Responses to Reviewers

We would like to thank the reviewers for your constructive comments. We have carefully revised this manuscript according to your comments, and the revisions in the revised manuscript were presented in red font. Enclosed please find the point-by-point responses to the reviewers' comments.

Responses to Referee #2's comments

General comment: I would like to thank the authors for the response and their efforts to improve and clarify this manuscript. The supplementary data is very useful and the discussion about the influence of the aerosol microphysics to the SOA formation provides a better understanding of the processes happening during guaiacol oxidation in the presence of SO_2 and seed aerosols. I still have a few comments about some of the updated paragraphs.

Response to comment: Many thanks for your constructive comments and valuable suggestions, which would be much helpful to improve the scientific merits of this manuscript. Your concerns have been carefully addressed in the revised manuscript.

Comment 1: l. 309 please provide the definition of CHOgt1

Response to comment 1: The definition of CHO_{gt1} ion group has been added in the revised manuscript as follows.

Revision in the manuscript:

Line 311, Add: "containing more than one oxygen atom"

Comment 2: l. 332 I would recommend to clarify this quantification by saying that these values were obtained if considering that all S-containing compounds are organosulfates and having the same response factor and fragmentation as methyl sulfate

Response to comment 2: According to your valuable suggestion, the descriptions of organosulfates concentration have been modified in the revised manuscript, shown in the following revisions.

Revisions in the manuscript:

Lines 335-336, Add: "assuming that all organic S-containing compounds are organosulfates and have the same response factor and fragmentation as methyl sulfate"

Lines 336-339, Change: "the conservative lower-bound concentration of organosulfates increased with the increase of SO_2 concentration, and was in the range of (2.1 ±0.8) to (4.3 ±1.7) ng m^{-3}, calculated using the method described by Huang et al. (2015), shown in the Supplement." **To** "the conservative lower-bound concentration of organosulfates was calculated to be in the range of (2.1 ±0.8) to (4.3 ±1.7) ng m^{-3} using the method described by Huang et al. (2015) shown in the Supplement, and increased with the increase of SO_2 concentration."

Comment 3: l. 340 Is SO_2 favorable for the uptake of low-MW species or at the contrary, sulfuric acid + SOA retain low-MW in the aerosol phase? It could be both.

Response to comment 3: According to your valuable suggestion, this sentence has been rewritten in the revised manuscript as follows.

Revision in the manuscript:

Lines 343-346, Change: "sulfuric acid formed from SO_2 may be favorable of the uptake of water-soluble low-MW species (e.g., small carboxylic acids and aldehydes)"

To "sulfuric acid formed from SO_2 may be favorable for the uptake of water-soluble low-MW species (e.g., small carboxylic acids and aldehydes) and also be helpful to retain them in aerosol phase"

Comment 4: l. 390 add value of O:C ratios in parenthesis

Response to comment 4: The O/C ratios have been added in parenthesis in the revised manuscript as follows.

Revisions in the manuscript:

Line 394, Add: "(0.94−0.99)"

Line 395, Add: "(0.90−0.93)"

Comment 5: l. 507 I would add "physic" and chemistry of SOA formation

Response to comment 5: According to your valuable suggestion, "chemistry" has been changed to "physics and chemistry" in the revised manuscript.

Revision in the manuscript:

Line 513, Change: "chemistry" **To** "physics and chemistry"

Comment 6: Figure 3. I would reverse the colors. Red more SOA and blue less SOA.

Response to comment 6: Colors in Figure 3 have been modified in the revised manuscript according to your valuable suggestion, shown as Figure R1.
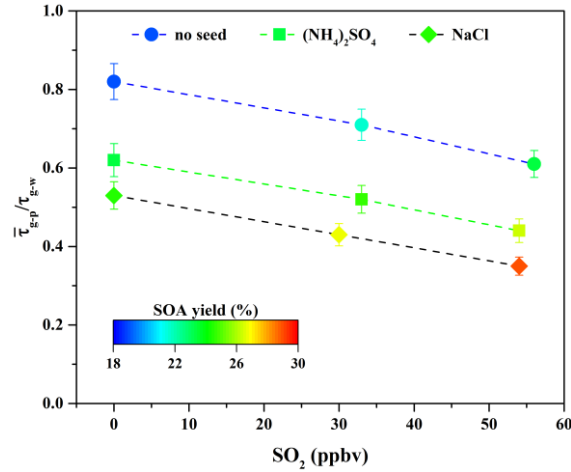
Figure R1. Variations in $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio in the presence of various seed particles as a function of SO$_2$ concentration.

Revision in the manuscript:

Figure R1 has been added in the revised manuscript.

Comment 7: In the supplement:

(1) l.54 In Zhang et al., 2014, Avogadro was misspelled to Avagadro. Change to Avogadro and also Boltzman to Boltzmann.

(2). Figure S7: make sure that the trace (NH$_4$)$_2$SO$_4$ blue triangles is not actually the NaCl data. Because SO$_2$ concentrations for ammonium sulfate seeds is 33 ppbv and for NaCl is 30 ppbv while in the figure the NaCl trace is higher than the (NH$_4$)$_2$SO$_4$ trace.

(3). l. 36 change to mass accommodation coefficient of vapors deposition to the wall

(4). l. 38 the coefficient of eddy diffusion will be chamber dependent. The k_e used here is the one corresponding to the chamber used in Zhang et al., 2014. Please explain your choice for this value that may or may not be the best fit for your study.

(5). Please provide the same discussion for the choice of the mass accommodation

values (to the walls and particles).

Response to comment 7: Thank you very much. The detailed responses to these comments are listed as follows.

(1). "Avagadro" and "Boltzman" have been changed to "Avogadro" and "Boltzmann", respectively.

(2). Figure traces in Figure S7 have been corrected in the revised Supplement, shown as Figure R2.
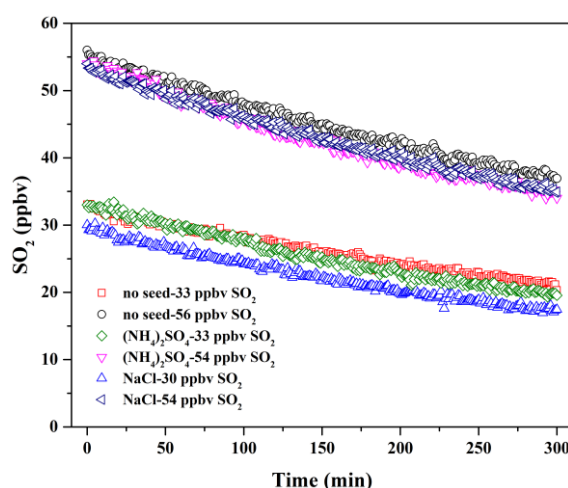
Figure R2. Decays of SO_2 as a function of irradiation time with different seed particles.

(3). "Mass accommodation coefficient of eddy diffusion" has been changed to "mass accommodation coefficient of vapors deposition to the wall".

(4) and (5). We agree that the values of k_e and α_w are chamber dependent. In this work, considering that the chamber volume (30 m^3) is very close to that (28 m^3) used by Zhang et al. (2014), thus the values of k_e and α_w reported by them were selected to calculate the overall wall loss rate of organic vapor (k_w).

Revisions in the manuscript:

(1). Line 64, Change: "Avagadro" and "Boltzman" **To** "Avogadro" and "Boltzmann",

respectively.

(2). Figure R2 has been added in the revised Supplement.

(3). Lines 36-37, Change: "mass accommodation coefficient of eddy diffusion" **To**

"mass accommodation coefficient of vapors deposition to the wall"

(4) and (5). Lines 39-41, Add "Considering that the chamber volume in this work (30 m^3) is very close to that (28 m^3) used by Zhang et al. (2014), thus the values of k_e and α_w reported by them were applied to calculate k_w."

Comment 8. The authors are not considering the vapor wall loss as a reversible process. Can you explain this choice? I would expect this process to be reversible.

Response to comment 8: Thank you very much. We agree that the vapor wall loss is a reversible process. In this work, we considered that the equilibrium was established for vapor wall losses after four hours photooxidation, because Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014) reported the rapid equilibrium established within less than an hour for vapor wall losses in Teflon chambers. In addition, assuming that the chamber wall was essential an absorbing medium of infinite extent, the overall wall loss rate of organic vapor (k_w) could be calculated using Eq. (S3) (Zhang et al., 2015), shown in the Supplement. Since this method could not separate the evaporation of adsorbed organic materials from the wall, the effect of vapor wall loss in this calculation might be overestimated. The detailed descriptions have been added in the revised Supplement.

Revision in the manuscript:

Supplement, Lines 41-49, Add: "In addition, we considered that the equilibrium was established for vapor wall losses after 4 hours photooxidation, because Matsunaga and Ziemann (2010) and Yeh and Ziemann (2014) reported the rapid equilibrium established within less than an hour for vapor wall losses in Teflon chambers. Meanwhile, it was assumed that the chamber wall was essential an absorbing medium of infinite extent. In this case, k_w could be calculated using Eq. (S3) (Zhang et al., 2015). Since this method could not separate the evaporation of adsorbed organic materials from the wall, the effect of vapor wall loss in this calculation might be overestimated."

Comment 9: Typing errors: I would recommend that the authors read carefully their paper to make sure no typing errors remain in the paper.

l. 69 direct

l. 90 Smog

l. 269 trace of NH_3

l. 329 low-MW

l. 403, 404 change to "might explain"

l. 438 when SO2 concentration raised from 0 to 30 ppbv for NaCl, M_o increased from 84.91 to 90.89 $\mu g\ m^{-3}$ and not from 63.62 to 90.89. Change the percentage too and the same changes has to be done for $(NH_4)_2SO_4$.

l. 487 add parenthesis before 26.37

l. 501 attention

l. 576 mass spectrometer

Response to comment 9: We have carefully checked the grammar and typing errors. The mistakes mentioned above have been corrected in the revised manuscript, listed as follows.

Revisions in the manuscript:

Line 69, Change: "direact" **To** "direct"

Line 90, Change: "Somg" **To** "Smog"

Line 270, Change: "trace NH_3" **To** "trace of NH_3"

Line 331, Change: "low-WM" **To** "low-MW"

Line 409, Change: "might be potentially explain" **To** "might explain"

Line 445, Change: "63.62 ±1.71" **To** "84.91 ±2.01"

Line 446, Change: "42.86% and 55.39%" **To** "7.04% and 16.43%"

Line 448, Change: "63.62 ±1.71" **To** "79.44 ±1.86"

Lines 449-450, Change: "32.58% and 41.34%" **To** "6.18% and 13.19%"

Line 493, Add: "("

Line 507, Change: "attenion" **To** "attention"

Line 590, Change: "aass spectrometer" **To** "mass spectrometer"

Responses to Referee #3's comments

Comment 1: Thank you for a very careful and thorough response to the suggestions presented in the review. I have one remaining concern: the mass spectra are communicated as being normalized to a sum of intensities of 1. However, when they are subtracted, there is net more intensity on one side. This is especially clear in Figure S13, please also check Figure 7c. If the mass spectra are normalized as described, the sum of the difference intensities should equal zero. Please double check this and the corresponding conclusions drawn from these figures.

Response to comment 1: Thank you very much. We are very sorry not to accurately response your comment in the previous version. In this work, the mass spectra were normalized to the mass concentration of SOA while not the sum intensity, which were obtained directly from AMS data analysis software (ToF-AMS analysis toolkit SQUIRREL 1.57I/PIKA 1.16I version, in Igor Pro version 6.37). Considering that the product distribution and SOA composition were different under different experimental conditions, the sum of difference intensities would not equal to zero. The similar phenomena were also reported by Tuet et al. (2017).

References

Matsunaga, A. and Ziemann, P. J.: Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements, Aerosol Sci. Technol., 44, 881-892, https://doi.org/10.1080/02786826.2010.501044, 2010.

Tuet, W. Y., Chen, Y., Fok, S., Gao, D., Weber, R. J., Champion, J. A., and Ng, N. L.: Chemical and cellular oxidant production induced by naphthalene secondary organic aerosol (SOA): Effect of redox-active metals and photochemical aging, Sci. Rep., 7, 15157, https://doi.org/10.1038/s41598-017-15071-8, 2017.

Yeh, G. K. and Ziemann, P. J.: Alkyl nitrate formation from the reactions of C8-C14 n-alkanes with OH radicals in the presence of NO_x: meausred yields with essential corections for gas-wall partitioning, J. Phys. Chem. A, 118, 8147–8157, https://doi.org/10.1021/jp500631v, 2014.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proc. Natl. Acad. Sci. U. S. A., 111, 5802-5807, https://doi.org/10.1073/pnas.1404727111, 2014.

Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos. Chem. Phys., 15, 4197-4214, https://doi.org/10.5194/acp-15-4197-2015, 2015.

Enhancement of secondary organic aerosol formation and its oxidation state by SO₂ during photooxidation of 2-methoxyphenol

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19   **Abstract.** 2-Methoxyphenol (guaiacol) is derived from the lignin pyrolysis and taken

20   as a potential tracer for wood smoke emissions. In this work, the effect of SO_2 at

21   atmospheric levels (0−56 ppbv) on secondary organic aerosol (SOA) formation and its

22   oxidation state during guaiacol photooxidation was investigated in the presence of

23   various inorganic seed particles (i.e., NaCl and $(NH_4)_2SO_4$). Without SO_2 and seed

24   particles, SOA yields ranged from (9.46 $\pm$ 1.71) % to (26.37 $\pm$ 2.83) % and could be

25   well expressed by a one-product model. According to the ratio of the average gas-

26   particle partitioning timescale ($\overline{\tau}_{g\text{-}p}$) over the course of experiment to the vapor wall

27   deposition timescale ($\tau_{g\text{-}w}$), the determined SOA yields were underestimated by a factor

28   of ~2 times. The presence of SO_2 resulted in enhancing SOA yield by 14.04 %−23.65 %.

29   With $(NH_4)_2SO_4$ and NaCl seed particles, SOA yield was enhanced by 23.07 % and

30   29.57 %, respectively, which further increased significantly to 29.78 %−53.43 % in the

31   presence of SO_2, suggesting that SO_2 and seed particles have a synergetic contribution

32   to SOA formation. The decreasing trend of $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio in the presence of seed

33   particles and SO_2 suggested that more SOA-forming vapors were partitioned onto

34   particle phase, consequently increasing SOA yields. It should be noted that SO_2 was

35   found to be in favor of increasing the carbon oxidation state (OS_C) of SOA, indicating

36   that the functionalization reaction or the partitioning of highly oxidized products onto

37   particles should be more dominant than oligomerization reaction. In addition, the

38   average N/C ratio of SOA was 0.037, which revealed that NO_x participated in the

39   photooxidation process, consequently leading to the formation of organic N-containing

40   compounds. The experimental results demonstrate the importance of SO_2 on the

41   formation processes of SOA and organic S-containing compounds, and also are helpful

42   to further understand SOA formation from the atmospheric photooxidation of guaiacol

43   and its subsequent impacts on air quality and climate.

1 Introduction

Biomass burning is considered as one of the major sources of gas and particulate pollutants in the atmosphere (Lauraguais et al., 2014b; Yang et al., 2016). Therefore, it has significant adverse impacts on regional and global air quality (Bari and Kindzierski, 2016; Lelieveld et al., 2001), climate (Chen and Bond, 2010), and human health (Naeher et al., 2007). The chemical species emitted by biomass burning is mainly dependent on fuel source and combustion conditions (O'Neill et al., 2014). Natural wood is composed of cellulose (40−50 wt.%), hemicelluloses (25−35 wt.%), and lignin (18−35 wt.%) (Nolte et al., 2001). During the burning process, lignin pyrolysis could result in the formation of methoxyphenols, mainly including guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol), and their derivatives (Nolte et al., 2001; Schauer et al., 2001). Due to the high emission rate of methoxyphenols (900−4200 mg kg^{-1} wood), methoxyphenols are considered as the potential tracers for wood burning (Hawthorne et al., 1989, 1992; Simoneit et al., 1993).

As a representative type of methoxyphenols, guaiacol mainly exists in the gas phase and is widely found in the atmosphere (Schauer et al., 2001). Its emission factor of wood burning is in the range of 172−279 mg kg^{-1} wood (Schauer et al., 2001). In recent years, the reactivity of gas-phase guaiacol toward OH radicals (Coeur-Tourneur et al., 2010a), NO$_3$ radicals (Lauraguais et al., 2016; Yang et al., 2016), Cl atom (Lauraguais et al., 2014a), and O$_3$ (El Zein et al., 2015) has been investigated, suggesting that its degradation by OH and NO$_3$ radicals might be predominant in the atmosphere.

65 Meanwhile, several studies have reported the significant SOA formation from guaiacol

66 oxidation by OH radicals, produced from the photolysis of the OH precursors (i.e., H_2O_2

67 and CH_3ONO) (Ahmad et al., 2017; Lauraguais et al., 2014b; Yee et al., 2013). However,

68 SOA formation from the photooxidation of guaiacol in the presence of NO_x has not

69 been investigated without adding the direct OH precursor, even though it has been

70 recently reported that the atmospheric level of NO_x could reach up to close 200 ppbv in

71 the severely polluted climate in China (Li et al., 2017).

72   Although many studies concentrated on the SOA production from the oxidation of

73 volatile organic compounds (VOCs), the reported SOA yields showed high variability

74 for a given precursor (Chu et al., 2016, 2017; Ge et al., 2017a; Lauraguais et al., 2012,

75 2014b; Ng et al., 2007; Sarrafzadeh et al., 2016; Yee et al., 2013). This variability is

76 mainly dependent on the numerous factors, e.g., pre-existing seed particles, SO_2 level,

77 NO_x level, humidity, and temperature. Two of the critical factors are the impacts of pre-

78 existing seed particles and SO_2 level on SOA formation (Chu et al., 2016, 2017; Ge et

79 al., 2017a). In addition, the atmospheric concentration of SO_2 could be up to close 200

80 ppbv in the severely polluted atmosphere in China, and SOA from biomass burning and

81 sulfate formation could significantly contribute to severe haze pollution (Li et al., 2017).

82 During the transport process, smoke plumes from biomass burning would be inevitably

83 mixed with suspended particles (e.g., $(NH_4)_2SO_4$ particles), SO_2, and NO_x in the

84 atmosphere. However, the influences of these co-existed pollutants on the

85 transformation of guaiacol and its SOA formation are still unclear. For these reasons,

86 the aim of this work was to investigate the SOA formation from guaiacol

87 photooxidation in the presence of NO_x in a 30 m^3 indoor smog chamber, as well as the

88 effect of SO_2 on SOA fromation with various inorganic seed particles.

2 Experimental section

2.1 Smog Chamber

91 The photooxidation experiments were performed in a 30 m^3 indoor smog chamber (4

92 m (height) $\times$ 2.5 m (width) $\times$ 3 m (length)), which was built in a temperature-controlled

93 room located at the Research Center for Eco-Environment Sciences, Chinese Academy

94 of Sciences (RCEES-CAS). Its schematic structure is shown in Fig. S1. Briefly, 120

95 UV lamps (365 nm, Philips TL 60/10R) were taken as the light source with a NO_2

96 photolysis rate of 0.55 min^{-1}, which was comparable to the irradiation intensity at noon

97 in Beijing (Chou et al., 2011). A maglev fan installed at the bottom center of the smog

98 chamber was used to mix sufficiently the introduced gas species and seed particles.

99 Temperature (T) and relatively humidity (RH) in the chamber were (302 $\pm$1) K and (39

100 $\pm$1) %, respectively. Before each experiment, the chamber was flushed by purified dry

101 zero air for ~36 h with a flow rate of 100 L min^{-1} until the particle number concentration

102 in the chamber was lower than 20 cm^{-3}.

2.2 Experimental procedures

104 Gas-phase guaiacol was firstly introduced into the chamber by purified dry zero air

105 flowing through the gently heated injector with a known volume of pure liquid guaiacol

106 until guaiacol fully vaporized. Its concentration in the chamber was online monitored

107 by a high-resolution proton-transfer reaction time-of-flight mass spectrometer (HR-

108 ToF-PTRMS) (Ionicon Analytik GmbH), and was calibrated by a commercial

109 permeation tube (VICI AG INTERNATIONAL Valco Instruments Co., Inc.). When

110 guaiacol concentration was stable, NO and SO_2 were introduced into the chamber by a

111 mass flow meter using purified dry zero air as the carrier gas. Their concentrations were

112 controlled by the injection time preset through the electromagnetic valve, and were

113 measured by a NO_x analyzer (model 42i-TL, Thermo Fisher Scientific, Inc.) and a SO_2

114 analyzer (model 43i, Thermo Fisher Scientific Inc.), respectively. In this work, the

115 initial ratio (V/V) of guaiacol concentration to NO_x concentration in the chamber was

116 similar in all experiments (~1.2) (Tables 1 and 2). In addition, sodium chloride (NaCl)

117 and ammonium sulfate (($NH_4)_2SO_4$) were used as the inorganic seeds. The seed aerosols

118 in the chamber were generated by the atomization of a 0.02 M aqueous solution.

119 Through atomization, the size distribution of seed particles peaked at 51−58 nm was

120 achieved, with a number concentration of 10100−11400 cm^{-3} (Table 2). After gas

121 species and seed particles in the chamber were mixed well, the photooxidation

122 experiment was carried out with the fan turned off. In this work, the OH concentrations

123 in the chamber were $(1.3−2.2) \times 10^6$ molecules cm^{-3}, calculated based on the

124 degradation rate (7.53×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) of guaiacol with OH radicals (Coeur-

125 Tourneur et al., 2010a). The chemicals and gas samples used in this work were

126 described in Supplement.

127 **2.3 Data analysis**

128   The HR-ToF-PTRMS with a time resolution of 1 min was used online to measure the

129   gas phase concentration of guaiacol, and its m/z range was 10−500 in the process of

130   data acquisition. Before data collection, the peaks of the protonated water ($[H_3^{18}O]^+$)

131   and protonated acetone ($[C_3H_7O]^+$) ions at m/z 21.0246 and 59.0491 were used for mass

132   calibration, with the aim to obtain accurate mass determination during experimental

133   process. All data obtained by the HR-ToF-PTRMS were analyzed with the PTR-MS

134   Viewer software (version 3.1.0, IONICON Analytik).

135   An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-

136   AMS) was applied to online measure the chemical composition of particles and the non-

137   refractory submicron aerosol mass (DeCarlo et al., 2006). For all experiments, the

138   acquisition time of the HR-ToF-AMS was 2 min. The inlet flow rate, ionization

139   efficiency, and particle sizing of the HR-ToF-AMS were calibrated at regular intervals,

140   according to the standard protocols using the size-selected pure ammonium nitrate

141   particles (Drewnick et al., 2005; Jimenez et al., 2003). All date obtained by the HR-

142   ToF-AMS were analyzed by the ToF-AMS analysis toolkit SQUIRREL 1.57I/PIKA

143   1.16I version, in Igor Pro version 6.37. The size distribution and concentration of

144   particles were monitored by a scanning mobility particle sizer (SMPS), which is

145   composed of a differential mobility analyzer (DMA) (model 3082, TSI Inc.) and a

146   condensation particle counter (CPC) (model 3776, TSI Inc.). Assuming that particles

147   are spherical and non-porous, the average particle density could be calculated to be 1.4

148   g cm^{-3} using the equation $\rho=d_{va}/d_m$ (DeCarlo et al., 2004), where d_{va} is the mean vacuum

149 aerodynamic diameter measured by the HR-ToF-AMS and d_m is the mean volume-

150 weighted mobility diameter measured by the SMPS. The mass concentration of

151 particles measured by the HR-ToF-AMS was corrected by the SMPS data in this work

152 using the same method as Gordon et al. (2014). In this work, the wall loss rate (k_{dep}) of

153 $(NH_4)_2SO_4$ particles could be expressed as $k_{dep} = 4.15 \times 10^{-7} \times D_p^{1.89} + 1.39 \times D_p^{-0.88}$

154 (D_p is the particle diameter (nm)), which was measured according to the literature

155 method (Takekawa et al., 2003) and was used to correct the wall loss of SOA. In

156 addition, its wall loss rate was determined at predetermined time intervals, which only

157 had a slight change among different experiments.

158 **2.4 Vapor wall-loss correction**

159 Previous studies have indicated that the losses of SOA-forming vapors to chamber wall

160 can result in the substantial and systematic underestimation of SOA (Zhang et al., 2014,

161 2015). Therefore, SOA yields obtained in this work were also corrected by vapor wall

162 loss. The effect of vapor wall deposition on SOA yields mainly depends on the

163 competition between the uptake of organic vapors by aerosol particles and the chamber

164 wall (Zhang et al., 2015). Thus, the ratio of the average gas-particle partitioning

165 timescale ($\overline{\tau}_{g-p}$) over the course of experiment to the vapor wall deposition timescale

166 (τ_{g-w}) could be reasonably used to evaluate the underestimation of SOA yields. The

167 detailed calculation of $\overline{\tau}_{g-p}$ and τ_{g-w} was shown in the Supplement.

168 **3   Results and discussion**

169 **3.1   SOA yields**

170   A series of experiments were conducted at different guaiacol/NO_x concentrations under

171   atmospheric pressure. The experimental conditions and results are shown in Table 1.

172   SOA yield was calculated to be the ratio of SOA mass concentration (M_o, μg m^{-3}) to the

173   consumed guaiacol concentration (Δ[guaiacol], μg m^{-3}) at the end of each experiment

174   (Kang et al., 2007). The results showed that SOA yield was dependent on the initial

175   guaiacol concentration ([Guaiacol]$_0$). Higher precursor concentration would result in

176   higher amount of condensable products, subsequently enhancing SOA formation

177   (Lauraguais et al., 2012). In addition, it should be noted that SOA mass could directly

178   affect the gas/particle partitioning via acting as the adsorption medium of oxidation

179   products, thus higher SOA mass generally leads to higher SOA yield (Lauraguais et al.,

180   2014b).

181   SOA yield (Y) could be represented by a widely-used semi-empirical model based

182   on the absorptive gas-particle partitioning of semi-volatile products, typically

183   calculated using the following equation (Odum et al., 1996):

184   $$Y = \sum_i M_o \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \tag{1}$$

185   where α_i is the mass-based stoichiometric coefficient for the reaction producing the

186   semi-volatile product i, $K_{om,i}$ is the gas-particle partitioning equilibrium constant, and

187   M_o is the total aerosol mass concentration.

188   The yield curve for guaiacol photooxidation is shown in Fig. 1, obtained by plotting

189   the SOA yield data in Table 1 according to Eq. (1). The yield data were accurately

190   reproduced by a one-product model ($R^2 = 0.97$), while two or more products used in the

191 model did not significantly improve the fitting quality. The obtained values of α_i and

192 $K_{om,i}$ for one-product model were (0.27 ±0.01) and (0.033 ±0.008) $m^3 \mu g^{-1}$, respectively.

193 In previous studies, the one-product model was widely applied to describe SOA yields

194 from the oxidation of aromatic compounds including methoxyphenols (Coeur-Tourneur

195 et al., 2010b; Lauraguais et al., 2012, 2014b). In this work, this simulation suggests that

196 the products in SOA have similar values of α_i and $K_{om,i}$, i.e., the obtained α_i and $K_{om,i}$

197 are the average values. The plot shown in Fig. S2 is the relationship between M_o versus

198 Δ[guaiacol], of which slope (0.28) is slightly higher than α_i value (0.27). This suggests

199 that the formed low-volatile products almost completely partitioned on the particle-

200 phase according to the theoretical partition model (Lauraguais et al., 2012, 2014b).

201   In the previous studies, the significant SOA formation from the OH-initiated

202 reaction of guaiacol has been reported (Lauraguais et al., 2014b; Yee et al., 2013). In

203 this work, SOA yields for guaiacol photooxidation range from (9.46 ±1.71) % to (26.37

204 ± 2.83) %, shown in Table 1. According to the ratios of $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ (0.61−0.93), the

205 determined SOA yields were underestimated by a factor of ~2 times, suggesting that

206 vapor wall loss in the chamber could significantly affect SOA formation. The similar

207 results were reported previously by Zhang et al. (2014), who indicated that SOA yields

208 for toluene photooxidation were substantially underestimated by factors as much as 4

209 times, caused by vapor wall loss. As shown in Fig. 1, the vapor wall-loss corrected SOA

210 yields were in the range of (15.24 ± 0.85) % to (50.89 ± 2.87) %, and could also be

211 reproduced by a one-product model (R^2 = 0.96). This range overlaps SOA yields of

212 0.6 %−87 % for guaiacol oxidation under high NO_x condition (~10 ppmv NO), reported

213 by Lauraguais et al. (2014b), using CH_3ONO as the OH source. Under low NO_x

214 conditions (< 5 ppbv NO), SOA yields for guaiacol oxidation were in the range of

215 44 %−50 %, reported by Yee et al. (2013) using H_2O_2 as the OH source and $(NH_4)_2SO_4$

216 as seed particles; they also indicated that high NO_x concentration (> 200 ppbv NO)

217 played an opposite role in SOA formation. Overall, the vapor wall-loss corrected SOA

218 yields in this work are well in agreement with those reported previously (Lauraguais et

219 al., 2014b; Yee et al., 2013), but the determined SOA yields are much lower. Therefore,

220 the effect of vapor wall loss on SOA formation should be seriously taken into account.

221 In addition, the average N/C ratio of SOA for guaiacol photooxidation in the

222 presence of NO_x is 0.037, calculated according to the element analysis by the HR-ToF-

223 AMS. This indicates that NO_x incorporates in guaiacol photooxidation. This

224 phenomenon is well supported by the previous studies, which have reported that the

225 nitro-substituted products are the main products of the OH-initiated reaction of guaiacol

226 in the presence of NO_x (Ahmad et al., 2017; Lauraguais et al., 2014b). The relative low

227 volatility of these products could reasonably contribute to SOA formation (Duporté et

228 al., 2016; Liu et al., 2016a). The average NO^+ / NO_2^+ ratio of SOA from guaiacol

229 photooxidation is 4.08, which is higher than that (2.06−2.54) for ammonium nitrate,

230 determined by the HR-ToF-AMS in this work. The possible explanation might be that

231 nitro-organics and organonitrates both exist in SOA (Farmer et al., 2010; Sato et al.,

232 2010). The relative abundance of organic N-containing compounds could be estimated

233   from the average N/C ratio. Assuming that the oxidation products in the SOA retain 7

234   carbon atoms, the yield of organic N-containing compounds is 25.9 %, which is the

235   upper limit due to the possible C－C bond scission during photooxidation process.

236   **3.2   Effect of SO$_2$ on SOA formation**

237   **3.2.1   SOA yields**

238   In China, atmospheric SO$_2$ concentration is always in the range of several to dozens of

239   ppbv, while in the severely polluted atmosphere it could be up to close 200 ppbv (Han

240   et al., 2015; Li et al., 2017). In addition, a recent field measurement study has reported

241   that the decrease of biogenic SOA mass concentration in the atmosphere has a positive

242   correlation with SO$_2$ emission controls (Marais et al., 2017). Therefore, the effect of

243   SO$_2$ at atmospheric levels on SOA formation from guaiacol photooxidation under

244   atmospheric NO$_x$ conditions was investigated. The experimental conditions and results

245   are shown in Table 2. The formation of SOA, sulfate, and nitrate as a function of SO$_2$

246   concentration for guaiacol photooxidation is shown in Fig. S3, and the time-series

247   variations in the concentrations of sulfate and nitrate are shown in Fig. S4. The decays

248   of guaiacol, NO$_x$, and SO$_2$ are shown in Figs. S5a, S6a, and S7, respectively, which

249   have the similar changing trends for different experiments. As illustrated in Fig. 2, the

250   induction period became shorter with the increase of SO$_2$ concentration. The similar

251   results caused by SO$_2$ have also been reported previously (Chu et al., 2016; Liu et al.,

252   2016b). Meanwhile, M$_o$ for the experiment without SO$_2$ (Exp. 1 in Table 2) increased

253   from (63.62 ± 1.71) to (71.88 ± 1.43) and (78.59 ± 2.06) μg m^{-3}, enhanced by 12.98 %

254 and 23.53 %, respectively, when SO_2 concentration raised from 0 to 33 and 56 ppbv.

255 The corresponding SOA yields were (21.60 ± 1.27) % and (23.42 ± 1.80) %,

256 respectively. The similar results were reported by previous studies (Kleindienst et al.,

257 2006; Lin et al., 2013; Liu et al., 2016b), which observed the significant enhancement

258 of SOA yields for VOCs oxidation and the photochemical aging of gasoline vehicle

259 exhaust in the presence of SO_2.

260 As shown in Fig. 3, $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio decreased from 0.82 to 0.71 and 0.61 when SO_2

261 concentration increased from 0 to 33 and 56 ppbv. It suggests that the formed sulfate

262 via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008) and increase the

263 surface areas of particles (Xu et al., 2016). These roles are favorable to partition more

264 SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing

265 SOA yields. At the same time, as shown in Fig. S4 and Table 2, the sulfate concentration

266 increased significantly from 7.42 to 17.89 μg m^{-3} when SO_2 concentration increased

267 from 33 to 56 ppbv. Nevertheless, the particle peak attributed to sulfate formed via SO_2

268 oxidation was not observed by the SMPS during experimental process due to the quick

269 particle growth in the presence of organic vapors. In this work, it is difficult to

270 completely remove trace of NH_3 from zero air, thus the formed sulfate should be the

271 mixture of H_2SO_4 and $(NH_4)_2SO_4$. The time-series changes in the concentration of

272 ammonium salt at different SO_2 concentrations are shown in Fig. S8. Its concentration

273 increased obviously with increasing SO_2 concentration, suggesting that the more

274 amount of $(NH_4)_2SO_4$ was produced. The similar results have also been reported

275 recently by Chu et al. (2016). In addition, the surface area concentration of aerosol

276 particles at the end time were calculated. As shown in Table 2, the final surface area of

277 aerosol particles formed via guaiacol photooxidation increased from 1.25×10^3 to 1.68

278 $\times 10^3$ and 2.04×10^3 μm^2 cm^{-3} when SO_2 concentration increased from 0 to 33 and 56

279 ppbv. The increased surface area could be in favor of outcompeting the wall loss for

280 low-volatility vapors produced from guaiacol photooxidation, i.e., more low-volatility

281 vapors would be diverted from wall loss to the particles, consequently increasing SOA

282 yields (Kroll et al., 2007). This is well supported by the decrease of $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio with

283 increasing SO_2 concentration, shown in Fig. 3.

284   The time-series changes in the mass concentrations of NO^+ and NO_2^+ are shown

285 in Fig. S9a. The mass concentration of NO^+ increased more quickly than that of NO_2^+,

286 and had a positive correlation with SO_2 concentration. But, compared to the experiment

287 without SO_2, the presence of SO_2 had little impact on NO^+ / NO_2^+ and N/C ratios

288 obtained at the end time, shown in Figs. S9b and S10b, respectively. These ratios

289 indicated that organic N-containing compounds were also produced in this system

290 (Farmer et al., 2010; Sato et al., 2010).

291 **3.2.2 Oxidation state of SOA**

292   The average carbon oxidation state ($OS_C = 2O/C - H/C$) of OA is widely used to

293 represent the oxidation degree of atmospheric OA, because it takes into account the

294 saturation level of carbon atoms in the OA (Kroll et al., 2011). As shown in Table 2,

295 increasing SO_2 concentration (0−56 ppbv, Exps. 1−3) leads to the increase of OS_C

296   (0.11−0.18). The variations in H/C, O/C, and N/C ratios as a function of irradiation time

297   are shown in Fig. S10. In order to further identify the effect of SO_2 on the chemical

298   properties of SOA, positive matrix factorization (PMF) analysis for all AMS data

299   obtained at different SO_2 concentrations over the courses of experiments was carried

300   out. Two factors were obtained from the PMF analysis, and their mass spectra are shown

301   in Fig. 4. The organic mass fraction of m/z 44 (CO_2^+), named f_{44}, was 0.122 for Factor

302   2, which is higher than that (0.094) for Factor 1. Therefore, Factor 2 was tentatively

303   assigned to the more-oxidized SOA, while Factor 1 was the less-oxidized SOA (Ulbrich

304   et al., 2009). During the photooxidation process, these two factors had different

305   variations as a function of irradiation time. As shown in Fig. S11, Factor 1 increased

306   along with the reaction and then decreased, while Factor 2 had an increasing trend.

307   Compared to Exps. 1 and 2 in Table 2, the higher fraction of Factor 2 mass obtained at

308   56 ppbv SO_2 (Exp. 3 in Table 2) suggests that the formed SOA mainly consists of more-

309   oxidized products with relatively low volatility. This is well supported by the time-

310   series variations in the fraction of organic ion groups (CH^+, CHO^+, and CHO_{gt1}^+

311   (containing more than one oxygen atom)) (Fig. S12a), which shows the higher fraction

312   of CHO_{gt1}^+ and lower fraction of CH^+ obtained at higher SO_2 concentration,

313   consequently resulting in higher OS_C of SOA.

314   Previous studies mostly reported that the enhancement of SOA yield in the presence

315   of SO_2 was ascribed to the functionalization and oligomerization reactions (Cao and

316   Jang, 2007; Jaoui et al., 2008 ; Liu et al., 2016b; Xu et al., 2016). If the oligomerization

317   reaction plays a predominant role in the presence of SO_2 which will lead to particle

318   phase H_2SO_4, the carbon number of oligomers will increase but their net O/C or H/C

319   values have little change, consequently resulting in little change in the oxidation state

320   of SOA (Chen et al., 2011). Nevertheless, we observed that SO_2 not only enhanced SOA

321   yields, but also resulted in higher OS_C (Table 2 and Fig. 5). This suggests that the

322   functionalization reaction might be predominant with SO_2, which leads to higher OS_C

323   of products with low molecular weight (MW) (Ye et al., 2018), consequently resulting

324   in an overall increase in OS_C and SOA yields. More recently, Ye et al. (2018) also found

325   the similar results in the ozonolysis of limonene. Fig. S13 shows the differences among

326   the normalized mass spectra of SOA formed at different SO_2 concentrations. As shown

327   in Fig. S13a, the signal fractions from the low-MW species were enhanced significantly

328   in the presence of SO_2, and were much higher than those from the high-MW species

329   (m/z > 300). The similar results were also observed in Fig. S13b when increasing SO_2

330   concentration. In other words, SO_2 played a more important role in the formation of

331   organic S-containing compounds and the formation or uptake of low-MW species,

332   compared to the formation of high-MW species (i.e., oligomers) that should be

333   reasonably produced via the acid-catalyzed heterogeneous reactions (Cao and Jang,

334   2007; Jaoui et al., 2008; Liu et al., 2016b; Xu et al., 2016).

335   In this work, assuming that all organic S-containing compounds are organosulfates

336   and have the same response factor and fragmentation as methyl sulfate, the conservative

337   lower-bound concentration of organosulfates was calculated to be in the range of (2.1

338 ± 0.8) to (4.3 ± 1.7) ng m^{-3} using the method described by Huang et al. (2015) shown

339 in the Supplement, and increased with the increase of SO$_2$ concentration. This

340 concentration range is close to those derived from the atmospheric oxidation of

341 polycyclic aromatic hydrocarbons and alkane (Meade et al., 2016; Riva et al., 2015).

342 Fig. S14 is the examples of the ions (i.e., CSO^+, $CH_3SO_2^+$, and $CH_3SO_3^+$) of methyl

343 sulfate obtained at 56 ppbv SO$_2$ (Exp. 3 in Table 2). On the other hand, sulfuric acid

344 formed from SO$_2$ may be favorable for the uptake of water-soluble low-MW species

345 (e.g., small carboxylic acids and aldehydes) and also be helpful to retain them in aerosol

346 phase, which would result in the increase of OS$_C$. This is well supported by the time-

347 series variations in the concentrations of acetic acid at different SO$_2$ concentrations

348 measured by the HR-ToF-PTRMS (Fig. S15a), which shows that acetic acid

349 concentration decreased with the increase of SO$_2$ concentration (0−56 ppbv). These

350 results were in good agreement with those reported by Liggio et al. (2005) and Liu et

351 al. (2010), who observed that the uptake of organic compounds under acidic conditions

352 would be enhanced significantly. Recently, Huang et al. (2016) have also reported that

353 acetic acid is present in SOA formed via α-pinene ozonolysis and its uptake would

354 increase in the presence of seed particles. In addition, Krapf et al. (2016) have indicated

355 that peroxides in SOA are unstable and liable to decompose into volatile compounds,

356 consequently leading to decrease SOA yield and OS$_C$. But, Ye et al. (2018) found that

357 the reactions of SO$_2$ with organic peroxides were the dominant sink of SO$_2$, initiated by

358 the heterogeneous uptake of SO$_2$ under humidity condition. These reactions would

359   result in the formation of organic S-containing compounds, consequently increasing

360   SOA yields and OS_C.

3.3   Effect of inorganic seed particles on SOA formation

362   Seed particle is one of the critical factors influencing SOA formation (Ge et al., 2017a),

363   thus the effects of inorganic seeds (i.e., NaCl and $(NH_4)_2SO_4$) on SOA formation from

364   guaiacol photooxidation were investigated. As shown in Fig. 6, the presence of

365   inorganic seed particles could accelerate SOA growth rate at the initial stage of

366   photooxidation (i.e., shorten induction period), followed by the decrease of growth rate

367   along with the reaction, because the presence of inorganic seeds could promote the

368   condensation of SOA-forming organic products and consequently increase SOA

369   formation (Yee et al., 2013). The results showed that M_o for the experiment without

370   seed particles (Exp. 1 in Table 2) increased from (63.62 ± 1.71) to (79.44 ± 1.86) and

371   (84.91 ± 2.01) μg m^{-3} (Table 2), enhanced by 24.87 % and 33.46 %, respectively, with

372   $(NH_4)_2SO_4$ and NaCl seed particles. The corresponding SOA yields were (23.31 ± 1.59) %

373   and (24.54 ± 1.73) %, respectively. In previous work, the similar results about the

374   enhancements of SOA formation by NaCl and $(NH_4)_2SO_4$ seed particles were reported

375   in the oxidation of VOCs (Ge et al., 2017a, 2017b; Huang et al., 2013, 2017). As shown

376   in Fig. 3, $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratios with $(NH_4)_2SO_4$ and NaCl seed particles were 0.62 and 0.54,

377   respectively, which suggested that more SOA-forming vapors were partitioned onto

378   particle phase in the presence of NaCl seed particles (Zhang et al., 2014), consequently

379   resulting in relatively higher SOA yield.

380   As shown in Table 2 and Fig. 6, the SOA mass concentration in the presence of

381   NaCl seed particles was higher than that in the presence of $(NH_4)_2SO_4$ seed particles.

382   In addition, OS_C of SOA in the presence of NaCl seed particles is 0.29, slightly higher

383   than that (0.20) in the presence of $(NH_4)_2SO_4$ seed particles. Recently, it has been also

384   reported that the presence of $(NH_4)_2SO_4$ and $NaNO_3$ seed particles could enhance

385   significantly the oxidation state of SOA, compared to without seed particles (Huang et

386   al., 2016). In this work, the experimental conditions for seed experiments are almost

387   the same (Table 2), including reactant concentration, temperature, RH, and the number

388   and diameter of seed particles. Therefore, the differences in the yield and oxidation state

389   of SOA were reasonably resulted from the different chemical compositions of SOA in

390   the presence of different inorganic seeds. As shown in Figs. S12b and S12c, compared

391   to $(NH_4)_2SO_4$ seed particles, the higher fraction of CHO_{gt1}^{+} and lower fraction of CH^{+}

392   were obtained with NaCl seed particles, consequently resulting in higher OS_C of SOA.

393   The time-series evolution of O/C, H/C, and N/C ratios is shown in Figs. S16 and S17,

394   which indicate that O/C ratios (0.94−0.99) with NaCl seed particles at the end of

395   experiments are higher than those (0.90−0.93) with $(NH_4)_2SO_4$ seed particles. Fig. 7

396   shows the mass spectra of SOA in the presence of NaCl and $(NH_4)_2SO_4$ seed particles

397   obtained by the HR-ToF-AMS, as well as their difference mass spectrum. As shown in

398   Fig. 7, f_{44} for SOA in the presence of NaCl seed particles was higher than that obtained

399   in the presence of $(NH_4)_2SO_4$ seed particles, while the mass fractions of m/z 15 (CH_3)

400   and 29 (CHO) fragments were both lower. The m/z 44 ion (CO_2^{+}) is mainly contributed

401   from acids or acid-derived species, such as esters (Ng et al., 2011). The higher f_{44} of

402   SOA with NaCl than $(NH_4)_2SO_4$ seed particles suggests that the distribution of highly

403   oxidized small carboxylic acids onto seed particles plays an important role in SOA

404   formation, consequently resulting in higher oxidation state of SOA (Huang et al., 2016;

405   Ng et al., 2011). Compared to $(NH_4)_2SO_4$, the hygroscopicity of NaCl is stronger (Ge

406   et al., 2017a; Gysel et al., 2002). The molar ratio of H_2O to NaCl is about 0.1 at 40 %

407   RH, and water is mainly adsorbed on NaCl particles (Weis and Ewing, 1999). Thus, the

408   greater water content on the particle surface could facilitate the uptake of highly

409   oxidized small carboxylic acids onto NaCl particles, which might explain the higher

410   SOA oxidation state observed in the presence of NaCl seed particles (Huang et al.,

411   2016). As shown in Fig. S15, the concentration of acetic acid in the gas phase with

412   NaCl seed particles was lower than that with $(NH_4)_2SO_4$ seed particles. It suggests that

413   the uptake of acetic acid on NaCl seed particles might be higher than that on $(NH_4)_2SO_4$

414   seed particles under the similar experimental conditions (i.e., NO_x and guaiacol

415   concentrations, temperature, and RH). Moreover, the adsorbed acid products would also

416   generate H^+ ions, which could catalyze heterogeneous reactions to produce more-

417   oxidized products or oligomers with relatively low volatility (Fig. S18), consequently

418   resulting in the enhancement of SOA formation (Huang et al., 2013, 2017; Cao and

419   Jang, 2007; Jaoui et al., 2008; Liu et al., 2016b; Xu et al., 2016).

420   In addition, the possible formation of Cl atoms from the photolysis of nitryl

421   chloride ($ClNO_2 \xrightarrow{hv} Cl + NO_2$, $k_1 = \sim 10^{-4}$ s^{-1}) (Mielke et al., 2011) and the reaction

422 of OH radical with Cl^- ($Cl^- + OH \rightarrow Cl + OH^-$, $k_2 = \sim10^9$ M^{-1} s^{-1}) (Fang et al., 2014)

423 would also initiate a series of reactions to oxidize SOA composition, which might be

424 another reason for higher OS_C observed with NaCl seed particles. According to the rate

425 constant (10^9 M^{-1} s^{-1}) (Fang et al., 2014), the uptake coefficient (3.4×10^{-3}) of OH

426 radicals on NaCl particles (Park et al., 2008), and the concentrations of OH radicals and

427 Cl^-, the concentration of Cl atoms produced from the reaction of OH radical with Cl^-

428 was estimated to be less than 38 molecules cm^{-3}, which was much higher than that from

429 the photolysis of $ClNO_2$ due to the slow photolysis rate constant of $\sim10^{-4}$ s^{-1} (Mielke

430 et al., 2011). Compared to OH concentration in the chamber, the oxidation of SOA

431 composition by Cl atoms should be insignificant.

432 **3.4 Synergetic effect of SO_2 and inorganic seed particles on SOA formation**

433 According to the former results obtained in this work, it is clearly known that SO_2 and

434 inorganic seed particles both have a positive role in enhancing SOA formation.

435 Therefore, their possible synergetic effects on SOA formation were investigated.

436 Considering the experiments performed under the comparable conditions (Table 2), the

437 results should be reasonably reliable. The decays of guaiacol, NO_x, and SO_2 are shown

438 in Figs. S5, S6, and S7, respectively, which have the similar changing trends for

439 different experiments. Fig. S19 shows the time-series evolution in the sulfate

440 concentration in the presence of different SO_2 concentrations and seed particles, which

441 indicates that sulfate concentration is dependent on SO_2 concentration. As shown in Fig.

442 8, the addition of SO_2 into the chamber in the presence of inorganic seed particles

443   significantly promoted SOA formation from guaiacol photooxidation, but had an

444   ignorable impact on the induction period. When SO_2 concentration raised from 0 to 30

445   and 54 ppbv in the presence of NaCl seed particles, M_o increased from (84.91 $\pm$ 2.01)

446   to (90.89 $\pm$ 2.28) and (98.86 $\pm$ 2.11) µg m^{-3}, enhanced by 7.04 % and 16.43 %,

447   respectively, and the corresponding SOA yields were (26.78 $\pm$ 1.97) % and (29.06 $\pm$

448   1.82) %. For $(NH_4)_2SO_4$ seed particles, M_o increased from (79.44 $\pm$ 1.86) to (84.35 $\pm$

449   2.09) for 33 ppbv SO_2 and (89.92 $\pm$ 2.31) µg m^{-3} for 54 ppbv SO_2, enhanced by 6.18 %

450   and 13.19 %, respectively, and the corresponding SOA yields were (24.58 $\pm$ 1.78) %

451   and (26.37 $\pm$ 1.98) %. As shown in Fig. 3, $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio had a decreasing trend when

452   increasing SO_2 concentration in the presence of seed particles, suggesting that the

453   underestimation of SOA yields caused by vapor wall loss was weakened significantly

454   because of the additional sulfate formed from SO_2 oxidation. Thus, inorganic seed

455   particles and SO_2 have a synergestic effect on SOA formation.

456   As shown in Table 2 and Fig. 5, it should be noted that OS_C of SOA increased in

457   the presence of SO_2, which was well supported by the time-series variations in H/C,

458   O/C, and N/C ratios at different SO_2 concentrations with NaCl and $(NH_4)_2SO_4$ as seed

459   particles, shown in Figs. S16 and S17. In addition, as shown in Figs. S12b and S12c,

460   the higher fraction of CHO_{gt1}^+ and lower fraction of CH^+ were obtained at higher SO_2

461   concentration, consequently resulting in higher OS_C of SOA. Fig. S20 shows the mass

462   spectra of SOA with NaCl and $(NH_4)_2SO_4$ as seed particles at different SO_2

463   concentrations obtained by the HR-ToF-AMS. As illustrated in Fig. S20, SO_2 addition

464   was in favor of increasing the value of f_{44}, suggesting that more products with higher

465   OS_C are produced by the functionalization reaction (Ye et al., 2018). Meanwhile, Table

466   2 shows that the final surface area of aerosol particles increased in the presence of SO_2,

467   which played a positive role in diverting more low-volatility vapors from wall loss to

468   the particles, consequently enhancing SOA yields (Kroll et al., 2007). In addition, the

469   presence of inorganic seeds could promote the condensation of SOA-forming organic

470   products and the heterogeneous uptake of SO_2 (Yee et al., 2013), providing favorable

471   conditions for the following reactions. Meanwhile, the higher hygroscopicity of NaCl

472   than $(NH_4)_2SO_4$ might be helpful to dissolve more acid substances on NaCl particle

473   surface (e.g., H_2SO_4 and organic acid), especially in the presence of SO_2. This

474   hypothesis could be supported by the variations in acetic acid concentration in the

475   presence of different seed particles and SO_2 concentrations (Fig. S15), which shows

476   that acetic acid concentration decreased with the increase of SO_2 concentration (0−54

477   ppbv). The dissolved acid compounds might be helpful to catalyze heterogeneous

478   reactions (Cao and Jang, 2007; Huang et al., 2013, 2017; Jaoui et al., 2008; Liu et al.,

479   2016b; Xu et al., 2016). Figs. S21 and S22 show the differences among the normalized

480   mass spectra of SOA formed at different SO_2 concentrations with various seed particles.

481   The results indicated that the signal fractions from the low-MW species increased

482   significantly in the presence of SO_2, and were much higher than those from the high-

483   MW species (m/z > 300). Compared to Exps. 2 and 3 in Table 2 with no seed particles,

484   the conservative lower-bound concentrations of organosulfates formed with seed

485 particles were similar and in the range of (2.2 ±0.7) to (4.6 ±1.8) ng m^{-3}, which might

486 be caused by the similar SO_2 concentrations applied for experiments. With NaCl and

487 $(NH_4)_2SO_4$ as seed particles, SOA yields and OS_C both increased with the increase of

488 SO_2, suggesting that the functionalization reaction should be more dominant than

489 oligomerization reaction during photooxidation process.

490 **4   Conclusions and atmospheric implications**

491 In this work, SOA formation from guaiacol photooxidation in the presence of NO_x was

492 investigated in a 30 m^3 smog chamber. SOA yields for guaiacol photooxidation were in

493 the range of (9.46 ±1.71) % to (26.37 ±2.83) %, and could be expressed well by a one-

494 product model. These yields were underestimated by a factor of ~2 times according to

495 $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratios. The presence of SO_2 could increase SOA yield and OS_C, indicating

496 that the functionalization reaction should be more dominant than oligomerization

497 reaction. Meanwhile, the similar effect of SO_2 was also observed with NaCl and

498 $(NH_4)_2SO_4$ seed particles. But, SOA yield and OS_C in the presence of NaCl seed

499 particles were both slightly higher than those in the presence of $(NH_4)_2SO_4$ seed

500 particles. In addition, the results indicated the synergetic contribution of SO_2 and

501 inorganic seed particles to SOA formation. The decreasing trend of $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio in

502 the presence of seed particles and SO_2 suggested that more SOA-forming vapors were

503 partitioned onto particle phase, consequently increasing SOA yields. The average N/C

504 ratio (0.037) of SOA suggested that NO_x participated in the process of guaiacol

505 photooxidation, resulting in the formation of organic N-containing compounds.

The significant SOA formation from guaiacol photooxidation at the atmospheric levels of SO_2 and NO_x in this work suggests that it should pay more attention to the SOA formation from biomass burning and its subsequent effects on haze evolution, especially in China with nationwide biomass burning, because recent studies have indicated that SOA formed from biomass burning plays an important role in haze pollution in China (Ding et al., 2017; Li et al., 2017). In addition, the results imply that the oxidation of SO_2 and VOCs should be tightly combined, and SO_2 has a direct impact on the physics and chemistry of SOA formation. Although guaiacol concentrations in the chamber study are higher than those in the ambient atmosphere, the results obtained in this work could provide new information for SOA formation from the photooxidation of methoxyphenols, and might be useful for SOA modeling, especially for air quality simulation modeling of the specific regions experiencing serious pollution caused by fine particulate matter. In addition, the results would help to further understand the photochemical aging process of smoke plumes from biomass burning in the atmosphere.

Data availability

The experimental data are available upon request to the corresponding authors.

Author contributions

CL, TC, YL, and HH designed the research and wrote the paper. CL, TC, and JL performed the experiments. CL, TC, YL, JL, HH, and PZ carried out the data analysis. All authors contributed to the final paper.

Competing interests

The authors declare that they have no conflict of interest.

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823 **Table 1.** Experimental conditions and results for guaiacol photoxidation in the presence

824 NO_x.

Exp.	[Guaiacol]$_0$ ($\mu g\ m^{-3}$)	$\triangle$[Guaiacol] ($\mu g\ m^{-3}$)[a]	[NO$_x$]$_0$ (ppbv)	[NO]$_0$ (ppbv)	RH (%)	T (K)	M$_o$ ($\mu g\ m^{-3}$)[b]	Yield (%)
1	136.83	112.34	25.1	13.2	39	302	10.63 ± 0.65	9.46 ± 1.71
2	309.06	282.33	52.7	34.4	38	302	34.72 ± 0.94	12.30 ± 0.98
3	375.19	335.94	58.3	44.5	40	302	63.62 ± 1.71	18.94 ± 1.49
4	718.49	613.25	116.7	98.5	38	302	130.19 ± 3.28	21.23 ± 1.56
5	1321.25	1116.20	209.2	184.1	39	302	256.88 ± 6.69	23.01 ± 1.75
6	1470.66	1175.03	248	200	38	302	297.65 ± 8.85	25.33 ± 2.21
7	2197.36	1664.29	335	286	38	302	438.82 ± 10.25	26.37 ± 2.83

825 [a] The consumed guaiacol concentration at the end of each experiment.

826 [b] M$_o$ is the mass concentration of SOA.

Table 2. Experimental conditions and results for guaiacol photoxidation in the presence of seed particles and SO_2.

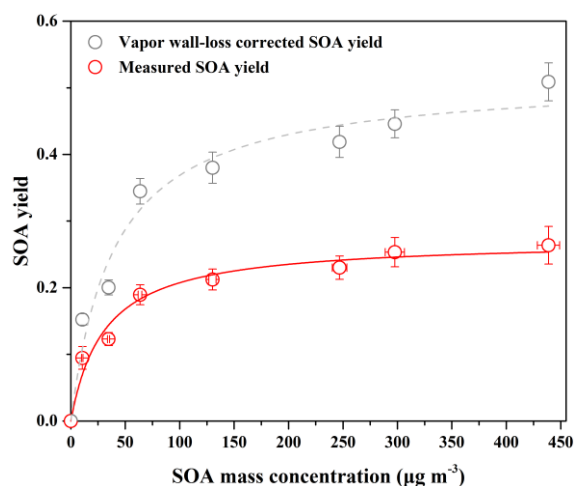
Exp.	[Guaiacol]$_0$ ($\mu g\ m^{-3}$)	$\triangle$[Guaiacol] ($\mu g\ m^{-3}$)[a]	Seed	[SO$_2$]$_0$ (ppbv)	[NO$_x$]$_0$ (ppbv)	[NO]$_0$ (ppbv)	RH (%)	T (K)	N$_S$ (m^{-3})[b]	D$_S$ (nm)[c]	C$_{seed}$ ($\mu g\ m^{-3}$)[d]	C$_{sulfate}$ ($\mu g\ m^{-3}$)[e]	S$_0$ ($\mu m^2\ cm^{-3}$)[f]	S$_f$ ($\mu m^2\ cm^{-3}$)[g]	$\overline{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ [h]	M$_o$ ($\mu g\ m^{-3}$)[i]	Yield (%)	OS$_C$[j]
1	375.19	335.94	–	–	58.3	44.5	40	302	–	–	–	–	–	1.25×10^3	0.82	63.62 ± 1.71	18.94 ± 1.49	0.11 ± 0.007
2	363.53	332.79	–	33	54.5	37.4	38	302	–	–	–	7.42	–	1.68×10^3	0.71	71.88 ± 1.43	21.60 ± 1.27	0.14 ± 0.006
3	370.12	335.58	–	56	57.3	41.8	38	302	–	–	–	17.89	–	2.04×10^3	0.61	78.59 ± 2.06	23.42 ± 1.80	0.18 ± 0.006
4	379.05	346.03	NaCl	–	58.8	40.7	39	302	10700	56	15.63	–	2.69×10^2	1.47×10^3	0.54	84.91 ± 2.01	24.54 ± 1.73	0.29 ± 0.007
5	378.44	339.34	NaCl	30	57.4	41.9	38	302	11300	58	13.84	7.51	2.64×10^2	2.32×10^3	0.43	90.89 ± 2.28	26.78 ± 1.97	0.30 ± 0.008
6	380.77	340.15	NaCl	54	60.1	46.1	39	301	11200	56	14.28	16.67	2.81×10^2	2.91×10^3	0.35	98.86 ± 2.11	29.06 ± 1.82	0.33 ± 0.008
7	373.57	340.86	(NH$_4$)$_2$SO$_4$	–	58.3	42.6	39	302	10400	53	15.45	–	2.75×10^2	1.53×10^3	0.62	79.44 ± 1.86	23.31 ± 1.59	0.20 ± 0.006
8	376.26	343.19	(NH$_4$)$_2$SO$_4$	33	56.8	38.9	38	302	10100	53	14.38	7.84	2.80×10^2	2.57×10^3	0.53	84.35 ± 2.09	24.58 ± 1.78	0.22 ± 0.007
9	381.33	341.01	(NH$_4$)$_2$SO$_4$	54	57.8	39.2	38	303	10700	51	14.90	17.25	2.82×10^2	3.10×10^3	0.44	89.92 ± 2.31	26.37 ± 1.98	0.23 ± 0.004

[a] The consumed guaiacol concentration at the end of each experiment. [b] N_S is the initial seed number. [c] D_S is the average diameter of seed particles.

[d] C_{seed} is the initial concentration of seed. [e] $C_{sulfate}$ is the sulfate concentration formed by SO_2 oxidation. [f] The initial surface area of seed particles.

[g] The final surface area of aerosol particles (seed + organic aerosol), measured by the SMPS. [h] The ratio of the average gas-particle partitioning

timescale ($\overline{\tau}_{g\text{-}p}$) over the course of experiment to the vapor wall deposition timescale ($\tau_{g\text{-}w}$). [i] M_o is the mass concentration of SOA. [j] OS_C is the

average oxidation state of carbon of SOA.

833

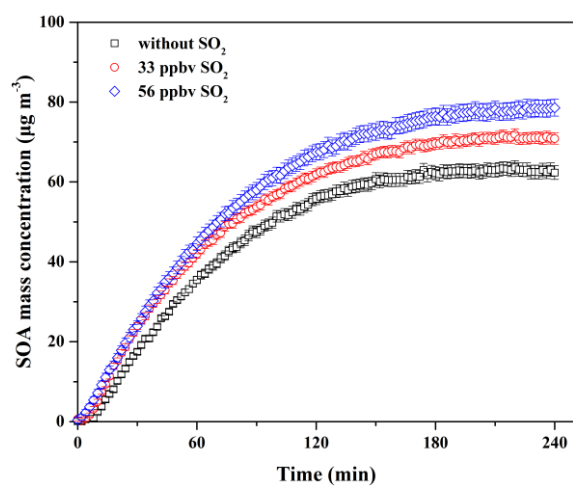
834 **Figure 1.** SOA yield as a function of SOA mass concentration (M_o) for guaiacol

835 photooxidation in the presence of NO_x at different guaiacol concentrations. The lines

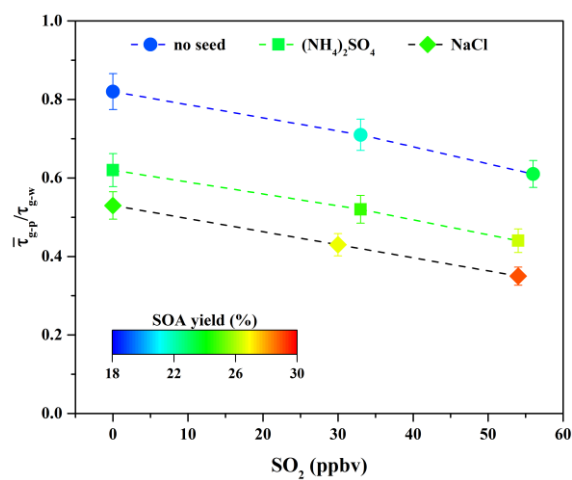
836 were fit to the experimental data using a one-product model. Values of α and $K_{om,i}$ used

837 to generate the solid line were (0.27 ± 0.01) and (0.033 ± 0.008), and their values for

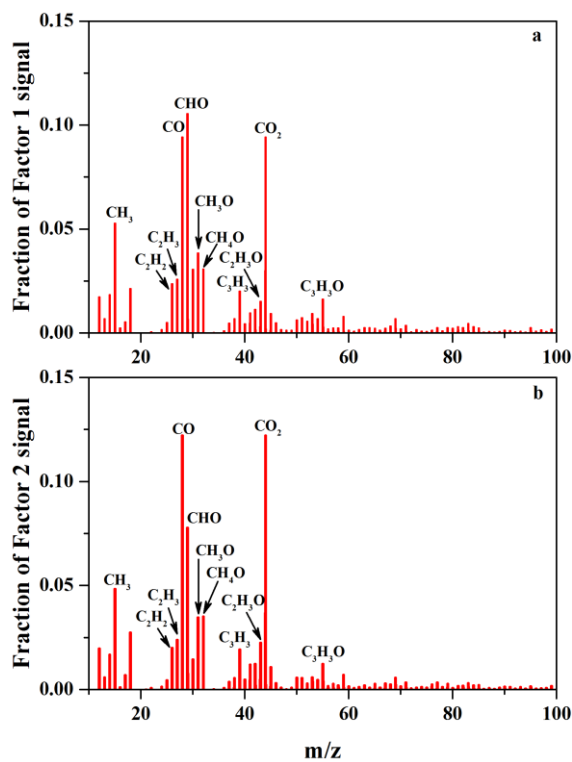
838 the dot line were (0.52 ± 0.03) and (0.025 ± 0.006), respectively.

839

840 **Figure 2.** Time-dependent growth curves of SOA mass concentration for guaiacol

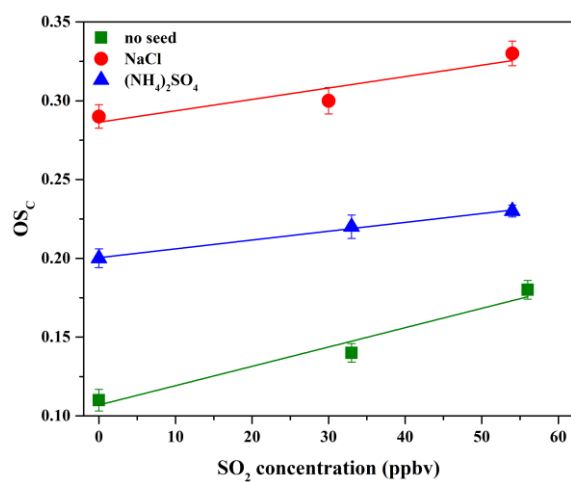
841 photooxidation at different SO_2 levels (Exps. 1−3 in Table 2).

842

843 **Figure 3.** Variations in $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio in the presence of various seed particles as a

844 function of SO_2 concentration.

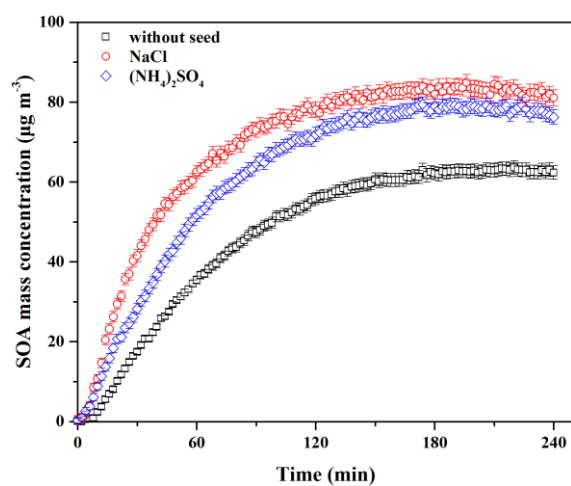
845

846 **Figure 4.** Mass spectra of Factor 1 (a) and Factor 2 (b) for the formed SOA identified

847 by applying PMF analysis to the AMS data, obtained at different SO_2 concentrations

848 over the courses of experiments.

849

850   **Figure 5.** OS_C of SOA formed in the presence of various seed particles as a function of

851   SO_2 concentration.

852

853 **Figure 6.** Time-dependent growth curves of SOA mass concentration for guaiacol

854 photooxidation in the presence of inorganic seed particles (Exps. 1, 4 and 7 in Table 2).

855

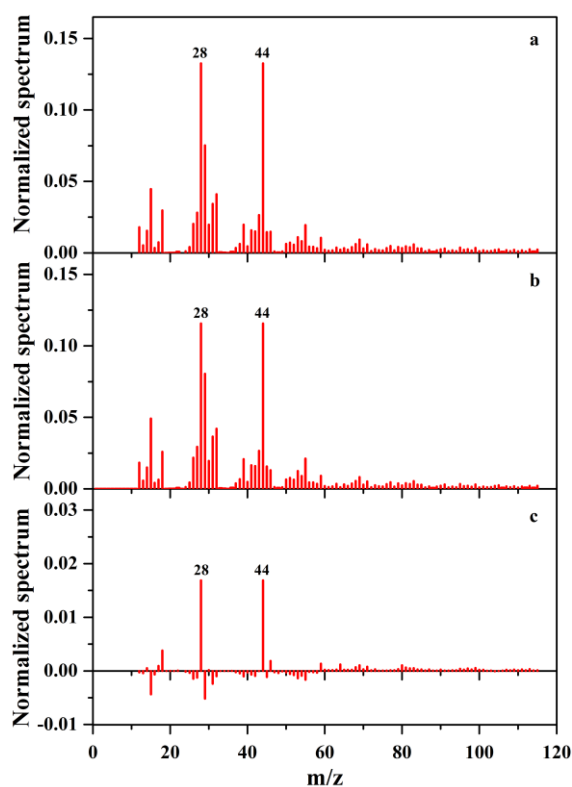
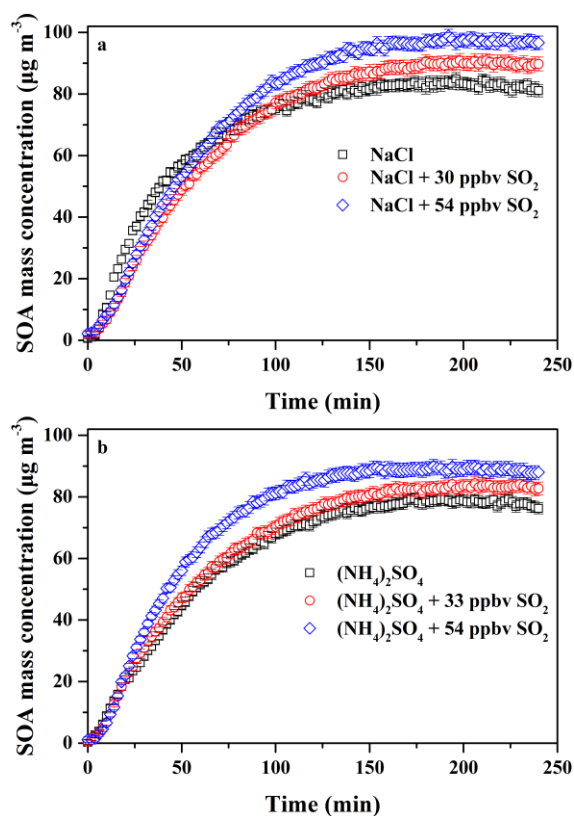



Figure 7. Mass spectra of SOA with NaCl (a) and $(NH_4)_2SO_4$ (b) as seed particles

obtained by the HR-ToF-AMS, as well as their difference mass spectrum (c) obtained

by a minus b.

859

860 **Figure 8.** Time-dependent growth curves of SOA mass concentration for guaiacol

861 photooxidation in the presence of SO_2 and inorganic seed particles (a: NaCl; b:

862 $(NH_4)_2SO_4$) (Exps. 4−9 in Table 2).