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Enhancement of Secondary Organic Aerosol Formation and its Oxidation State by SO_2 during Photooxidation of 2-Methoxyphenol

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Abstract. 2-Methoxyphenol (guaiacol) is derived from the lignin pyrolysis and taken as a potential tracer for wood smoke emissions. In this work, the effect of SO_2 at atmospheric levels (0−56 ppb) on secondary organic aerosol (SOA) formation and its oxidation state during guaiacol photooxidation was investigated in the presence of various inorganic seed particles (NaCl and $(NH_4)_2SO_4$). Without SO_2 and seed particles, SOA yields (9.46−26.37%) obtained at different guaiacol concentration (138.83−2197.36 μg m^{-3}) could be well expressed by a one-product model. The presence of SO_2 resulted in enhancing SOA yield by 14.05−23.66%. With $(NH_4)_2SO_4$ and NaCl seed particles, SOA yield was enhanced by 23.06% and 29.57%, respectively, which further increased significantly to 29.78−53.47% in the presence of SO_2, suggesting that SO_2 and seed particles have a synergetic contribution to SOA formation. It should be noted that SO_2 was found to be in favor of increasing the carbon oxidation state (OS_C) of SOA, indicating that the functionalization reaction should be more dominant than oligomerization reaction. In addition, the average N/C ratio of SOA was 0.037, which revealed that NO_x participated in the photooxidation process, consequently leading to the formation of organic nitrates. The experimental results demonstrate the importance of SO_2 on the formation processes of SOA and organosulfates, and also are helpful to further understand SOA formation from the atmospheric photooxidation of guaiacol and its subsequent impacts on air quality and climate.

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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 of fuel)$^{-1}$), 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} fuel (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), chlorine atom (Lauraguais et al., 2014a), and O_3 (El Zein et al., 2015) has been investigated, suggesting that its degradation by OH radicals and NO_3 radicals might be predominant

in the atmosphere. Meanwhile, several studies have reported the significant SOA formation from guaiacol oxidation by OH radicals (Ahmad et al., 2017; Lauraguais et al., 2014b; Ofner et al., 2011; Sun et al., 2010; Yee et al., 2013). However, SOA formation from the photooxidation of guaiacol in the presence of NO_x has not been determined yet, even though it has been recently reported that the atmospheric level of NO_x could reach up to close 200 ppb in the severely polluted climate in China (Li et al., 2017).

Although many studies concentrated on the SOA production from the oxidation of volatile organic compounds (VOCs), the reported SOA yields showed high variability for a given precursor (Chu et al., 2016, 2017; Ge et al., 2017a; Lauraguais et al., 2012, 2014b; Ng et al., 2007; Sarrafzadeh et al., 2016; Yee et al., 2013). This variability is mainly dependent on the numerous factors, e.g., pre-existing seed particles, SO_2 level, NO_x level, humidity, and temperature. Two of the critical factors are the impacts of pre-existing seed particles and SO_2 level on SOA formation (Chu et al., 2016, 2017; Ge et al., 2017a). In addition, the atmospheric concentration of SO_2 could be up to close 200 ppb in the severely polluted atmosphere in China, and SOA from biomass burning and sulfate formation could significantly contribute to severe haze pollution (Li et al., 2017). During the transport process, smoke plumes from biomass burning would be inevitably mixed with suspended particles (e.g., $(NH_4)_2SO_4$ particles), SO_2, and NO_x in the atmosphere. However, the influences of these co-existed pollutants on the transformation of guaiacol and its SOA formation are still unclear. For these reasons,

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the aim of this work was to investigate the SOA formation from guaiacol photooxidation in the presence of NO_x in a 30 m^3 indoor smog chamber, as well as the effect of SO_2 on SOA fromation with various inorganic seed particles.

2 Experimental section

The photooxidation experiments were performed in a 30 m^3 indoor smog chamber (4 m (high) × 2.5 m (wide) × 3 m (length)), which was built in a temperature-controlled room located at the Research Center for Eco-Environment Sciences, Chinese Academy of Sciences (RCEES-CAS). Its schematic structure is shown in Fig. S1. Briefly, 120 UV lamps (365 nm, Philips TL 60/10R) were taken as the light source with a NO_2 photolysis rate of 0.55 min^{-1}, which is comparable to the irradiation intensity at noon in Beijing (Chou et al., 2011). A maglev fan installed at the bottom center of the smog chamber was used to mix sufficiently the introduced gas species and seed particles. Temperature and relatively humidity (RH) in the chamber were (302 ± 1) K and (39 ± 1)%, respectively. Before each experiment, the chamber would be flushed by purified dry zero air for ~36 h with a flow rate of 100 L min^{-1} until the particle number concentration in the chamber was lower than 20 cm^{-3}.

Gas-phase guaiacol was firstly introduced into the chamber by purified dry zero air flowing through the gently heated injector with a known volume of pure liquid guaiacol until guaiacol fully vaporized. Its concentration in the chamber was online monitored by a proton-transfer reaction time-of-flight mass spectrometer (PTR-QiToF-MS) (Ionicon Analytik GmbH), and was calibrated by a commercial permeation tube (VICI

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AG INTERNATIONAL Valco Instruments Co., Inc.). When guaiacol concentration was stable, NO and SO_2 were introduced into the chamber by a gas controller using purified dry zero air as the carrier gas. Their concentrations were controlled by the injection time preset through the electromagnetic valve, and were measured by a NO_x analyzer (Model 42i-TL, Thermo Fisher Scientific, Inc.) and a SO_2 analyzer (Model 43i, Thermo Fisher Scientific Inc.), respectively. In this work, the initial ratio (V/V) of guaiacol concentration to NO_x concentration in the chamber was similar in all experiments (~1.2) (Tables 1 and 2). In addition, sodium chloride (NaCl) and ammonium sulfate ($(NH_4)_2SO_4$) were used as the inorganic seeds. The seed aerosols in the chamber were generated by the atomization of a 0.02 M aqueous solution. Through atomization, the size distribution of seed particles peaked at 51−58 nm with a number concentration of 10100−11400 cm^{-3} was achieved (Table 2). After gas species and seed particles in the chamber were mixed well, the photooxidation experiment was carried out with the fan turned off. In this work, the OH concentrations in the chamber were (1.3−2.2) × 10^6 molecules cm^{-3}, calculated based on the degradation rate (7.53 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}) of guaiacol with OH radicals (Coeur-Tourneur et al., 2010a). The chemicals and gas samples used in this work were described in Supporting Information.

An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was applied to online measure the chemical composition of particles and the non-refractory submicron aerosol mass (DeCarlo et al., 2006). The size distribution and concentration of particles were monitored by a scanning mobility particle sizer (SMPS),

which is composed of a differential mobility analyzer (DMA) (Model 3082, TSI Inc.) and a condensation particle counter (CPC) (Model 3776, TSI Inc.). Assuming that particles are spherical and non-porous, the average particle density could be calculated to be 1.4 g cm^{-3} using the equation $\rho=d_{va}/d_m$ (DeCarlo et al., 2004), where d_{va} is the mean vacuum aerodynamic diameter measured by HR-ToF-AMS and d_m is the mean volume-weighted mobility diameter measured by SMPS. The mass concentration of particles measured by HR-ToF-AMS was corrected by SMPS data in this work using the same method as Gordon et al. (2014). In this work, the wall loss rate (k_{dep}) of $(NH_4)_2SO_4$ particles could be expressed as $k_{dep} = 4.15 \times 10^{-7} \times D_p^{1.89} + 1.39 \times D_p^{-0.88}$ (D_p is the particle diameter (nm)), which was measured according to the literature method (Takekawa et al., 2003) and used to correct the wall loss of SOA. In addition, its wall loss rate was determined at predetermined time intervals, which only had a slight change among different experiments.

3 Results and discussion

3.1 SOA yields

A series of experiments were conducted at different guaiacol/NO_x concentrations under atmospheric pressure. The experimental conditions and results are shown in Table 1. SOA yield was calculated to be the ratio of SOA mass concentration (M_0, μg m^{-3}) to the consumed guaiacol concentration (Δ[guaiacol], μg m^{-3}) at the end of each experiment (Kang et al., 2007). The results showed that SOA yield was dependent on the initial guaiacol concentration. Higher precursor concentration would result in higher amount

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of condensable products, subsequently enhancing SOA formation (Lauraguais et al., 2012). In addition, it should be noted that SOA mass could directly affect the gas/particle partitioning via acting as the adsorption medium of oxidation products, thus higher SOA mass generally leads to higher SOA yield (Lauraguais et al., 2014b).

SOA yield (Y) could be represented by a widely-used semi-empirical model based on the absorptive gas-particle partitioning of semi-volatile products, typically calculated using the following equation (Odum et al., 1996):

$$Y = \sum_i M_0 \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_0} \quad (1)$$

where α_i is the mass-based stoichiometric coefficient for the reaction producing the semi-volatile product i, $K_{om,i}$ is the gas-particle partitioning equilibrium constant, and M_0 is the total aerosol mass concentration.

The yield curve for guaiacol photooxidation is shown in Fig. 1, obtained by plotting the SOA yield data in Table 1 according to Eq. (1). The yield data were accurately reproduced by a one-product model (R^2 = 0.97), while two or more products used in the model did not significantly improve the fitting quality. The obtained values of α_i and $K_{om,i}$ for one-product model were (0.27 ±0.01) and (0.033 ±0.008) $m^3\ \mu g^{-1}$, respectively. In previous studies, the one-product model was widely applied to describe SOA yields from the oxidation of aromatic compounds including methoxyphenols (Coeur-Tourneur et al., 2010b; Lauraguais et al., 2012, 2014b). In this work, this simulation suggests that the products in SOA have similar values of α_i and $K_{om,i}$, i.e., the obtained α_i and $K_{om,i}$ are the average vaules. The plot shown in Fig. S2 is the relationship between M_0 versus

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165 Δ[guaiacol], of which slope (0.28) is slightly higher than α_i value (0.27). This suggests
166 that the formed low-volatile products almost completely paritioned on the particle-
167 phase according to the theoretical partition model (Lauraguais et al., 2012, 2014b).
168 In the previous studies, the significant SOA formation from the OH-initiated
169 reaction of guaiacol has been reported (Lauraguais et al., 2014b; Sun et al., 2010; Yee
170 et al., 2013). In this work, SOA yields for guaiacol photooxidation range from
171 9.46−26.37%, shown in Table 1. This range overlaps SOA yields of 0.6−87% for
172 guaiacol oxidation under high NO_x condition (~10 ppm NO), reported by Lauraguais et
173 al. (2014b), using CH_3ONO as the OH source. Under low NO_x conditions (<5 ppb NO),
174 SOA yields for guaiacol oxidation were in the range of 44−50%, reported by Yee et al.
175 (2013) using H_2O_2 as the OH source and $(NH_4)_2SO_4$ as seed particles; they also
176 indicated that high NO_x concentration (>200 ppb NO) played an opposite role in SOA
177 formation. Compared to the reported results, SOA yields obtained in this work were
178 lower, which might be explained by the different experimental conditions, e.g., OH
179 concentrations and seed particles. For example, Sun et al. (2010) have reported that
180 SOA mass formed from the aqueous-phase photochemical reaction of guaiacol in the
181 presence of H_2O_2 is about one-fold higher than that in the absence of H_2O_2.
182 In addition, the average N/C ratio of SOA for guaiacol photooxidation in the
183 presence of NO_x is 0.037, calculated according to the element analysis by HR-ToF-
184 AMS. This indicates that NO_x incorporates in guaiacol photooxidation. This
185 phenomenon is well supported by the previous results, which reported that the nitro-

substituted products are the main products of the OH-initiated reaction of guaiacol in the presence of NO_x (Ahmad et al., 2017; Lauraguais et al., 2014b). The relative low volatility of these products could reasonably contribute to SOA formation (Duporté et al., 2016; Liu et al., 2016a). The average NO^+/NO_2^+ ratio of SOA from guaiacol photooxidation is 4.08, which is within the range of 3.82−5.84 for organic nitrates of SOA from the photooxidation of aromatics (Sato et al., 2010). In this work, the measured NO^+/NO_2^+ ratios for inorganic nitrates are in the range of 2.06 to 2.54, determined by HR-ToF-AMS using ammonium nitrate as calibration sample. The relative abundance of organic nitrates could be estimated from the average N/C ratio. Assuming that the oxidation products in the SOA retain 7 carbon atoms, the yield of organic nitrates is 25.9%, which is the upper limit due to the possible C−C bond scission during photooxidation process.

3.2 Effect of SO_2 on SOA formation

In China, atmospheric SO_2 concentration is always in the range of several to dozens of ppb, while in the severely polluted atmosphere it could be up to close 200 ppb (Han et al., 2015; Li et al., 2017). In addition, a recent field measurement study has reported that the decrease of biogenic SOA mass concentration in the atmosphere has a postive correlation with SO_2 emission controls (Marais et al., 2017). Therefore, the effect of SO_2 at atmospheric levels on SOA formation from guaiacol photooxidation under atmospheric NO_x conditions was investigated. The experimental conditions and results are shown in Table 2. The formation of SOA, sulfate, and nitrate as a function of SO_2

concentration for guaiacol photooxidation is shown in Fig. S3. As illustrated in Fig. 2, M_0 for the blank experiment (Expt. 1 in Table 2) increased from 63.62 to 71.88 and 78.59 μg m^{-3}, enhanced by 12.98% and 23.53%, respectively, when SO_2 concentration raised from 0 to 33 and 56 ppb. The corresponding SOA yield increased by 14.05% and 23.66%, respectively. The similar results were reported by previous studies (Kleindienst et al., 2006; Lin et al., 2013; Liu et al., 2016b), which observed the significant enhancements of SOA yields for VOCs oxidation and the photochemical aging of gasoline vehicle exhaust in the presence of SO_2.

The average carbon oxidation state (OS_C = 2O/C – H/C) of OA is widely used to represent the oxidation degree of atmospheric OA, because it takes into account the saturation level of carbon atoms in the OA (Kroll et al., 2011). As shown in Table 2, increasing SO_2 concentration (0−56 ppb) leads to the increase of OS_C (0.11−0.18). In order to further identify the effect of SO_2 on the chemical properties of SOA, positive matrix factorization (PMF) analysis for the AMS data obtained at different SO_2 concentrations was carried out. Two factors were obtained from the PMF analysis, and their mass spectra are shown in Fig. 3. The organic mass fraction of m/z 44 (CO_2^+), named f_{44}, was 0.122 for Factor 2, which is higher than that (0.094) for Factor 1. Therefore, Factor 2 was tentatively assigned to the more-oxidized SOA, while Factor 1 was the less-oxidized SOA (Ulbrich et al., 2009). During the photooxidation process, these two factors had different variations as a function of reaction time. As shown in Fig. S4, Factor 1 decreased along with the reaction, while Factor 2 had an opposite

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trend. Compared to Expts. 1 and 2 in Table 2, the higher fraction of Factor 2 mass obtained at 56 ppb SO_2 (Expt. 3 in Table 2) suggests that the formed SOA mainly consists of more-oxidized products with relatively low volatility, which is well supported by the obtained OS_C of SOA.

Previous studies mostly reported that the enhancement of SOA yield in the presence of SO_2 was ascribed to the functionalization and oligomerization reactions (Cao and Jang, 2007; Jaoui et al., 2008 ; Liu et al., 2016b; Xu et al., 2016). If the oligomerization reaction plays a predominant role in the presence of SO_2 which will lead to particle phase H_2SO_4, the oxidation state of SOA will decrease. Nevertheless, we observed that SO_2 not only enhanced SOA yields, but also resulted in higher OS_C (Table 2 and Fig. 4). This suggests that the functionalization reaction should be predominant with SO_2, which leads to higher OS_C of products with low molecular weight (MW) (Ye et al., 2018), consequently resulting in an overall increase in OS_C and SOA yields. More recently, Ye et al. (2018) also found the similar results in the ozonolysis of limonene. Fig. S5 shows the differences among the normalized mass spectra of SOA formed at different SO_2 concentrations. As shown in Fig. S5a, the signal fractions from the low-MW species are enhanced significantly in the presence of SO_2, and are much higher than those from the high-MW species (m/z >300). The similar results are also observed in Fig. S5b when increasing SO_2 concentration. In other words, SO_2 played a more important role in the formation of organosulfate and the formation or uptake of low-WM species, compared to the formation of high-MW species (i.e., oligomerics). In this

work, organosulfate concentration increased with the increase of SO_2 concentration, and was in the range of 2.1−4.3 ng m^{-3}, calculated using the method described by Huang et al. (2015). This concentration range is close to those derived from the atmospheric oxidation of polycyclic aromatic hydrocarbons and alkane (Riva et al., 2015; Meade et al., 2016). Fig. S6 is the examples of the ions (i.e., CSO^+, $CH_3SO_2^+$, and $CH_3SO_3^+$) in the calibration of methyl sulfate obtained at 56 ppb SO_2. On the other hand, 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), which also results in the increase of OS_C. In addition, Krapf et al. (2016) have indicated that peroxides in SOA are unstable and liable to decompose into volatile compounds, consequently leading to decrease SOA yield and OS_C. But, Ye et al. (2018) recently found that the reactions of SO_2 with organic peroxides were the dominant sink of SO_2, initiated by the heterogeneous uptake of SO_2 under humidity condition. These reactions would result in the formation of organosulfates, consequently increasing SOA yields and OS_C.

In addition, it has been reported that the formed sulfate by SO_2 oxidation not only serves as the substrate for the condensation of low-volatility vapors (Jaoui et al., 2008), but also increases the surface areas of particles (Xu et al., 2016). These roles of sulfate are also favorable for increasing SOA yields. In the presence of SO_2, however, we did not observe the particle mode attributed to H_2SO_4 formed from SO_2 oxidation. Therefore, we calculated the surface area concentration of aerosol particles at the end time. As shown in Table 2, the final surface area of aerosol particles formed via guaiacol

photooxidation increased from 1.25 $\times 10^3$ to 1.68 $\times 10^3$ and 2.04 $\times 10^3$ μm^2 cm^{-3} when SO_2 concentration increased from 0 to 33 and 56 ppb. The increased surface area could be in favor of outcompeting the wall loss for low-volatility vapors produced from guaiacol photooxidation, i.e., more low-volatility vapors will be diverted from wall loss to the particles, consequently increasing SOA yields (Kroll et al., 2007). But, the surface area of aerosol particles is still much lower than that (1.97 $\times 10^6$ μm^2 cm^{-3}) of smog chamber used in this work. Therefore, the enhancement of SOA yields by the increased surface area from H_2SO_4 by SO_2 oxidation might be limited.

3.3 Effect of inorganic seed particles on SOA formation

Seed particle is one of the critical factors influencing SOA formation (Ge et al., 2017a), thus the effects of inorganic seeds (NaCl and $(NH_4)_2SO_4$) on SOA formation from guaiacol photooxidation were investigated. As shown in Fig. 5, the presence of inorganic seed particles could accelerate SOA growth rate at the initial stage of photooxidation, followed by the decrease of growth rate along with the reaction, because the presence of inorganic seeds could promote the condensation of SOA-forming organic products and consequently increase SOA formation (Yee et al., 2013). The results showed that M_0 for the blank experiment (Expt. 1 in Table 2) increased from 63.62 to 79.44 and 84.91 μg m^{-3} (Table 2), enhanced by 24.87% and 33.46%, respectively, with $(NH_4)_2SO_4$ and NaCl seed particles. The corresponding SOA yield increased by 23.06% and 29.57%, respectively. In previous work, the similar results about the enhancements of SOA formation by NaCl and $(NH_4)_2SO_4$ seed particles were

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

As shown in Table 2 and Fig. 5, the SOA mass concentration in the presence of NaCl seed particles is higher than that in the presence of $(NH_4)_2SO_4$ seed particles. In addition, OS_C of SOA in the presence of NaCl seed particles is 0.29, slightly higher than that (0.20) in the presence of $(NH_4)_2SO_4$ seed particles. Recently, it has been also reported that the presence of $(NH_4)_2SO_4$ and $NaNO_3$ seed particles could enhance significantly the oxidation state of SOA, compared to without seed particles (Huang et al., 2016). In this work, the experimental conditions for seed experiments are almost the same (Table 2), including reactant concentration, temperature, RH, and the number and diameter of seed particles. Therefore, the differences in the yield and oxidation state of SOA were reasonably resulted from the different chemical compositions of SOA with different inorganic seeds. Fig. 6 shows the mass spectra of SOA in the presence of NaCl and $(NH_4)_2SO_4$ seed particles obtained by HR-ToF-AMS, as well as their difference mass spectrum. As shown in Fig. 6, f_{44} and the organic mass fraction of m/z 28 (CO^+) for SOA in the presence of NaCl seed particles are both higher than those in the presence of $(NH_4)_2SO_4$ seed particles, while the mass fractions of CH_3 and CHO fragments are both lower. The m/z 44 ion (CO_2^+) is mainly contributed from acids or acid-derived species, such as esters (Ng et al., 2011). The higher f_{44} of SOA with NaCl than $(NH_4)_2SO_4$ seed particles suggests that the distribution of highly oxidized small carboxylic acids onto seed particles plays an important role in SOA formation, consequently resulting in higher oxidation state of SOA (Ng et al., 2011; Huang et al.,

2016). Compared to $(NH_4)_2SO_4$, the hygroscopicity of NaCl is stronger (Ge et al., 2017a; Gysel et al., 2002). The molar ratio of H_2O to NaCl is about 0.1 at 40% RH, and water is mainly adsorbed on NaCl particles (Weis and Ewing, 1999). Thus, the greater water content on the particle surface could facilitate the uptake of highly oxidized small carboxylic acids onto NaCl particles, which might be potentially explain the higher SOA oxidation state observed in the presence of NaCl seed particles (Huang et al., 2016). The adsorbed acid products would also generate H^+ ions, which could catalyze heterogeneous reactions to produce more-oxidized products or oligomerics with relatively low volatility (Fig. S7), consequently resulting in the enhancement of SOA formation (Huang et al., 2013, 2017; Cao and Jang, 2007; Jaoui et al., 2008; Liu et al., 2016b; Xu et al., 2016).

In addition, the possible formation of Cl atoms from the photolysis of nitryl chloride ($ClNO_2 \xrightarrow{h\nu} Cl + NO_2$, k_1 = ~10^{-4} s^{-1}) (Mielke et al., 2011) and the reaction of OH radical with Cl^- ($Cl^- + OH \rightarrow Cl + OH^-$, k_2 = ~10^9 M^{-1} s^{-1}) (Fang et al., 2014) would also initiate a series of reactions to oxidize SOA composition, which might be another reason for higher OS_C observed with NaCl seed particles. According to the rate constant (10^9 M^{-1} s^{-1}) (Fang et al., 2014), the uptake coefficient (3.4×10^{-3}) of OH radicals on NaCl particles (Park et al., 2008), and the concentrations of OH radicals and Cl^-, the concentration of Cl atoms from the reaction of OH radical with Cl^- was estimated to be less than 38 molecules cm^{-3}, which was much higher than that from the photolysis of $ClNO_2$ due to the slow photolysis rate constant of ~10^{-4} s^{-1} (Mielke et

al., 2011). Compared to OH concentration in the chamber, the oxidation of SOA composition by Cl atoms should be insignificant.

3.4 Synergetic effect of SO_2 and inoragnic seed particles on SOA formation

According to the former results obtained in this work, it is clearly known that SO_2 and inorganic seed particles both have a positive role in enhancing SOA formation. Therefore, their possible synergetic effects on SOA formation were investigated. In view of the experiments performed under the comparable conditions (Table 2), the results should be reasonably reliable. As shown in Fig. 7, the addition of SO_2 into the chamber in the presence of inorganic seed particles significantly promotes SOA formation from guaiacol photooxidation. When SO_2 concentration raised from 0 to 30 and 54 ppb in the presence of NaCl seed particles, M_0 was enhanced by 42.86% and 55.39%, respectively, and the corresponding SOA yield increased by 41.43% and 53.47%, compared to the blank experiment (Expt. 1 in Table 2). For $(NH_4)_2SO_4$ seed particles, M_0 was enhanced by 32.58% for 33 ppb SO_2 and 41.34% for 54 ppb SO_2, respectively, and the corresponding SOA yield increased by 29.78% and 39.24%. Therefore, inorganic seed particles and SO_2 have a synergestic effect on SOA formation.

As shown in Table 2 and Fig. 4, it should be noted that OS_C of SOA increases in the presence of SO_2. Fig. S8 shows the mass spectra of SOA with NaCl and $(NH_4)_2SO_4$ as seed particles at different SO_2 concentrations obtained by HR-ToF-AMS. As illustrated in Fig. S8, SO_2 addition is in favor of increasing the value of f_{44}, suggesting that more products with higher OS_C are produced by the functionalization reaction (Ye

et al., 2018). Meanwhile, Table 2 shows that the final surface area of aerosol particles increased in the presence of SO_2, which played a positive role in diverting more low-volatility vapors from wall loss to the particles, consequently enhancing SOA yields (Kroll et al., 2007). But, this impact should be insignificant due to the much lower surface area of aerosol particles compared to that (1.97×10^6 μm^2 cm^{-3}) of smog chamber in this work. In addition, the presence of inorganic seeds could promote the condensation of SOA-forming organic products and the heterogeneous uptake of SO_2 (Yee et al., 2013), providing favorable conditions for the following oxidation reactions. Meanwhile, the higher hygroscopicity of NaCl than $(NH_4)_2SO_4$ might be helpful to dissolve more acid substances on NaCl particle surface (e.g., H_2SO_4 and organic acid), especially in the presence of SO_2, which might be helpful to catalyze heterogeneous reactions (Cao and Jang, 2007; Huang et al., 2013, 2017; Jaoui et al., 2008; Liu et al., 2016b; Xu et al., 2016). Figs. S9 and S10 show the differences among the normalized mass spectra of SOA formed at different SO_2 concentrations with various seed particles, which both shows that the signal fractions from the low-MW species are increased significantly in the presence of SO_2, and are much higher than those from the high-MW species (m/z >300). Compared to Expts. 2 and 3 in Table 2 with no seed particles, organosulfate concentrations formed with seed particles were similar and in the range of 2.2−4.6 ng m^{-3}, which might be caused by the similar SO_2 concentrations applied for experiments. With NaCl and $(NH_4)_2SO_4$ as seed particles, SOA yields and OS_C both also increased with the increase of SO_2, suggesting that the functionalization reaction

should be more dominant than oligomerization reaction during photooxidation process.

4 Conclusions and atmospheric implications

In this work, SOA formation from guaiacol photooxidation in the presence of NO_x was investigated in a 30 m^3 smog chamber. SOA yields for guaiacol photooxidation were in the range of 9.46−26.37% at the initial guaiacol concentrations ranging from 138.83−2197.36 μg m^{-3}, and could be expressed well by a one-product model. The presence of SO_2 could increase SOA yield and OS_C, indicating that the functionalization reaction should be more dominant than oligomerization reaction. Meanwhile, the similar effect of SO_2 was also observed with NaCl and $(NH_4)_2SO_4$ seed particles. But, SOA yield and OS_C in the presence of NaCl seed particles were both slightly higher than those in the presence of $(NH_4)_2SO_4$ seed particles. In addition, the results indicated the synergetic contribution of SO_2 and inorganic seed particles to SOA formation. The average N/C ratio (0.037) of SOA suggested that NO_x participated in the process of guaiacol photooxidation, resulting in the formation of organic nitrates.

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 attenion on 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 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.

Competing interests

The authors declare that they have no conflict of interest.

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Atmospheric Chemistry and Physics Discussions

671 **Table 1.** Experimental condtions and results for guaiacol photoxidation in the presence

672 NO_x.

Expt.	$[Guaiacol]_0$ (μg m^{-3})	△[Guaiacol] (μg m^{-3})[a]	$[NO_x]_0$ (ppb)	$[NO]_0$ (ppb)	RH (%)	T (K)	M_0 (μg m^{-3})[b]	Yield (%)
1	136.83	112.34	25.1	13.2	39	302	10.63	9.46
2	309.06	282.33	52.7	34.4	38	302	34.72	12.30
3	375.19	335.94	58.3	44.5	40	302	63.62	18.94
4	718.49	613.25	116.7	98.5	38	302	130.19	21.23
5	1321.25	1116.20	209.2	184.1	39	302	256.88	23.01
6	1470.66	1175.03	248	200	38	302	297.65	25.33
7	2197.36	1664.29	335	286	38	302	438.82	26.37

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

674 [b] M_0 is the mass concentration of SOA.

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

Expt.	$[Guaiacol]_0$ ($\mu g\ m^{-3}$)	$\triangle$[Guaiacol] ($\mu g\ m^{-3}$)[a]	Seed	$[SO_2]_0$ (ppb)	$[NO_x]_0$ (ppb)	$[NO]_0$ (ppb)	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]	M_0 ($\mu g\ m^{-3}$)[h]	Yield (%)	OS_C[i]
1	375.19	335.94	–	–	58.3	44.5	40	302	–	–	–	–	–	1.25×10^3	63.62	18.94	0.11
2	363.53	332.79	–	33	54.5	37.4	38	302	–	–	–	7.42	–	1.68×10^3	71.88	21.60	0.14
3	370.12	335.58	–	56	57.3	41.8	38	302	–	–	–	17.89	–	2.04×10^3	78.59	23.42	0.18
4	379.05	346.03	NaCl	–	58.8	40.7	39	302	10700	56	15.63	–	2.69×10^2	1.47×10^3	84.91	24.54	0.29
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	90.89	26.78	0.30
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	98.86	29.06	0.33
7	373.57	340.86	$(NH_4)_2SO_4$	–	58.3	42.6	39	302	10400	53	15.45	–	2.75×10^2	1.53×10^3	79.44	23.31	0.20
8	376.26	343.19	$(NH_4)_2SO_4$	33	56.8	38.9	38	302	10100	53	14.38	7.84	2.80×10^2	2.57×10^3	84.35	24.58	0.22
9	381.33	341.01	$(NH_4)_2SO_4$	54	57.8	39.2	38	303	10700	51	14.90	17.25	2.82×10^2	3.10×10^3	89.92	26.37	0.23

676 [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.

677 [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.

678 [g] The final surface area of aerosol particles (seed + organic aerosol), measured by SMPS. [h] M_0 is the mass concentration of SOA. [i] OS_C is the

679 average oxidation state of carbon of SOA.

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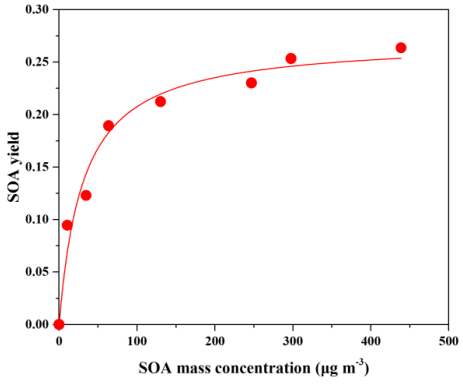

680

681 **Figure 1.** SOA yield as a function of SOA mass concentration (M_0) for guaiacol

682 photooxidation in the presence of NO_x at different guaiacol concentrations. The solid

683 lines was fit to the experimental data using a one-product model. Values of α and $K_{om,i}$

684 used to generate the solid line were (0.27 ± 0.01) and (0.033 ± 0.008) in this work.

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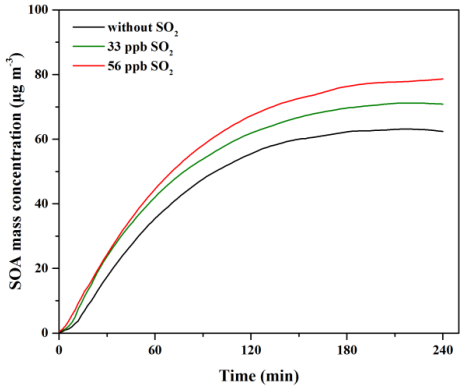

685

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

687 photooxidation at different SO_2 levels (Expts. 1−3 in Table 2).

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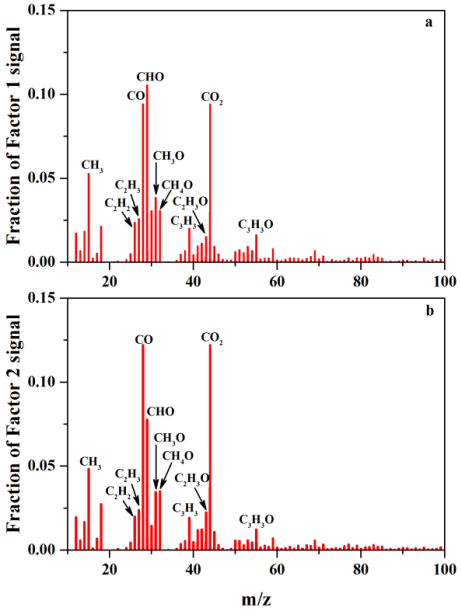

688

689 **Figure 3.** Mass spectra of Factor 1 (a) and Factor 2 (b) for the formed SOA identified

690 by applying PMF analysis to the AMS data.

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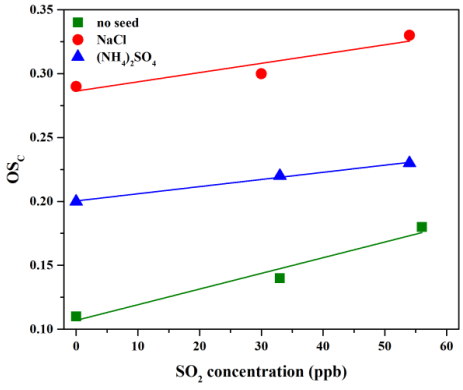

691

692 **Figure 4.** OS_C of SOA formed in the presence of various seed particles as a function of

693 SO_2 concentration.

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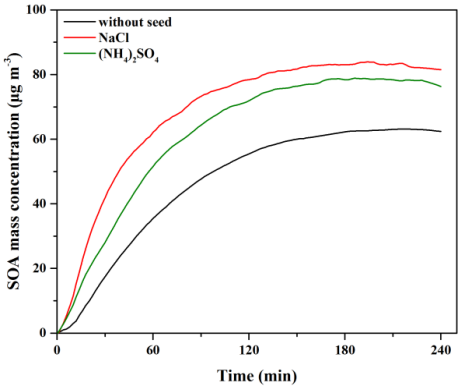

694

695 **Figure 5.** Time-dependent growth curves of SOA mass concentration for guaiacol

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

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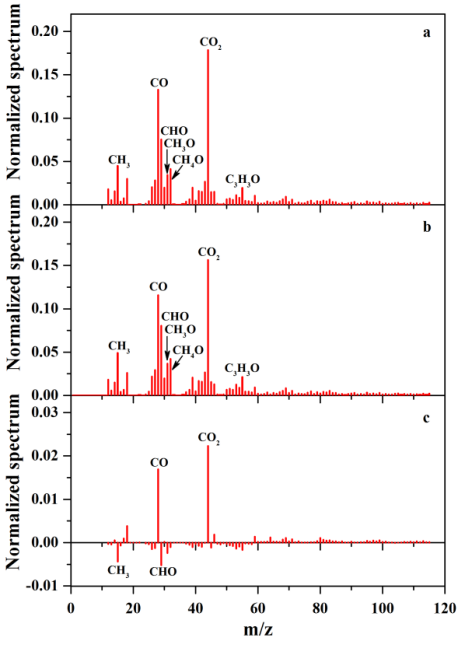

Figure 6. Mass spectra of SOA with NaCl (a) and $(NH_4)_2SO_4$ (b) as seed particles obtained by HR-ToF-AMS, as well as their difference mass spectrum (c) obtained by a minus b.

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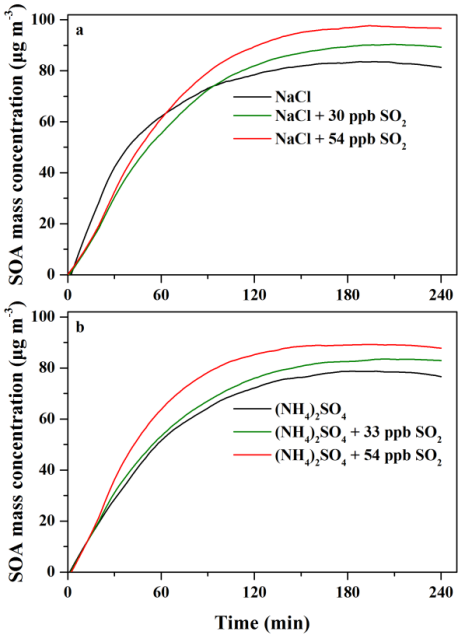

Figure 7. Time-dependent growth curves of SOA mass concentration for guaiacol photooxidation in the presence of SO_2 and inorganic seed particles (a, NaCl; b, $(NH_4)_2SO_4$) (Expts. 4−9 in Table 2).