

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

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

275 chamber, which might possibly lead to an underestimation of the reported SOA yields. Y_{SOA} varied between 4

276 and 7% dependent on reaction conditions and is in good agreement to literature values.

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

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

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

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

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

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

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

284 1,3,5-TMB. Cao and Jang (2007) found also only a small influence of seed particle acidity on SOA formation.

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

286 an influence on the phase state of the particles which, in turn, has an effect on the partitioning of the compounds

287 into the particles as well as on particle-phase reactions (Ziemann, 2010; Saukko et al., 2012). The

288 deliquescence RH of $(NH_4)_2SO_4$ and NH_4HSO_4 seed particles are known from literature to be 79% and 39%,

289 respectively (Cziczo et al., 1997). Thus, pure NH_4HSO_4 seed particles are liquid at the applied RH values of

290 50% and 75% and solid at RH = 0% while $(NH_4)_2SO_4$ seed particles are solid over the whole RH range.

291 Nevertheless, in the present study the particles are a mixture of inorganic and partitioned organic compounds.

292 Organic compounds might change the phase state of the particles (Bertram et al., 2011) due to an influence on

293 the deliquescence point (Andrews and Larson, 1993; Lightstone et al., 2000) as well as the hygroscopic

294 behaviour of the particles (Lightstone et al., 2000; Prenni et al., 2003; Chen and Lee, 1999). Virtanen et al.,

295 2010 postulated that particles are in an amorphous solid state if oligomeric compounds are present in the

296   particles. Thus, it can be speculated that the particles in the present study containing a fraction of up to 8% of

297   oligomeric compounds might be in an amorphous solid phase state. It was assumed, that the further reactions

298   in the particle phase might be inhibited in solid particles (Saukko et al., 2012) thus, further oligomerisation or

299   other reactions might become less effective after a certain fraction of oligomers exist in the particles. In

300   addition, the partitioning of methylglyoxal monomers can be inhibited into solid particles (Saukko et al., 2012),

301   which then might also lead to lower oligomer fractions in SOA. Thus, it might be possible that the phase state

302   influences ΔM and the SOA yields. ΔM is the highest at RH = 0% (ΔM = 18.1 − 19.7 µg m^{-3}) whereas ΔM is

303   the lowest under humid conditions (RH = 50% and 75%, ΔM = 11.3 − 11.7 µg m^{-3} and 13.9 − 14.2 µg m^{-3}).

304   Due to the variation of RH in the aerosol chamber the liquid water content (LWC) of the particles is changing

305   (Table 5). The LWC was calculated using model II from the extended aerosol thermodynamic model (E-AIM;

306   Clegg et al., 1998). With increasing RH the LWC of the seed particle increases as well. The LWC of the seed

307   particles influences i) the partitioning of the compounds from the gas phase into the particle phase and ii) the

308   formation and/or further reaction in the particle phase (Zuend et al., 2010; Cocker et al., 2001; Seinfeld et al.,

309   2001; Fick et al., 2003). These two effects might influence the SOA formation under different relative

310   humidities.

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

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

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

314   Y_{SOA} values at elevated RH.

315   The influence of RH on SOA formation is controversial (Hennigan et al., 2008; Fick et al., 2003;

316   Edney et al., 2000; Saxena and Hildemann, 1996; Baker et al., 2001; Hasson et al., 2001, Cocker et al., 2001).

317   Edney et al. (2000) and Seinfeld et al. (2001) reported an enhanced SOA formation of hydrophilic compounds

318   under humid conditions and a lowered SOA formation of hydrophobic compounds. This is also supported by

319   Saxena and Hildemann (1996), which found an enhanced partitioning of organic compounds with several

320   hydroxyl groups at higher LWCs of the particles. This might lead to the conclusion that the OH-radical

321   oxidation of 1,3,5-TMB results in the formation of hydrophobic compounds which showed an enhanced

322   partitioning under dry conditions. Additionally, it can be speculated that the formation of oligomeric

323   compounds can be enhanced at lower RH values resulting in higher Y_{SOA} due to the increasing conversion of

324   the monomeric building blocks and their enhanced partitioning into the particle phase.

325

326   **3.3 Particulate methylglyoxal**

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

328   2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005;

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

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

331   phase between 0.7 and 2%.

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

333   in Fig. 5a, with resulting fractions between ≈ 0.6% and ≈ 2.2%. With increasing RH the fraction decreases for

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

335   2.17 ± 0.20% for NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$/H$_2$SO$_4$) and with (NH$_4$)$_2$SO$_4$/H$_2$SO$_4$ seed particles.

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

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

338 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

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

340 In comparison, Cocker et al., 2001 measured a particulate fraction of 0.72%.

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

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

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

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

345 Altieri et al., 2008).

346

347 **3.4 Heat-decomposable methylglyoxal oligomers**

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

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

350 decomposable methylglyoxal oligomers into monomers. Thus, the concentration of monomeric methylglyoxal

351 was determined prior and after thermal decomposition. The concentrations were converted into the fraction of

352 methylglyoxal oligomers of ΔM using the molar mass of methylglyoxal (Mw = 72.06 g mol^{-1}). An oligomer

353 fraction of ≈ 2 up to ≈ 8% was determined.

354   Fig. 5b shows the dependency of the detected heat-decomposable methylglyoxal oligomers on the

355 relative humidity with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles. In the presence of NH_4HSO_4 seed

356 particles the highest oligomer fraction (8.2 ± 0.7%) can be observed with RH = 0% whereas in the presence of

357 $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction is the lowest (2.1 ± 0.4%) under dry conditions

358 (RH = 0%). A possible explanation for the opposite trend of the oligomer fractions with RH between NH_4HSO_4

359 and $(NH_4)_2SO_4/H_2SO_4$ seed particles could be different oligomer formation mechanism caused by different

360 seed particle acidity. The type of accretion reaction might change with pH (Yasmeen et al., 2010). In Table 5

361 the pH of the seed particles was calculated with E-AIM. NH_4HSO_4 particles have pH = 0.1 and 1.2 at

362 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

363 pH = 4.2 at RH = 75%).

364   It was postulated by Yasmeen et al. (2010) that a lower pH (pH < 3.5) favor acetal/hemiacetal

365 formation whereas at high pH (pH = 4 - 5) aldol condensation are more relevant. This has been supported by

366 Sedehi et al. (2013) and Sareen et al. (2010).

367   Thus, in the presence of strong acidic NH_4HSO_4 seed particles acetal/hemiacetal formation might be

368 the favored oligomer formation mechanism. Oligomerisation via acetal/hemiacetal formation occurs under a

369 reversible water loss (Yasmeen et al., 2010). As higher RH values in the aerosol chamber LEAK leads to higher

370 LWCs of the seed particles (Table 5) the chemical equilibrium of the reaction shifts towards the precursor

371 compound resulting in a lower methylglyoxal oligomer fraction (Kalberer et al., 2004; Liggio et al., 2005). In

372 addition, the pH of NH_4HSO_4 particles decreases with decreasing RH (Table 5) thus acid-catalysed

373 acetal/hemiacetal formation might be enhanced under dry conditions due to a lower pH (Liggio et al., 2005).

374   In the presence of $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction increases with increasing

375 RH (Fig. 5b). As it was mentioned, aldol condensation can be assumed as the favored accretion reaction under

376 these conditions (Yasmeen et al., 2010). Aldol condensation includes as a first step aldol addition followed by
377 a loss of water. The loss of water is irreversible, thus the aldol condensation will not be inhibited with higher
378 LWC of the seed particles.

379   Other accretion reactions can contribute to the formation of heat-decomposable methylglyoxal
380 oligomers with $(NH_4)_2SO_4/H_2SO_4$ seed particles as well. Altieri et al. (2008) detected products formed through
381 acid-catalysed esterification at pH $\approx$ 4. This equilibrium reaction involves the reversible loss of water as it was
382 reported for acetal/hemiacetal formation (Lim et al., 2010). Thus, it can be expected that with higher LWCs
383 the contribution of esterification reactions to oligomer formation decreases due to the shift of the equilibrium
384 towards the monomers.

385   Imidazole formation was also postulated as possible oligomer-formation mechanism for
386 methylglyoxal (Sedehi et al., 2013; De Haan et al., 2011). It was found that imidazole formation is of minor
387 importance compared to aldol condensation (Sedehi et al., 2013). However, imidazole formation involves also
388 a reversible loss of water, thus it does not provide a feasible explanation for the higher oligomer fraction at
389 higher RH with $(NH_4)_2SO_4/H_2SO_4$ seed particles.

390   Radical – radical reactions are also postulated as a possible reaction pathway to form oligomers
391 (Schaefer et al., 2015; Lim et al., 2013; Rincon et al., 2009; Lim et al., 2010; Sun et al., 2010). Radical-radical
392 reactions of methylglyoxal might occur following the H - atom abstraction of methylglyoxal with OH radicals
393 and a subsequent recombination of the resulting alkyl radicals (as discussed for glyoxal in Schaefer et al.,
394 2015). The contribution of radical – radical reactions to oligomer formation is not well understood as
395 obviously, the reaction of alkyl radicals with oxygen tends to suppress this pathway. Nevertheless, it can be
396 expected, that with higher LWCs of the seed particles and thus with a higher reaction volume, the absolute
397 amount of methylglyoxal in the particle phase might increase, but not its particle-phase concentrations. For
398 aerosol particle systems, ionic strength effects (Herrmann et al., 2015) are able to influence the uptake of
399 methylglyoxal into the particle phase as well. Waxman et al. (2015) observed a salting-out effect for
400 methylglyoxal for all investigated seed particles at higher ionic strengths.

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

405   In summary, the present study provides a reliable quantification method for heat-decomposable
406 methylglyoxal oligomers formed by 1,3,5-TMB oxidation. The fraction of oligomeric substances formed solely
407 by methylglyoxal oligomerisation varied dependent on RH and seed particle acidity between 2 – 8%, which is
408 lower than the determined values by Kalberer et al. (2004) and Baltensperger et al. (2005) (varying between
409 50 and 80%). In the present study only heat-decomposable methylglyoxal oligomers were quantified, thus
410 there might be not heat-decomposable methylglyoxal oligomers or oligomers originating from other monomers
411 than methylglyoxal, which were not determined in the present study leading to lower oligomer fractions of ΔM
412 compared to the literature studies. The obtained data are not fully conclusive and literature studies are often
413 contradicting. Thus, more experiments are necessary to get a clearer picture about the influence of RH and
414 particle phase acidity on oligomer formation and to explain the non-linear relation between the oligomer
415 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 $\approx$ 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$_4$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**.
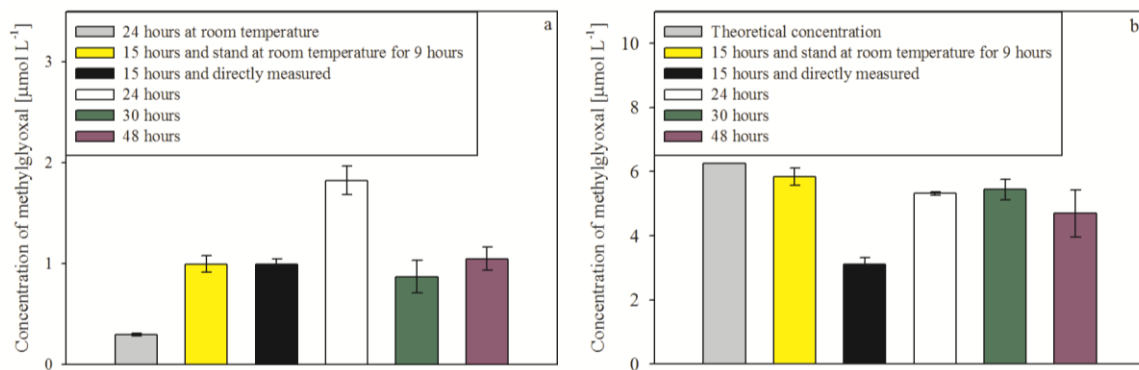
Figure 1: Influence of the heating time on the detected methylglyoxal concentrations in filter samples (a) and the methylglyoxal standard solution (b).
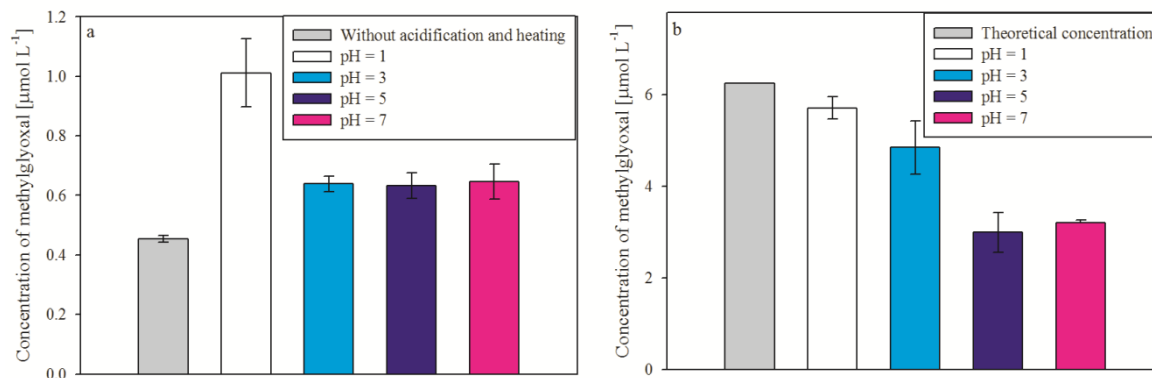
Figure 2: Influence of pH on the detected methylglyoxal concentration in filter samples (a) and the methylglyoxal standard solution (b).
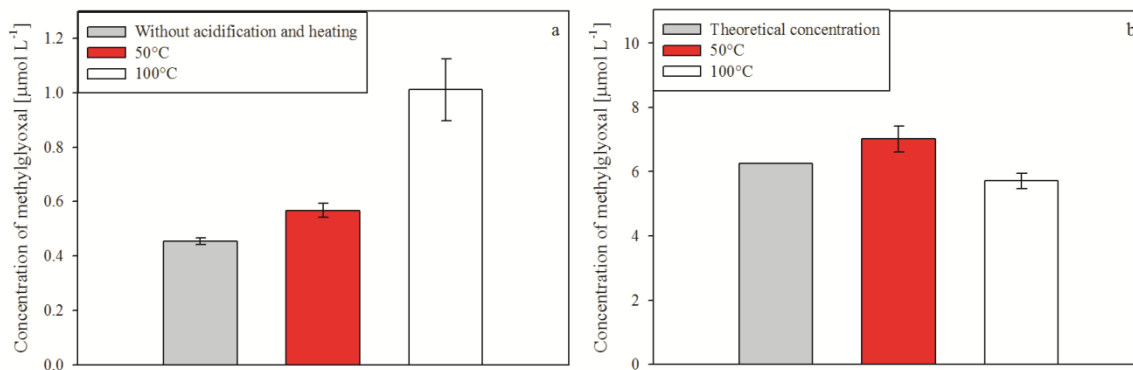
Figure 3: Influence of the heating temperature on the detected methylglyoxal concentration in filter samples (a) and the standard solution (b).

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 ± 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
4.12 – 7.00	This work
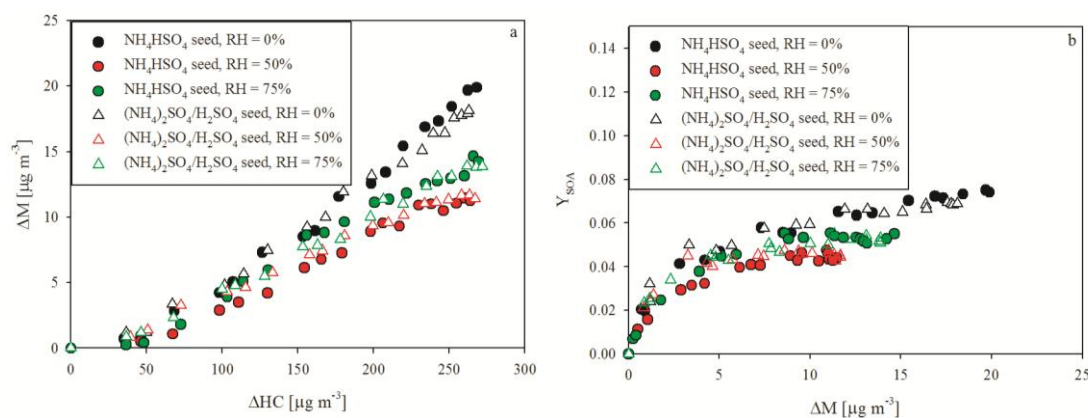
Figure 4: SOA growth curve (a) and yield curve (b) of the OH radical oxidation of 1,3,5-TMB in the presence of NH_4HSO_4 or $(NH_4)_2SO_4/H_2SO_4$ seed under variation of RH.

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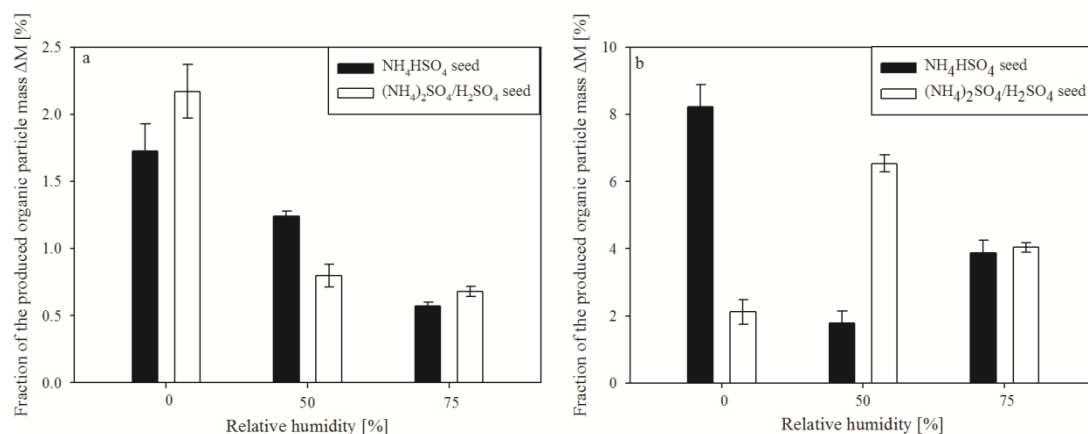
Figure 5: Contribution of methylglyoxal (a) and their heat-decomposable oligomers (b) to the produced organic particle mass (ΔM) with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles under variation of the relative humidity.