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 #1's comments

General comment: This is an interesting manuscript describing experiments on SOA formation from guaiacol oxidation by OH radicals in various chamber conditions (seed concentrations, NO_x levels, and SO_2 levels). While the experimental results are certainly worth publishing, the interpretation of those results is extremely speculative and, while plausible, for the most part unsubstantiated. This discussion needs to be significantly restructured.

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: My first issue is with the discussion around seeds. First and foremost, seeds provide surface area for condensation. It is essential that the authors consider the microphysics of condensation. Specifically, the authors can integrate the smps data to determine the "Fuchs corrected surface area" and relate that to the condensation sink of vapors of some chosen molecular weight (conventionally, 98 g/mole is common because that is H_2SO_4, but a number more like 300 g/mole may be more representative of condensable organic vapors). It is essential to consider the condensation sink at the onset of precursor oxidation as well as the average condensation sink over the course of an experiment. The most straightforward consequence of having no seeds at all (so-called "nucleation" experiments) is an "induction" period first described by Kroll et al EST 2005). Simply put, ELVOC and LVOC products driving nucleation and growth are lost to the chamber walls with the vapor loss timescale (which MUST also be reported here, for some species with a known diffusion constant - it scales with sqrt(D)), and so the overall SOA mass yields are reduced because of this wall loss. This induction period is clearly evident in Figure 2. Because of this, the "null hypothesis" for the seed effects is that the condensation sink of the seeds differs for the different seed types, and that the condensation sink additionally grows when SO_2 is also oxidized, causing 20 ug/m^3 or so of added sulfate condensation as shown in Fig S3. Until there is a coherent discussion of the condensation sink for these various experiments (and, ideally, the ratio of the condensation sink to the vapor wall-loss timescale), it is difficult to assess all of the other interpretation.

Response to comment 1: Thank you very much. According to your valuable suggestions, the ratio of the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment to the vapor wall-loss timescale ($\tau_{\text{g-w}}$) under different experimental conditions in this work was calculated and discussed in the revised manuscript. Based on $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio, the underestimation of SOA yield caused by vapor wall loss could be determined. The descriptions of $\overline{\tau}_{\text{g-p}}$ and $\tau_{\text{g-w}}$ have been added in the revised manuscript (Lines 164-167), and their calculation methods have been added in the revised Supplement.

Under the experimental conditions without SO_2 and seed particles (Section 3.1), the determined SOA yields were underestimated by a factor of ~2 times in this work according to the ratios of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ (0.61−0.93), suggesting that vapor wall loss in the chamber could significantly affect SOA formation. The similar results were reported previously by Zhang et al. (2014), who indicated that SOA yields for toluene photooxidation were substantially underestimated by factors as much as 4 times, caused by vapor wall loss. The vapor wall-loss corrected SOA yields were in the range of (15.24 ± 0.85)% to (50.89 ± 2.87)%, and could also be reproduced by a one-product model ($R^2 = 0.96$). As shown in Sections 3.2-3.4 in the revised manuscript, the decreasing trend of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratios in the presence of seed particles and SO_2 have been observed (shown in Figure R1), suggesting that more intermediate products were partitioned onto particle phase, consequently increasing SOA yields. The details about the revisions in the manuscript were pointed out as follows.

In addition, the time-series variations in the concentrations of sulfate in the presence of different SO_2 concentrations and seed particles were added in the Supplement (Figure R2). As shown in Figure R2, the sulfate concentration increased with the increase of SO_2 concentration, suggesting that more sulfate aerosols were produced via SO_2 oxidation.

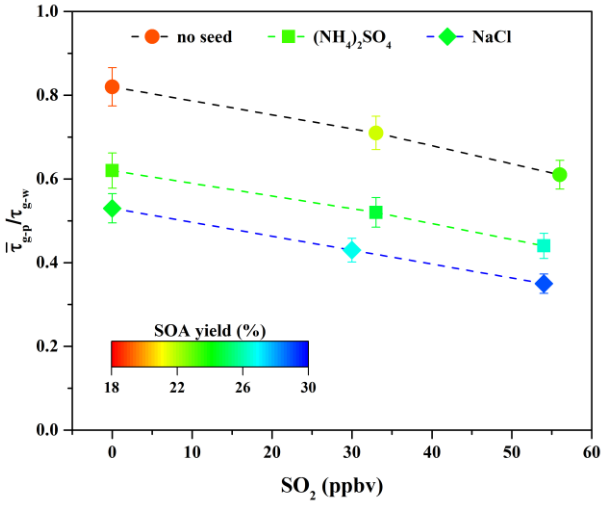

Figure R1. Variations in $\overline{\tau}_{g\text{-}p} / \tau_{g\text{-}w}$ ratio in the presence of various seed particles as a function of SO_2 concentration.

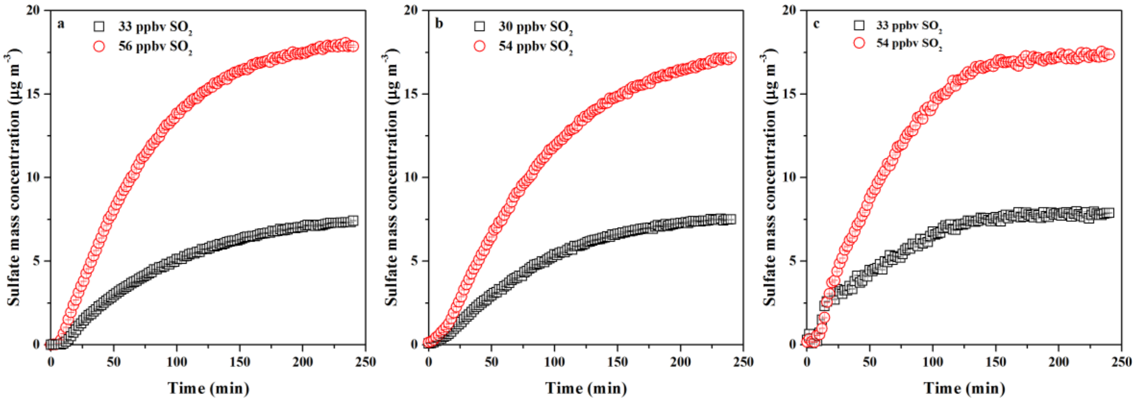

Figure R2. Variations in the concentrations of sulfate as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$). The sulfate concentrations shown in Figure R1c is the net concentrations formed via SO_2 oxidation, e.g., do not include the $(NH_4)_2SO_4$ concentration added in the smog chamber.

Revisions in the manuscript:

1. Abstract

Lines 25-27, Add: "According to the ratio of the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment to the vapor wall deposition timescale ($\tau_{\text{g-w}}$), the determined SOA yields were underestimated by a factor of ~2 times."

Lines 32-34, Add: "The decreasing trend of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio in the presence of seed particles and SO_2 suggested that more SOA-forming vapors were partitioned onto particle phase, consequently increasing SOA yields."

2. Experimental section: The descriptions of vapor wall-loss correction have been added in the revised manuscript as follows (**Lines 158-167**):

2.4 Vapor wall-loss correction

Previous studies have indicated that the losses of SOA-forming vapors to chamber wall can result in the substantial and systematic underestimation of SOA (Zhang et al., 2014, 2015). Therefore, SOA yields obtained in this work were also corrected by vapor wall loss. The effect of vapor wall deposition on SOA yields mainly depends on the competition between the uptake of organic vapors by aerosol particles and the chamber wall (Zhang et al., 2015). Thus, the ratio of the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment to the vapor wall deposition timescale ($\tau_{\text{g-w}}$) could be reasonably used to evaluate the underestimation of SOA yields. The detailed calculation of $\overline{\tau}_{\text{g-p}}$ and $\tau_{\text{g-w}}$ was shown in the Supplement.

3. Lines 203-210, Add: "According to the ratios of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ (0.61−0.93), the determined SOA yields were underestimated by a factor of ~2 times, suggesting that vapor wall loss in the chamber could significantly affect SOA formation. The similar results were reported previously by Zhang et al. (2014), who indicated that SOA yields for toluene photooxidation were substantially underestimated by factors as much as 4 times, caused by vapor wall loss. As shown in Fig. 1, the vapor wall-loss corrected SOA yields were in the range of (15.24 ± 0.85)% to (50.89 ± 2.87)%, and could also be reproduced by a one-product model ($R^2 = 0.96$)."

4. Vapor wall-loss corrected SOA yields have been added in Figure 1 in the revised manuscript, shown as Figure R3.

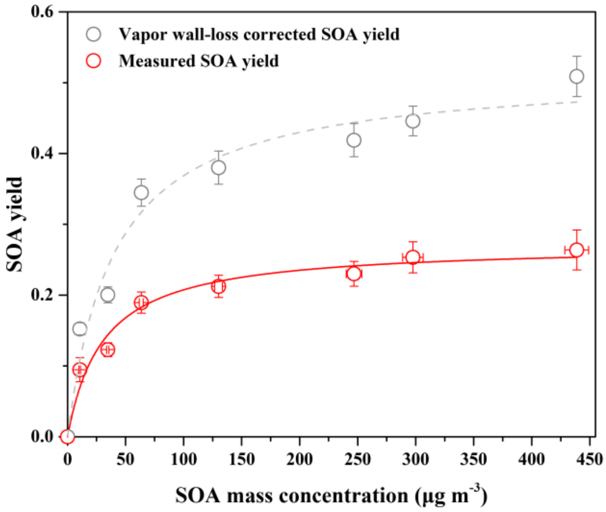

Figure R3. SOA yield as a function of SOA mass concentration (M_0) for guaiacol photooxidation in the presence of NO_x at different guaiacol concentrations. The solid lines was fit to the experimental data using a one-product model. Values of α and $K_{om,i}$ used to generate the solid line were (0.27 ± 0.01) and (0.033 ± 0.008) , and their values for the dot line were (0.52 ± 0.03) and (0.025 ± 0.006), respectively.

5. Figure R1 has been added in the revised manuscript and Figure R2 has been added in the revised Supplement.

6. Lines 248-251, Add: "As illustrated in Fig. 2, the induction period became shorter with the increase of SO_2 concentration. The similar results caused by SO_2 have also been reported previously (Chu et al., 2016; Liu et al., 2016b)."

7. Lines 259-264, Add: "As shown in Fig. 3, $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio decreased from 0.82 to 0.71 and 0.61 when SO_2 concentration increased from 0 to 33 and 56 ppbv. It suggests that the formed sulfate via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008) and increase the surface areas of particles (Xu et al., 2016). These roles are favorable to partition more SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields."

8. Lines 370-374, Add: "As shown in Fig. 3, $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratios with $(NH_4)_2SO_4$ and NaCl seed particles were 0.62 and 0.54, respectively, which suggested that more SOA-forming vapors were partitioned onto particle phase in the presence of NaCl seed particles (Zhang et al., 2014), consequently resulting in relatively higher SOA yield."

9. Lines 445-448, Add: "As shown in Fig. 3, $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio had a decreasing trend when increasing SO_2 concentration in the presence of seed particles, suggesting that the underestimation of SOA yields caused by vapor wall loss was weakened significantly because of the additional sulfate formed from SO_2 oxidation."

10. Lines 488-489, Add: "These yields were underestimated by a factor of ~2 times according to $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratios."

11. Lines 495-497, Add: "The decreasing trend of $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio in the presence of seed particles and SO_2 suggested that more SOA-forming vapors were partitioned onto particle phase, consequently increasing SOA yields."

12. The descriptions of timescale calculation in the Supplement are as follows:

3 Timescale calculation

The average gas-particle partitioning timescale ($\bar{\tau}_{\text{g-p}}$) over the course of experiment could be expressed as Eq. (S1) (Zhang et al., 2014; Seinfeld and Pandis, 2006), and the vapor wall deposition timescale ($\tau_{\text{g-w}}$) is calculated using Eq. (S2) (Zhang et al., 2015).

$$\bar{\tau}_{\text{g-p}} = \frac{1}{2\pi \bar{N}_{\text{p}} \bar{D}_{\text{p}} D_{\text{gas}} F_{\text{FS}}} \tag{S1}$$

$$\tau_{\text{g-w}} = \frac{1}{k_{\text{w}}} \tag{S2}$$

$$k_{\text{w}} = \left(\frac{A}{V}\right)\left(\frac{\alpha_{\text{w}}\bar{c}/4}{\pi\alpha_{\text{w}}\bar{c}/8\left(D_{\text{gas}}k_{\text{e}}\right)^{0.5}+1}\right) \tag{S3}$$

where $\bar{N}_{\text{p}}$ is the average particle number concentration for the whole experimental process since UV lamps were turned on, $\bar{D}_{\text{p}}$ is the number mean diameter, D_{gas} is the gas-phase diffusivity, F_{FS} is the Fuchs-Sutugin correction to the mass transfer flux due to noncontinuum effects and imperfect accommodation (Seinfeld and Pandis, 2006), k_{w} is the overall wall loss rate of organic vapor (Eq. (S3)), A/V is the surface to volume ratio of the chamber, α_{w} is the mass accommodation coefficient of eddy diffusion (~10^{-5}) (Zhang et al., 2014; Matsunaga and Ziemann, 2010), $\bar{c}$ is the mean thermal speed of the molecules, and k_{e} is the coefficient of eddy diffusion (0.015 s^{-1}) (Zhang et al., 2014).

It is assumed that D_{gas} of organic vapor changes with the molecular weight (MW) and is equal to $D_{\text{CO}_2}(\text{MW}_{\text{CO}_2}/\text{MW})$. The value of D_{CO_2} is 1.38×10^{-5} m^2 s^{-1} (Zhang et al., 2014). Conventionally, MW of 98 g mol^{-1} (H_2SO_4) is widely used for the Fuchs-Sutugin correction, but a number more like 300 g mol^{-1} might be more representative of the condensable organic vapors. Thus, MW of 300 g mol^{-1} was selected in this work. The Fuchs-Sutugin correction is expressed as the following equation:

$$F_{\mathrm{FS}} = \frac{0.75\alpha(1+Kn)}{Kn^2 + Kn + 0.283Kn\alpha + 0.75\alpha} \tag{S4}$$

where α is the mass accommodation coefficient onto particles (~0.002) (Zhang et al., 2014) and Kn is the Knudsen number, expressed as follows:

$$Kn = \frac{\lambda}{R_{\mathrm{p}}} \tag{S5}$$

R_{p} is the particle radius and λ is the gas mean free path, which is calculated using Eq. (S6):

$$\lambda = \frac{3D_{\mathrm{gas}}}{\bar{c}} \tag{S6}$$

$$\bar{c} = \sqrt{\frac{8N_{\mathrm{A}}kT}{\pi \mathrm{MW}}} \tag{S7}$$

where N_{A}, k, and T are Avagadro's number, Boltzman constant, and temperature, respectively.

Comment 2: My second issue is with the mechanism by which SO_2 might lead to an increased OSc. It is possible that the SO_2 simply results in a higher condensation sink, as discussed above, but it is suggested that the SO_2 oxidation catalyzes SOA formation (and specifically highly oxidized SOA formation). It seems implausible that SO_2 would act as an oxidant, and so it (or H_2SO_4) would need to enhance condensation of vapors that were already highly oxidized. This is NOT completely implausible (i.e. condensation of glyoxal via an acid catalyzed reactive uptake process) but we would need to see actual direct evidence for such a pathway.

Response to comment 2: We agree with you that SO_2 cannot catalytically oxidize organics. In the revised manuscript, we proposed out that uptake of highly oxidized compounds such as organic acids might lead to the observed enhancement of OS_C in the presence of SO_2 and/or seed particles. For example, we observed that acetic acid concentration decreased in the presence of SO_2 and seed particles compared with the corresponding control experiments, which suggested that the uptake of acetic acid might be enhanced. These results were in good agreement with those reported by Liggio et al. (2005) and Liu et al. (2010), who observed that that the uptake of organic compounds under acidic conditions would be enhanced significantly.

The time-series changes in the gas-phase concentrations of acetic acid under different conditions were discussed in the revised manuscript and added in the Supplement (Figure R4).

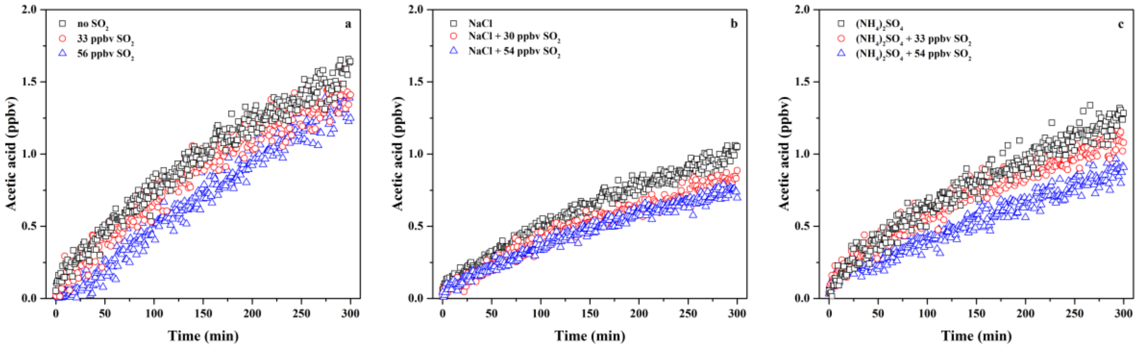

Figure R4. Variations in the gas-phase concentrations of acetic acid as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: (NH4)$_2$SO$_4$).

In addition, the time-series variations in the fraction of organic ion groups (CH^+,

CHO^+, and CHO^+_{gt1}) under different conditions were also discussed in the revised manuscript and added in the Supplement (Figure R5). The results showed that the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ were obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA.

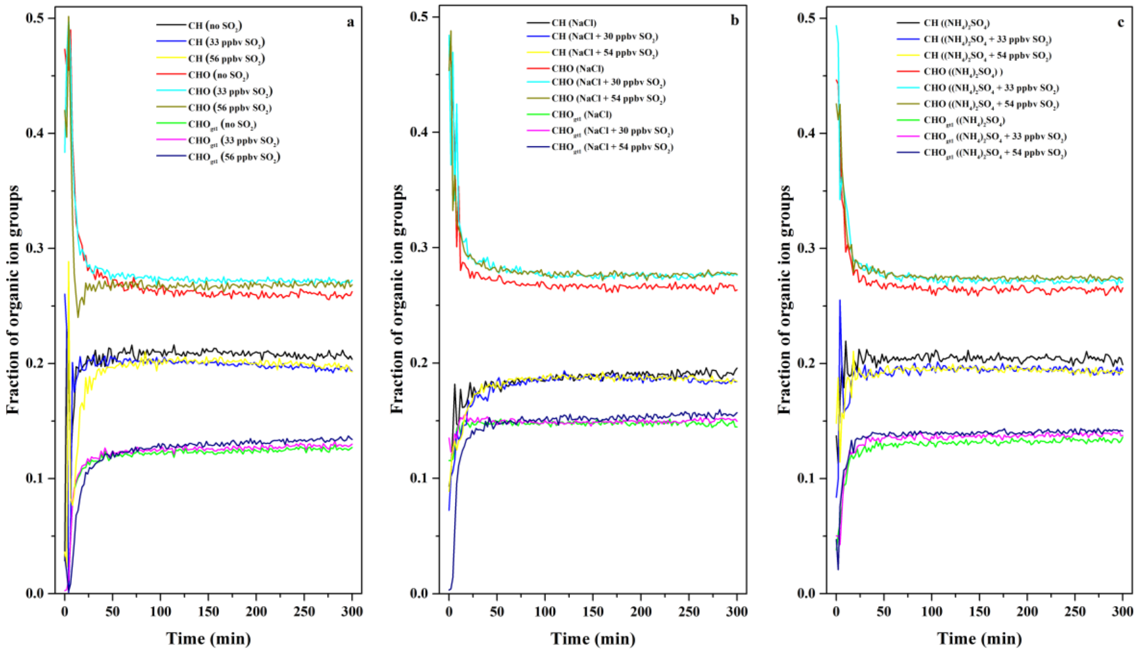

Figure R5. Variations in the fraction of organic ion groups as a function of irradiation time in the presence of different SO_2 concentrations and seed particles (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$).

Revisions in the manuscript:

1. Figures R4 and R5 have been added in the revised manuscript.

2. Lines 308-311, Add: "This is well supported by the time-series variations in the fraction of organic ion groups (CH^+, CHO^+, and CHO^+_{gt1}) (Fig. S12a), which shows the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA."

3. Lines 342-349, Add: "This is well supported by the time-series variations in the concentrations of acetic acid at different SO_2 concentrations measured by the HR-ToF-PTRMS (Fig. S15a), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−56 ppbv). These results were in good agreement with those reported by Liggio et al. (2005) and Liu et al. (2010), who observed that that the uptake of organic compounds under acidic conditions would be enhanced significantly. Recently, Huang et al. (2016) have also reported that acetic acid is present in SOA formed via α-pinene ozonolysis and its uptake would increase in the presence of seed particles."

4. Lines 385-387, Add: "As shown in Figs. S12b and S12c, compared to $(NH_4)_2SO_4$ seed particles, the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ were obtained with NaCl seed particles, consequently resulting in higher OS_C of SOA."

5. Lines 405-409, Add: "As shown in Fig. S15, the concentration of acetic acid in the gas phase with NaCl seed particles was lower than that with $(NH_4)_2SO_4$ seed particles. It suggests that the uptake of acetic acid on NaCl seed particles might be higher than that on $(NH_4)_2SO_4$ seed particles under the similar experimental conditions (i.e., NO_x and guaiacol concentrations, temperature, and RH)."

6. Lines 453-455, Add: "In addition, as shown in Figs. S12b and S12c, the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ were obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA."

7. Line 467-471, Add: "This hypothesis could be supported by the variations in acetic acid concentration in the presence of different seed particles and SO_2 concentrations (Fig. S15), which shows that acetic acid concentration decreased with the increase of

SO_2 concentration (0−54 ppbv).”

Responses to Referee #2's comments

General comment: This works describes the effect of the composition and presence of seed aerosol and gas-phase SO_2 (NO_x) on the SOA formation from guaiacol photooxidation. The topic is of great interest as methoxyphenols are largely emitted by biomass burning (BB) emissions and the evolution of these compounds in the atmosphere in a more complex environment is not fully understood yet. Some paragraphs of the discussion could be improved (in a quantitative way) in order to better appreciate the results provided by the authors.

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: The influence of SO_2 in the gas-phase as a source of seed aerosol should be addressed. The sulfate aerosol arising from SO_2 conversion has the potential to impact the surface area available for condensation and therefore enhance SOA formation. This question needs to be address in a more quantitative way. SOA yields could be corrected from this estimation and would help the reader to know whether the increase of SOA concentrations is due to the aerosol microphysics or chemical reactions. The AMS used in this study can provide a lot of information about the evolution of the aerosol all along the experiment. The evolution of the seed aerosol concentration for each experiment would help understanding and estimating the influence of both microphysics and chemistry on SOA formation.

Response to comment 1: Thank you very much. Sulfate formed via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008) and increase the surface areas of particles (Xu et al., 2016). These roles are favorable to partition more SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields. Therefore, the time-series variations in the concentrations of sulfate at different SO_2 concentrations were added in the Supplement (Figure R1). As shown in Figure R1, the sulfate concentration increased with the increase of SO_2 concentration, suggesting that more sulfate aerosols were produced via SO_2 oxidation.

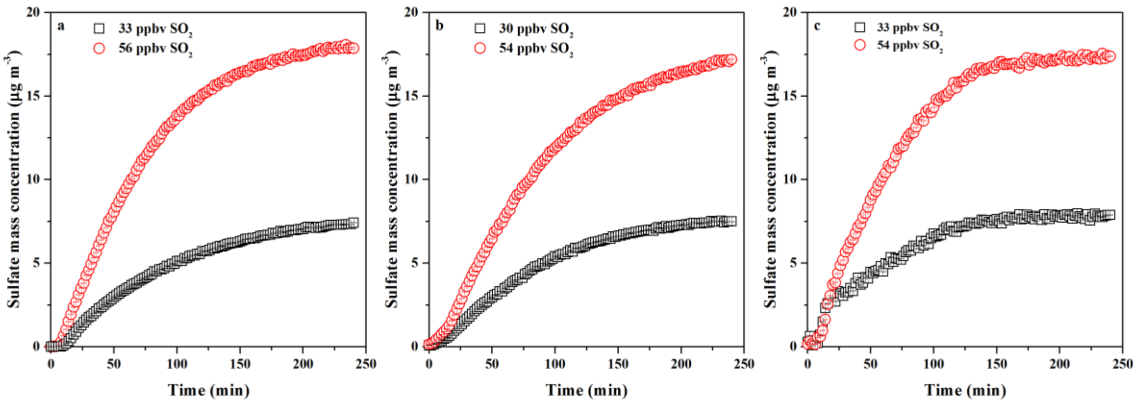

Figure R1. Variations in the concentrations of sulfate as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$). The sulfate concentrations shown in Figure R1c is the net concentrations formed via SO_2 oxidation, e.g., do not include the $(NH_4)_2SO_4$ concentration added in the smog chamber.

In order to further investigate the effect of sulfate formed via SO_2 oxidation on SOA yields, the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment and the vapor wall-loss timescale ($\tau_{\text{g-w}}$) under different experimental conditions were estimated and discussed in the revised manuscript. Based on

$\overline{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ ratio, the underestimation of SOA yield caused by vapor wall loss could be determined. The calculation methods of $\overline{\tau}_{g\text{-}p}$ and $\tau_{g\text{-}w}$ were added in the Supplement. As shown in Sections 3.2-3.4 in the revised manuscript, the decreasing trend of $\overline{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ ratios in the presence of seed particles and SO_2 have been observed (shown in Figure R2), suggesting that more SOA-forming vapors are partitioned onto particle phase, consequently increasing SOA yields. The detailed revisions of the discussion about $\overline{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ ratio have been pointed out in the responses to the Referee #1's Comment 1, thus these revisions were not listed. Other revisions in the manuscript were pointed out as follows.

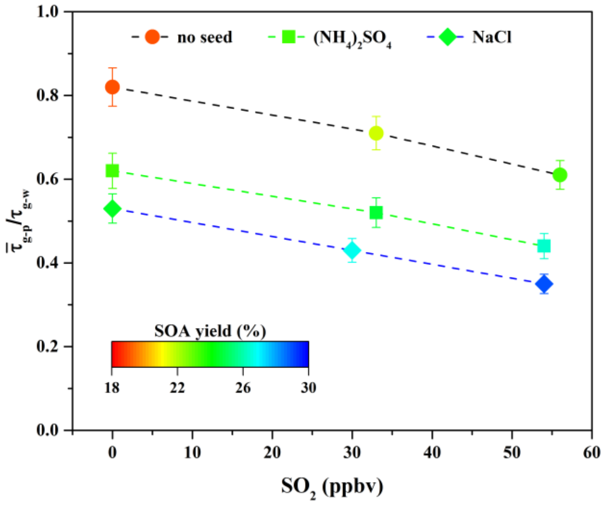

Figure R2. Variations in $\overline{\tau}_{g\text{-}p}/\tau_{g\text{-}w}$ ratio in the presence of various seed particles as a function of SO_2 concentration.

Revisions in the manuscript:

1. Figure R1 has been added in the revised Supplement.

2. Figure R2 has been added in the revised manuscript.

Comment 2: I would expect more details in the experimental section specifically for the instruments used (PTR and AMS). Also, it would be worth adding a section for the AMS data analysis (quantification, PMF…)

Response to comment 2: More details about HR-ToF-PTRMS and HR-ToF-AMS have been added in the Experimental section in the revised manuscript. In addition, the analysis of data from HR-ToF-PTRMS and HR-ToF-AMS has also added in the Experimental section. PMF analysis has been added in the Supplement. The detailed revisions in the revised manuscript were listed as follows.

Revisions in the manuscript:

1. Lines 128-134, Add: "The HR-ToF-PTRMS with a time resolution of 1 min was used online to measure the gas phase concentration of guaiacol, and its m/z range was 10−500 in the process of data acquisition. Before data collection, the peaks of the protonated water ($[H_3{}^{18}O]^+$) and protonated acetone ($[C_3H_7O]^+$) ions at m/z 21.0246 and 59.0491 were used for mass calibration, with the aim to obtain accurate mass determination during experimental process. All data obtained by the HR-ToF-PTRMS were analyzed with the PTR-MS Viewer software (version 3.1.0, IONICON Analytik)."

2. Lines 137-143, Add: "For all experiments, the acquisition time of the HR-ToF-AMS was 2 min. The inlet flow rate, ionization efficiency, and particle sizing of the HR-ToF-AMS were calibrated at regular intervals, according to the standard protocols using the size-selected pure ammonium nitrate particles (Drewnick et al., 2005; Jimenez et al., 2003). All date obtained by the HR-ToF-AMS were analyzed by the ToF-AMS analysis toolkit SQUIRREL 1.57I/PIKA 1.16I version, in

Igor Pro version 6.37."

3. Supplement, PMF analysis has been added as follows:

2 Positive matrix factorization (PMF) analysis

Positive Matrix Factorization (PMF) is a receptor model and a multivariate factor analysis tool, which could decompose a matrix of speciated sample data into two matrices, namely factor contributions and factor profiles (Paatero, 1997). In recent years, the PMF model was widely used for the analysis of high resolution (HR) mass spectra data, which could provide better separation of different organic components (DeCarlo et al., 2010; Docherty et al., 2008). This model is expressed as a bilinear factor model, namely, $x_{ij} = \sum_p g_{ip} f_{pj} + e_{ij}$, where i and j refer to values of j species in i samples, respectively, p is the number of factors in the solution and is used a least-squares fitting process to minimize the quality of fit parameter. In this work, the HR mass spectra (m/z 12–115) was analyzed by the PMF software coupled with a modified version of the CU AMS PMF Execute Calcs Tool version 2.06 developed by Ulbrich et al. (2009). The concentration and uncertainty matrices input into the PMF analysis were generated from the PIKA version 1.15D. Ions were classified and down-weighted according to the signal to noise ratios (SNR). $0.2 < \text{SNR} < 2$ was classified as the weak ions and down-weighted by a factor of 2, $\text{SNR} < 0.2$ was bad ions and removed from the analysis, and the uncertainty values of CO_2^+-related peaks at m/z 16 (O), 17 (HO), 18 (H_2O), 28 (CO), and 44 (CO_2) were down-weighted.

Comment 3: The authors used the AMS which is an instrument known to highly fragment molecules and does not allow molecular level chemical characterization for organics. Organosulfates and organonitrates can be positively identified only using appropriate instrumentation. I would suggest to use: organic sulfur-containing compounds and organic nitrogen-containing compounds (or something similar).

Response to comment 3: Thank you for your valuable suggestion. Organosulfates and organonitrates have been rewritten to be organic S-containing compounds and organic N-containing compounds, respectively.

Revisions in the manuscript:

1. Lines 39, 231, 233, 499, Change “organic nitrates” **To** “organic N-containing compounds”

2. Lines 41, 329, 354, Change “organosulfates” **To** “organic S-containing compounds”

Comment 4: For some results, an evaluation of the uncertainties would help knowing if the variability is due to the uncertainty of the measurement or really represents a difference in a physico-chemical process. It would be worth providing uncertainties for Mo, SOA yields and OSc. In Figure 7, the larger SOA mass in the first 2 hours of the experiment with NaCl only comparing with NaCl + 30 ppbv of SO_2 could be due to the uncertainty of the experiment. If not, this behavior needs to be discussed by the authors.

Response to comment 4: The uncertainties for M_o, SOA yields and OS_C have been added in the revised manuscript as follows.

Revisions in the manuscript:

1. Line 24, Change “(9.46−26.37%)” **To** “ranged from (9.46 ± 1.71)% to (26.37 ± 2.83)%”

2. Lines 202-203, Change “9.46−26.37%” **To** “(9.46 ± 1.71)% to (26.37 ± 2.83)%”

3. Line 252, Change “63.62 to 71.88 and 78.59” **To** “(63.62 ± 1.71) to (71.88 ± 1.43) and (78.59 ± 2.06)”

4. Line 254, Change “The corresponding SOA yield increased by 14.05% and 23.66%, respectively.” **To** “The corresponding SOA yields were (9.46 ± 1.71)%, (21.60 ± 1.27)%, and (23.42 ± 1.80)%, respectively.”

5. Lines 365-366, Change “63.62 to 79.44 and 84.91” **To** “(63.62 ± 1.71) to (79.44 ± 1.86) and (84.91 ± 2.01)”

6. Lines 367-368, Change “The corresponding SOA yield increased by 23.06% and 29.57%, respectively.” **To** “The corresponding SOA yields were (23.31 ± 1.59)% and (24.54 ± 1.73)%, respectively.”

7. Lines 439-440, Change “M_0 was enhanced by 41.43% and 53.47%” **To** “M_o increased from (63.62 ± 1.71) to (90.89 ± 2.28) and (98.86 ± 2.11) $\mu g\ m^{-3}$.”

8. Lines 441-442, Change “the corresponding SOA yield increased by 41.43% and 53.47%” **To** “the corresponding SOA yields were (26.78 ± 1.97)% and (29.06 ± 1.82)%.”

9. Lines 442-445, Change “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%.” **To** “M_o increased from (63.62 ± 1.71) to (84.35 ± 2.09) for 33 ppbv

SO_2 and (89.92 ± 2.31) μg m^{-3} for 54 ppbv SO_2, enhanced by 32.58% and 41.34%, respectively, and the corresponding SOA yields were (24.58 ± 1.78)% and (26.37 ± 1.98)%."

10. Line 487, Change "9.46−26.37%" **To** "(9.46 ± 1.71)% to (26.37 ± 2.83)%"

11. Tables and Figures: The uncertainties of M_o, SOA yields, and OS_C have been added in Tables 1 and 2, as well as Figures 1, 2, 5, 6, and 8 in the revised manuscript.

Comment 5: l-51 and elsewhere in the introduction: Specify the type of fuel used for the given emission factors.

Response to comment 5: The type of fuel has been specified in the revised manuscript.

Revisions in the manuscript:

Lines 56 and 60, Change "fuel" **To** "wood"

Comment 6: l-62 SOA formation from guaiacol photooxidation in the presence of NO_x has been studied in the past (Lauraguais et al., 2014; Yee et al., 2013). See your discussion paragraph. Experimental section: The experimental section could be improved by adding details about the the AMS/PTR-MS instrumental settings (experimental conditions) and data analysis (N:C, O:C, H:C, sulfur and nitrogen-containing compounds concentrations, PMF).

Response to comment 6: In previous studies, the significant SOA formation from guaiacol oxidation by OH radicals has been reported, and OH radicals are produced from the photolysis of the OH precursors (i.e., H_2O_2 and CH_3ONO) (Ahmad et al., 2017; Lauraguais et al., 2014; Yee et al., 2013). In order to describe accurately, this sentence has been rewritten in the revised manuscript.

More details about HR-ToF-PTRMS and HR-ToF-AMS have been added in the Experimental section in the revised manuscript. In addition, the analysis of data from HR-ToF-PTRMS and HR-ToF-AMS has also been added in the Experimental section. PMF analysis and the calculation of organosulfate concentration have been added in the Supplement. The supplementary revisions about HR-ToF-PTRMS, HR-ToF-AMS, and PMF analysis have been pointed out in the responses to the Referee #2's Comment 2, thus these revisions were not listed in the following revisions. Other detailed revisions in the revised manuscript were listed as follows.

Revisions in the manuscript:

1. Lines 65-68, Change "Meanwhile, several studies have reported the significant SOA formation from guaiacol oxidation by OH radicals." **To** "Meanwhile, several studies have reported the significant SOA formation from guaiacol oxidation by OH radicals, produced from the photolysis of the OH precursors (i.e., H_2O_2 and CH_3ONO) (Ahmad et al., 2017; Lauraguais et al., 2014b; Yee et al., 2013)."

2. Supplement, organosulfate concentration calculation have been added as follows:

4 Organosulfate concentration calculation

Considering that methyl sulfate is the simplest organosulfate, the fraction of $C_xH_yO_zS$ is more likely to be lower than that of methyl sulfate (Huang et al., 2015). In addition, more information about the varieties of organosulfates could not be obtained in this work. Therefore, a conservative low-bound of organosulfate concentration has been estimated according to the method described by Huang et al. (2015), as shown in Eq. (S8).

$$C_{\mathrm{OS}_{\mathrm{min}}} = f_{\mathrm{OS}} \times (C_{\mathrm{org}} + C_{\mathrm{SO_4}}) \qquad \text{(S8)}$$

$$f_{\mathrm{OS}} = \frac{\dfrac{\sum_h I_{\mathrm{OS},h}}{\mathrm{RIE_{OS}}}}{\dfrac{\sum_n I_{\mathrm{org},n}}{\mathrm{RIE_{org}}} + \dfrac{\sum_t I_{\mathrm{SO_4},t}}{\mathrm{RIE_{SO_4}}}} \qquad \text{(S9)}$$

where $C_{\mathrm{OS}_{\mathrm{min}}}$ is the minimum concentration of organosulfates; f_{OS} is the factor that represents for the fractional contribution of organosulfates to the lumped species of organics and sulfate in W-mode data; C_{org} and $C_{\mathrm{SO_4}}$ are the concentrations of organics and sulfate calculated from V-mode data, respectively; *h, n, and t* indicate the fragments of organosulfates, organics, and sulfate, respectively; $\sum_h I_{\mathrm{OS},h}$, $\sum_n I_{\mathrm{org},n}$, and $\sum_t I_{\mathrm{SO_4},t}$ are the total signal intensities of organosulfates, organics, and sulfate, respectively, obtained from W-mode data; $\mathrm{RIE_{OS}}$ is the relative ionization efficiency for organosulfates, which is estimated as the average of $\mathrm{RIE_{org}}$ = 1.4 and $\mathrm{RIE_{SO_4}}$ = 1.2 (Barnes et al., 2006).

Comment 7: l. 165-167 Do you see any low volatility products in the gas phase based on the PTRMS data?

Response to comment 7: According to the products of guaiacol oxidation by OH radicals in the presence of NO_x reported by Lauraguais et al. (2014) and Yee et al. (2013), we did not observe these low volatility products by the HR-ToF-PTRMS. The reason should be from the configuration of the HR-ToF-PTRMS (Ionicon Analytik

GmbH) because a capillary interface was used. This leads to a very low transmission efficiency of low volatile compounds. In fact, these compounds can be measured using an API-ToF-CIMS. Unfortunately, the API-ToF-CIMS is unavailable in our laboratory.

Comment 8: l.171 and all the paper: What is the estimated uncertainties of the reported SOA yields?

Response to comment 8: The uncertainties of SOA yields have been added in the revised manuscript. The corresponding revisions have been pointed out in the responses to the Referee #2's Comment 4, thus the detailed revisions were not listed.

Comment 9: l.170 How would you explain the difference in SOA yield between your study and Lauraguais et al., 2014? The SOA formation in their study is 3 times higher with the same guaiacol and OH concentrations and without seed particles.

Response to comment 9: In the original manuscript, the vapor wall-loss was not considered when calculating SOA yields. In the revised manuscript, the vapor wall-loss was corrected and the SOA yields were well consistent with the results reported by Lauraguais et al. (2014). Thus, the difference in SOA yields should be reasonably resulted from vapor wall loss which was not considered in the original manuscript. The vapor wall loss has been corrected in our revised manuscript.

Revisions in the manuscript:

1. Lines 203-210, Add: "According to the ratios of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ (0.61−0.93), the determined SOA yields were underestimated by a factor of ~2 times, suggesting that vapor wall loss in the chamber could significantly affect SOA formation. The similar results were reported previously by Zhang et al. (2014), who indicated that SOA yields for toluene photooxidation were substantially underestimated by factors as much as 4 times, caused by vapor wall loss. As shown in Fig. 1, the vapor wall-loss corrected SOA yields were in the range of (15.24 ± 0.85)% to (50.89 ± 2.87)%, and could also be reproduced by a one-product model ($R^2 = 0.96$)."

2. Lines 216-219, Add: "Overall, the vapor wall-loss corrected SOA yields in this work are well in agreement with those reported previously (Lauraguais et al., 2014b; Yee et al., 2013), but the determined SOA yields are much lower. Therefore, the effect of vapor wall loss on SOA formation should be seriously taken into account."

Comment 10: l. 179 Sun et al., 2010 presented results of aqueous-phase oxidation of guaiacol with and without an added source of OH. Their results are not really comparable to this study.

Response to comment 10: According to your valuable suggestion, the comparison has been deleted in the revised manuscript.

Revision in the manuscript:

Lines 180-182, Delete: "For example, Sun et al. (2010) have reported that SOA mass formed from the aqueous-phase photochemical reaction of guaiacol in the presence of H_2O_2 is about one-fold higher than that in the absence of H_2O_2."

Comment 11: l. 189-197 Organonitrates (-ONO2) are different than nitro-organics (nitro-aromatics, nitro-compounds…) containing a (-NO2) chemical group. The formation of nitroaromatics from the photooxidation of guaiacol under high NOx conditions has already been reported (i.e. nitroguaiaol, nitrocatechol) (Ahmad et al., 2017; Lauraguais et al., 2014).

Response to comment 11: According to your valuable suggestion, organonitrates have been rewritten to be organic N-containing compounds, respectively.

Revisions in the manuscript:

Lines 39, 231, 233, 499, Change "organic nitrates" **To** "organic N-containing compounds"

Comment 12: In this study, the reported NO^+/NO_2^+ is clearly different from the ammonium nitrate standard. This difference could be explained by the presence of both nitro and nitrate organics (Farmer et al., 2010; Sato et al., 2010). I would suggest to use organic nitrogen-containing compounds (or something similar) instead of "organonitrates" unless the authors provide molecular chemical characterization clearly showing the for mation of organonitrates.

Response to comment 12: According to your valuable suggestion, the difference between NO^+/NO_2^+ ratio observed in this work and that for ammonium nitrate was explained. In addition, organonitrates have been rewritten to be organic N-containing compounds, respectively. The detailed revisions were pointed out as follows.

Revisions in the manuscript:

1. Lines 39, 231, 233, 499, Change "organic nitrates" **To** "organic N-containing compounds"

2. Lines 227-231, Change "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." **To** "The average NO^+/NO_2^+ ratio of SOA from guaiacol photooxidation is 4.08, which is higher than that (2.06−2.54) for ammonium nitrate, determined by the HR-ToF-AMS in this work. The possible explanation might be that nitro-organics and organonitrates both exist in SOA (Farmer et al., 2010; Sato et al., 2010)."

Comment 13: l. 224 The results in Figure 3 arise from one specific condition or represent an average of MS for the three different conditions? Unclear. In the MS in Figure 3, we can see a large contribution of the m/z 44 in the factor 1. At t=0 min, the factor 1 dominates the aerosol fraction which means that before the photooxidation experiment there is already a large fraction of m/z 44 in the aerosol. Is there already oxidized organics and SOA in the aerosol before the photooxidation experiments? Does it correspond to guaiacol condensation on the aerosol phase? Something else? To illustrate these experiments, I would recommend to provide the evolution of the organics, sulfate, nitrate, over the course of an experiment (before and after lights on and corrected with wall loss). This would help visualizing the change in sulfate an organics concentrations. The impact of sulfate formation on SOA formation due to an increase of condensation or due to chemical processes needs to be addressed in a more quantitative way.

Response to comment 13: Figure 3 in the original manuscript is obtained by applying PMF analysis to the AMS data, collected at different SO_2 concentrations over the course of experiments. Thus, it represents an average of mass spectrum over the course of experiments at three different SO_2 concentrations. We are very sorry to make a mistake, e.g., Figure S4 in the original Supplement is wrong, caused by our carelessness. The right figure has been added in the Supplement (Figure R3). As shown in Figure R3, the relative fraction of Factor 1 at different SO_2 concentrations at the beginning of experiments was close to 0, which increased firstly and then decreased along with prolonging irradiation time.

In addition, the time-series variations in the concentrations of sulfate and nitrate over the course of experiments have been added in the Supplement (Figure R4). The time-dependent growth curves of SOA mass concentration for guaiacol photooxidation at different SO_2 levels are shown in Figure 2 in the manuscript (Figure R5).

In the revised manuscript, the quantitative analysis about the effect of sulfate formed via SO_2 oxidation on SOA yield has been discussed, according to the $\bar{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratios obtained at different SO_2 concentrations. The detailed revisions have been pointed out in the responses to the Referee #1's Comment 1, which were not listed as follows.

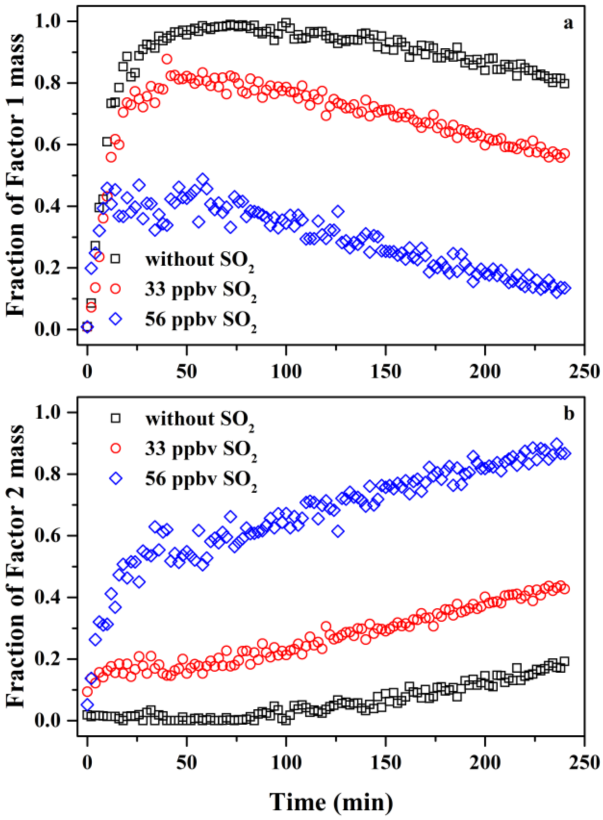

Figure R3. Time-dependent curves of Factor 1 (a) and Factor 2 (b) at three different SO2 concentrations (without seed particles).

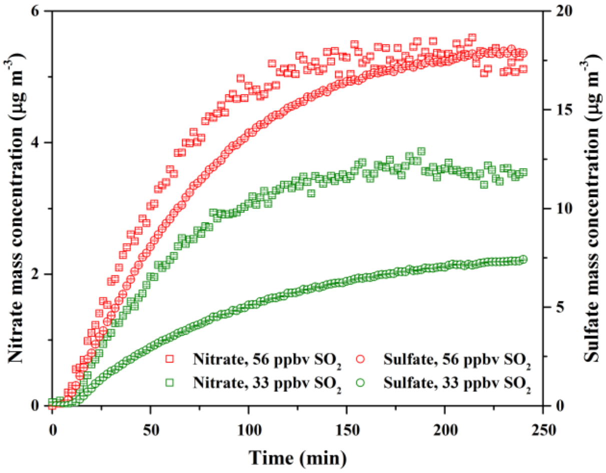

Figure R4. Variations in the concentrations of sulfate and nitrate in the presence of various SO2 concentrations as a function of reaction time (without seed particles).

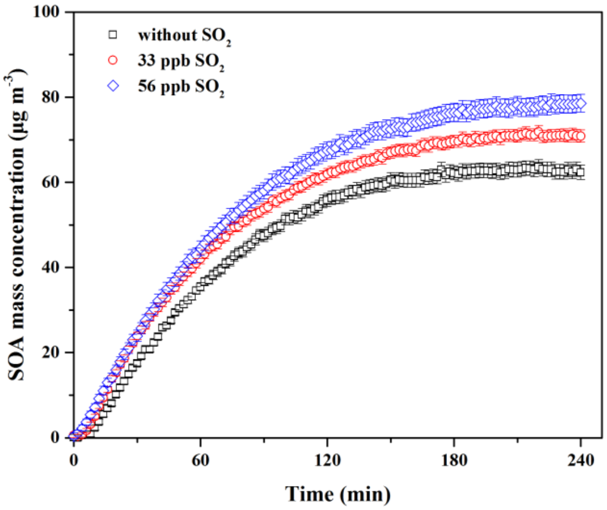

Figure R5. Time-dependent growth curves of SOA mass concentration for guaiacol photooxidation at different SO_2 levels.

Revisions in the manuscript:

1. Figures R3 and R4 have been added in the Supplement.

2. The caption of Figure 4 was changed to be "Mass spectra of Factor 1 (a) and Factor 2 (b) for the formed SOA identified by applying PMF analysis to the AMS data, obtained at different SO_2 concentrations over the course of experiments."

Comment 14: l 243-248 From the MS presented in Figure S5 we clearly see that in the presence of SO_2, low-MW compounds are more abundant. It also appears that high-MW compounds are in higher abundance in the presence of SO_2 (33 ppb vs no SO_2 and 56 ppb vs 33 ppb). Do you have an idea of the role of SO_2 in the formation of these compounds?

Response to comment 14: As shown in Figure S5 in the original manuscript, the signal fractions from the low-MW species were enhanced significantly in the presence of SO_2, and were much higher than those from the high-MW species (m/z >300). In other words, SO_2 played a more important role in the formation of organic S-containing compounds and the formation or uptake of low-WM species. For example, we observed that acetic acid concentration decreased in the presence of SO_2 and seed particles compared with the corresponding control experiments, which suggesting that the uptake of acetic acid might be enhanced. These results are in good agreement with those reported by Liggio et al. (2005) and Liu et al. (2010), who observed that that the uptake of organic compounds under acidic conditions would be enhanced significantly. The time-series changes in the gas-phase concentrations of acetic acid under different conditions were discussed in the revised manuscript and added in the Supplement (shown in Figure R6).

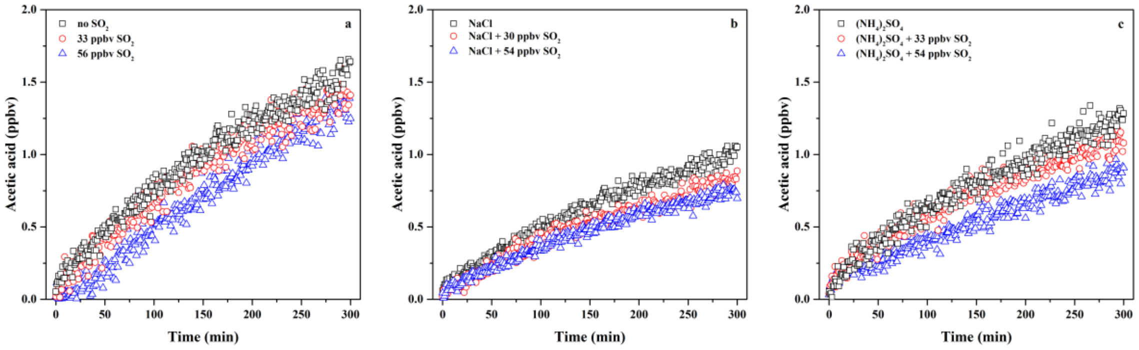

Figure R6. Variations in the gas-phase concentrations of acetic acid as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH4)_2SO_4$).

As shown in Figure S5 in the original Supplement, the formation of high-MW species (i.e., oligomers) was observed, which should be reasonably produced via the acid-catalyzed heterogeneous reactions (Cao and Jang, 2007; Jaoui et al., 2008; Liu et al., 2016; Xu et al., 2016). But, compared to low-MW species, the formation of oligomers should not be predominant due to the much lower signal fractions.

Revisions in the manuscript:

1. Figure R6 has been added in the Supplement.

2. Lines 330-332, Add: "compared to the formation of high-MW species (i.e., oligomers) that should be reasonably produced via the acid-catalyzed heterogeneous reactions (Cao and Jang, 2007; Jaoui et al., 2008; Liu et al., 2016b; Xu et al., 2016)."

Comment 15: l. 254 Do you see water soluble low-MW compounds in the gas-phase using the PTRMS and an increase of the uptake of these compounds with increasing SO_2 concentrations?

Response to comment 15: The time-series changes in the gas-phase concentrations of acetic acid under different conditions were discussed in the revised manuscript and added in the Supplement (shown in Figure R6). The results showed that acetic acid concentration decreased in the presence of SO_2, suggesting that the uptake of acetic acid might be enhanced.

Revisions in the manuscript:

1. Figure R6 has been added in the Supplement.

2. Lines 342-349, Add: "This is well supported by the time-series variations in the concentrations of acetic acid at different SO_2 concentrations measured by the HR-ToF-PTRMS (Fig. S15a), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−56 ppbv). These results were in good agreement with those reported by Liggio et al. (2005) and Liu et al. (2010), who observed that that the uptake of organic compounds under acidic conditions would be enhanced significantly. Recently, Huang et al. (2016) have also reported that acetic acid is present in SOA formed via α-pinene ozonolysis and its uptake would increase in the presence of seed particles.”

Comment 16: L 253 How did you quantify the amount of organosulfates? In Figure S6: Is this MS from a standard or from smog chamber experiment? Unclear. In Huang et al., 2015, they quantified using a commercial standard. What is the uncertainty in your measurement considering that the C_5H_3O and $C_5H_3O_2$ are highly abundant (and the resolution seems lower comparing to Huang et al. 2015) and can induce error during the peak fitting?

Response to comment 16: The calculation method of organosulfate concentration has been added in the Supplement, which has already been pointed out in the responses to Referee #2’s Comment 6. Thus, it was not listed in the following revisions.

Figure S6 in the original Supplement is the mass spectra obtained from smog chamber experiment. In addition, the uncertainties of the estimated concentration of organosulfate have been added in the revised manuscript.

Revisions in the manuscript:

Line 334, Change “2.1−4.3 ng m^{-3}” **To** “(2.1 ± 0.8) to (4.3 ± 1.7) ng m^{-3}”

Line 479, Change “2.2−4.6 ng m^{-3}” **To** “(2.2 ± 0.7) to (4.6 ± 1.8) ng m^{-3}”

Comment 17: L 261 Would it be possible to provide a potential chemical mechanism that could lead to the formation of organosulfate (or organic sulfur containing compounds) through heterogeneous uptake of SO_2?

Response to comment 17: According to the results reported previously, organic S-containing compounds might be produced by the nucleophillic addition of HSO_4^- or the electrophilic addition of H_2SO_4 on the corresponding groups of organic molecules (Liggio and Li, 2006; Surratt et al., 2008), or through the reactions initiated by sulfate radicals ($SO_4^{\bullet -}$) which are formed by sulfates under UV irradiation (Nozière et al., 2010). Considering that organic S-containing compounds are not identified in this work due to the lack of analytical instruments, it is very difficult for us to propose a chemical mechanism about the formation of organic S-containing compounds.

Comment 18: L 323 Do you see chlorine containing compounds (organics) or fragments using the AMS or the PTR-MS? Do you think they could participate to SOA formation?

Response to comment 18: Chlorine-containing compounds or fragments are not detected by HR-ToF-PTRMS and HR-ToF-AMS. Its concentration might below the detection limits of analytical instruments.

Comment 19: l-362 Do you see a higher SO_2 uptake in the presence of NaCl comparing with $(NH_4)_2SO_4$? This could illustrate the enhance SO_2 uptake and explain the higher SOA formation.

Response to comment 19: The time-series decays of SO_2 with different seed particles are shown in Figure R7, which shows that there is no significant difference of SO_2 decay with different seed particles. However, Figure R6 shows that acetic acid concentration decreases in the presence of SO_2 and seed particles, suggesting that the uptake of acetic acid might be enhanced.

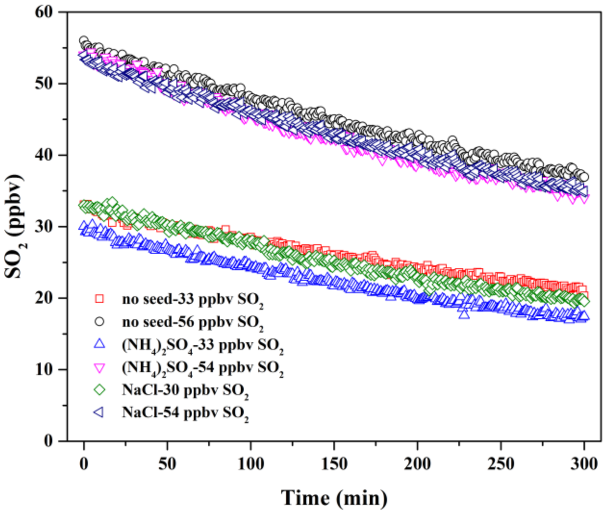

Figure R7. Decays of SO_2 as a function of irradiation time with different seed particles.

Revisions in the manuscript:

1. Figures R6 and R7 have been added in the Supplement.

2. Lines 467-471, Add: “This hypothesis could be supported by the variations in acetic acid concentration in the presence of different seed particles and SO_2 concentrations (Fig. S15), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−54 ppbv).”

Comment 20: l. 368 Do you see a difference in the PTR-MS signal for low MW compounds in the presence of SO_2 for NaCl and $(NH_4)_2SO_4$? (a larger uptake of these molecules in the presence of NaCl?).

Response to comment 20: In this work, we observed that acetic acid concentration decreased with increasing SO_2 concentration when using NaCl and $(NH_4)_2SO_4$ as seed particles, suggesting that the uptake of acetic acid might be enhanced. The time-series changes in the gas-phase concentrations of acetic acid under different conditions are shown in Figure R6. Compared to $(NH_4)_2SO_4$ as seed particles, the uptake of acetic acid on NaCl in the presence of SO_2 was larger.

Revisions in the manuscript:

1. Figure R6 has been added in the Supplement.

2. Lines 467-471, Add: "This hypothesis could be supported by the variations in acetic acid concentration in the presence of different seed particles and SO_2 concentrations (Fig. S15), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−54 ppbv)."

Comment 21: Typing errors: l. 164 values l. 166 partitioned l. 335 inorganic SI l. 31 Formation Figure S5: signal.

Response to comment 21: All type errors have been corrected in the revised manuscript.

Revisions in the manuscript:

1. Line 196, Change "vaules" **To** "values"

2. Line 198, Change "paritioned" **To** "partitioned"

3. Line 356, Change "inorganic" **To** "inorganic"

4. Supplement, Line 80, Change "Fomration" **To** "Formation"

5. Supplement, Figures S13, S21 and S22, Change “Singal” **To** “Signal”

Responses to Referee #3's comments

General comment: This manuscript presents results from a series of chamber experiments investigating the effect of SO_2 on the SOA yield for guaiacol oxidization in the presence of NO_x and seed aerosols. The authors report increased SOA yields for increasing amounts of SO_2 in the chamber and also observe an increased carbon oxidation state. This research is important for understanding the impact of gas-phase precursors on SOA formation, with relevance for severely polluted regions in China. This is a valuable set of experiments, however, the interpretation is not fully supported by the presented results. Before publication, I recommend the authors provide more detailed information on the results from the chamber experiments, as outlined below. These additional data sets will help support the conclusions made in the current manuscript.

Response to comment: Thank you 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: The big question I have for this paper is what part of the observations is due to chemical differences (i.e. different SOA formation mechanisms) and what part is due to changes in the physical system (i.e. more seed surface area = more SOA). To understand these results, it would really help to be able to compare the data sets for the experiments. Can you show experimental traces (AMS and PTR-MS) for some of these experiments?

For the particle phase: When/how does the particulate sulfate from SO_2 grow in? What is the NH_4^+ doing? Does it rise as well or is the pH of the particles dropping (forming H_2SO_4) or are you forming organic sulfate? What about the NO^+ and NO_2^+ ions? Do they grow in at the same rate for all experiments? When the lights are turned on for the different experiments, are there any differences in the induction period before SOA growth is observed? How do the chemical properties change with time (What is the time series for the O/C, H/C, and N/C)?

For the gas phase: What do the experimental traces from the PTR-MS look like? Does the decay in Guaiacol look the same in all experiments? Are any other VOC products observed during the experiments? If so, are there any differences between experiments and what do the time series for these products look like? What do the time traces for NO_x and SO_2 look like?

Response to comment 1: In this work, we compared the effect of sulfate formed via SO_2 oxidation on SOA formation with/without seed particles. The results suggested that the physical and chemical factors could be both helpful to enhance SOA yield, but their contributions were very difficult to quantify.

It is well known that sulfate formed via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008) and increase the surface areas of particles (Xu et al., 2016). These roles are favorable to partition more SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields. Therefore, the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment and the vapor wall-loss timescale ($\tau_{\text{g-w}}$) under different experimental conditions were estimated and discussed in the revised manuscript. Based on $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio, the underestimation of SOA yield caused by vapor wall loss could be determined. The calculation methods of $\overline{\tau}_{\text{g-p}}$ and $\tau_{\text{g-w}}$ were added in the Supplement. The detailed revisions of the discussion about $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio have been pointed out in the responses to the Referee #1's Comment 1. Thus, these revisions were not listed as follows.

For the particle phase: The time-series changes in the concentrations of sulfate and nitrate, as well as ammonium salts are shown in Figure R1 and Figure R2, respectively, which show that the concentrations of sulfate, nitrate, and ammonium salts increase along with the irradiation time. The time-series variations in the concentrations of NO^+ and NO_2^+ ions at different SO_2 concentrations are shown in Figure R3a, and their ratio (NO^+ / NO_2^+) is shown in Figure R3b. Figure 3 shows that the concentrations of NO^+ and NO_2^+ ions are both increase with increasing SO_2 concentration, but the impact of SO_2 on NO^+ / NO_2^+ ratio could be negligible. The induction periods under different conditions are discussed in the revised manuscript (lines 249, 361, and 437-438). For example, the induction period became shorter with the increase of SO_2 concentration (line 249).

The time-series changes in the ratios of O/C, H/C, and N/C are shown in Figures R4-R6. In addition, the time-series variations in the fraction of organic ion groups (CH^+, CHO^+, and CHO_{gt1}^+) are shown in Figure R7, which shows the higher fraction of CHO_{gt1}^+ and lower fraction of CH^+ obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA.

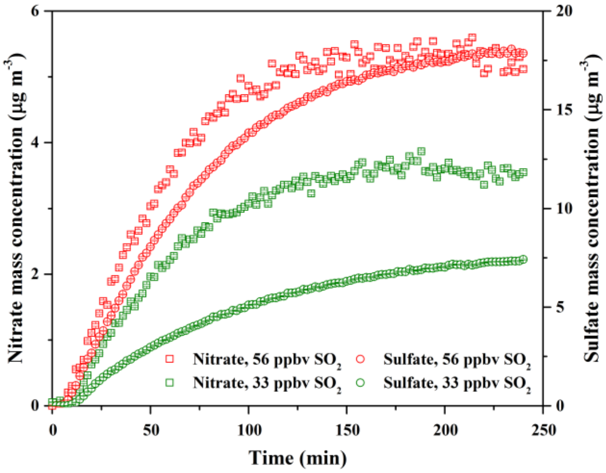

Figure R1. Variations in the concentrations of sulfate and nitrate in the presence of various SO_2 concentrations as a function of reaction time (without seed particles).

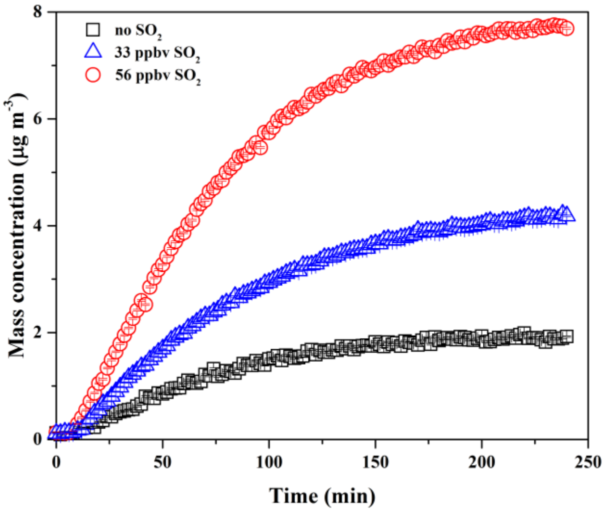

Figure R2. Variations in the concentrations of ammonium salt as function of irradiation time at various SO_2 concentrations (without seed particles).

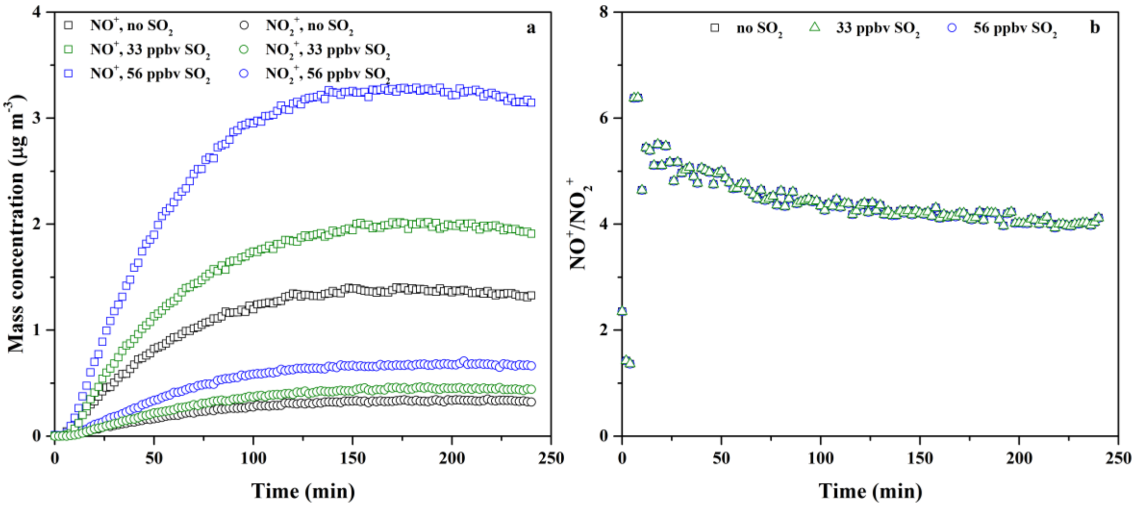

Figure R3. Variations in the mass concentrations of NO^{+} and NO_2^{+}, as well as $\mathrm{NO}^{+}/\mathrm{NO}_2^{+}$ ratio as a function of irradiation time at various SO2 concentrations (without seed particles).

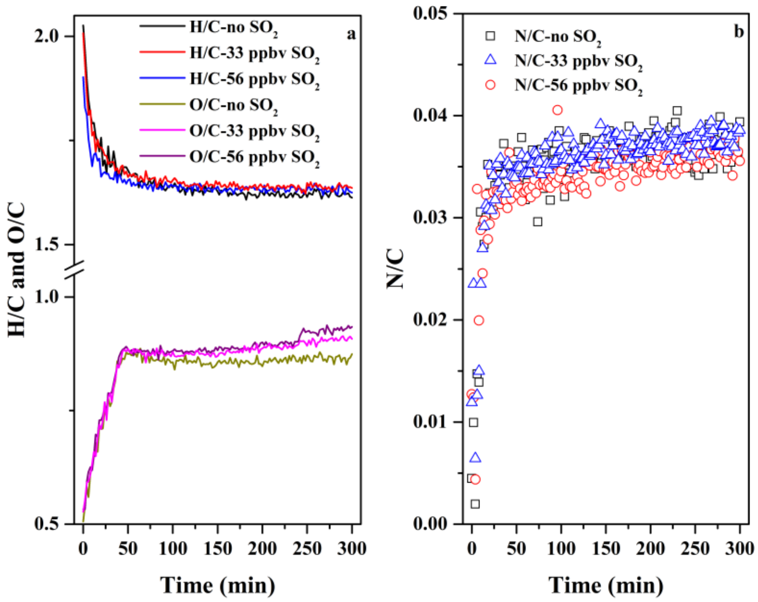

Figure R4. Variations in H/C, O/C, and N/C at various SO2 concentrations as a function of irradiation time (without seed particles).

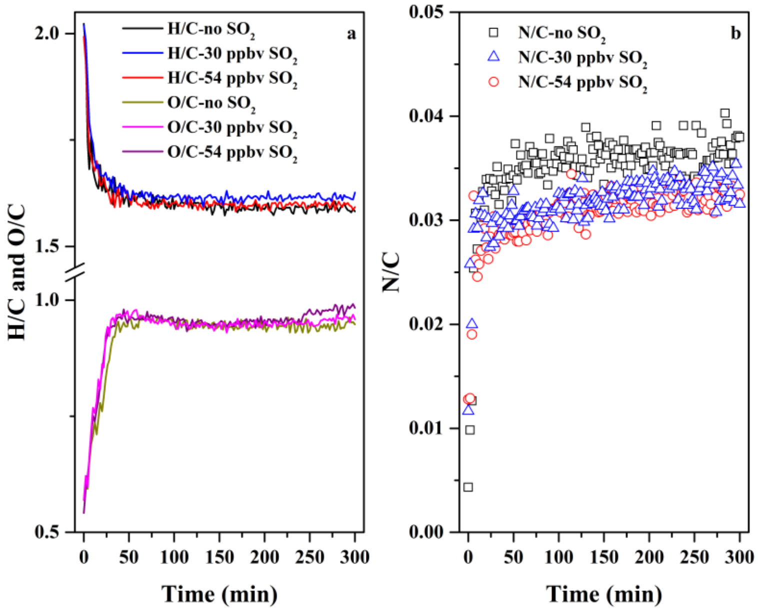

Figure R5. Variations in H/C, O/C, and N/C at various SO_2 concentrations as a function of irradiation time with NaCl seed particles.

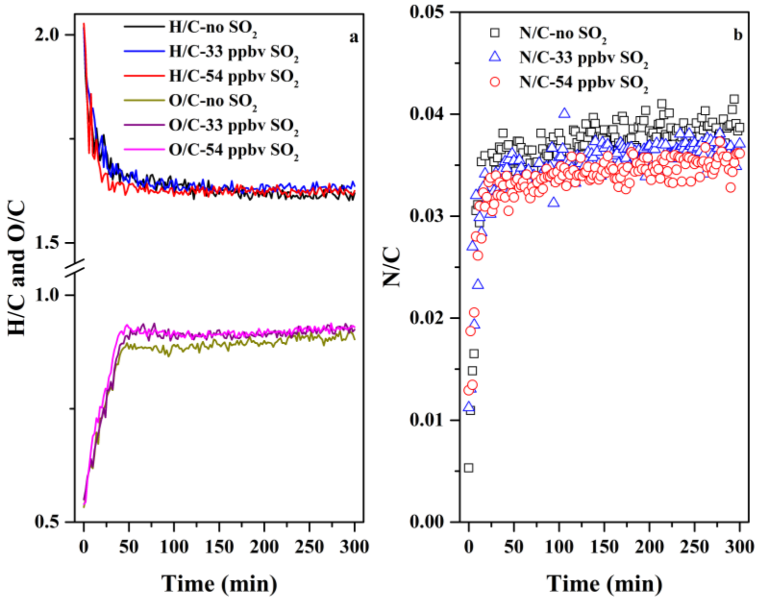

Figure S6. Variations in H/C, O/C, and N/C at various SO_2 concentrations as a function of irradiation time with $(NH_4)_2SO_4$ seed particles.

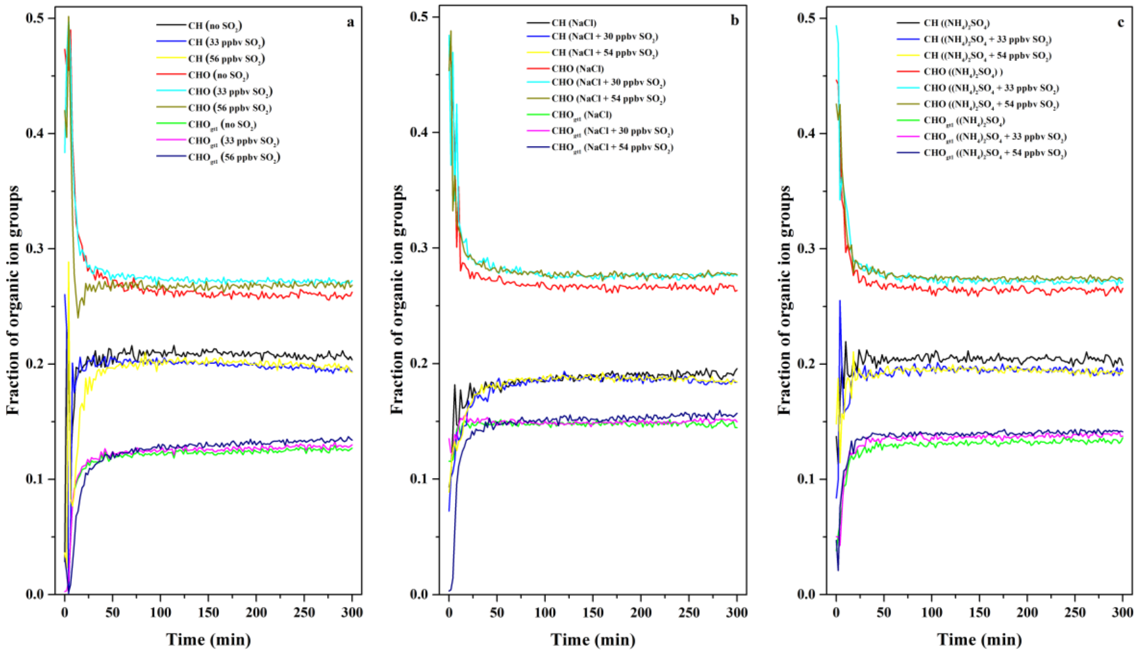

Figure R7. Variations in the fraction of organic ion groups as a function of irradiation time in the presence of different SO_2 concentrations and seed particles (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$).

For the gas phase: The decays of guaiacol, NO_x, and SO_2 as a function of irradiation time are shown in Figure R8, Figure R9, and Figure R10, respectively, which have the similar changing trends for different experiments. The time-series variations in the concentrations of acetic acid at different SO_2 concentrations measured by the HR-ToF-PTRMS are shown in Figure R11, which shows that acetic acid concentration decreases with the increase of SO_2 concentration, suggesting that the uptake of acetic acid might be enhanced in the presence of sulfate and seed particles.

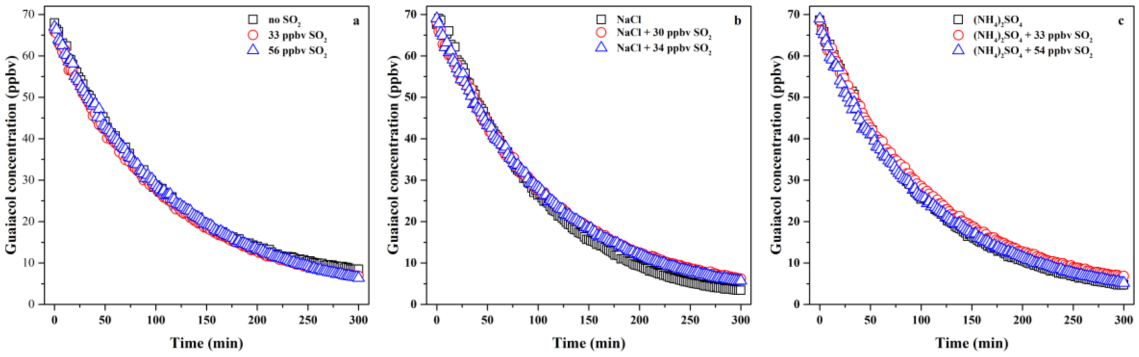

Figure R8. Decays of guaiacol as a function of irradiation time at different conditions (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$)).

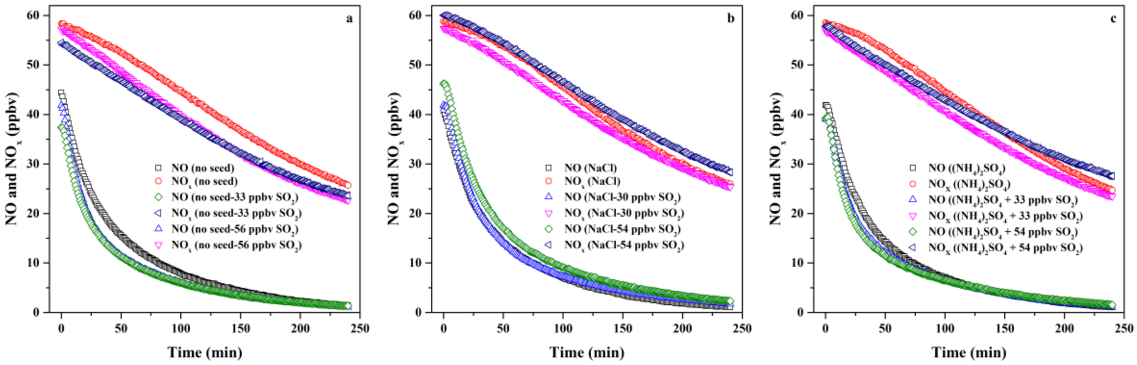

Figure R9. Decays of NO_x as a function of irradiation time at different conditions (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$)).

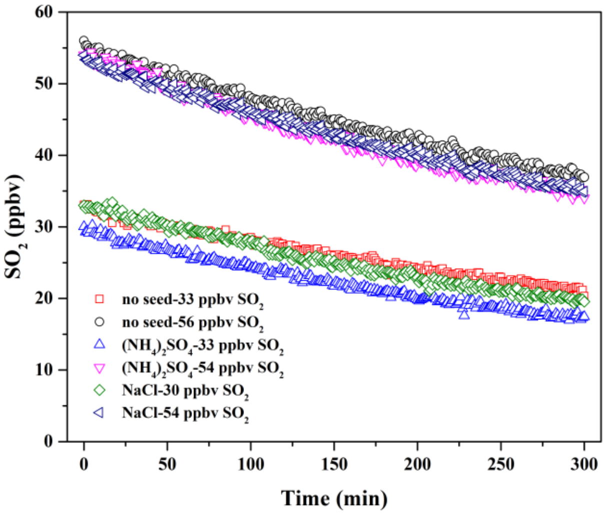

Figure R10. Decays of SO_2 as a function of irradiation time with different seed particles.

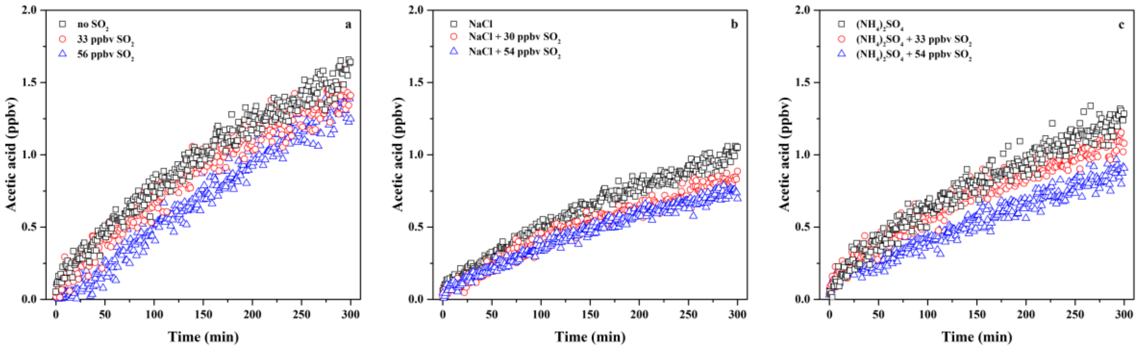

Figure R11. Variations in the gas-phase concentrations of acetic acid as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$).

Revisions in the manuscript:

1. Figures R1-R11 have been added in the revised Supplement.

2. Lines 245-251, Add: "the time-series variations in the concentrations of sulfate and nitrate are shown in Fig. S4. The decays of guaiacol, NO_x, and SO_2 are shown in Fig. S5a, Fig. S6a, and Fig. S7, respectively, which have the similar changing trends for different experiments. As illustrated in Fig. 2, the induction period became shorter with the increase of SO_2 concentration. The similar results caused by SO_2 have also been reported previously (Chu et al., 2016; Liu et al., 2016b)."

3. Lines 270-274 Add: "The time-series changes in the concentration of ammonium salt at different SO_2 concentrations are shown in Fig. S8. Its concentration increased obviously with increasing SO_2 concentration, suggesting that the more amounts of $(NH_4)_2SO_4$ was produced. The similar results have also been reported recently by Chu et al. (2016)."

4. Lines 295-296, Add: "The variations in H/C, O/C, and N/C ratios as a function of irradiation time are shown in Fig. S10."

5. Lines 308-311, Add: “This is well supported by the time-series variations in the fraction of organic ion groups (CH^+, CHO^+, and CHO^+_{gt1}) (Fig. S12a), which shows the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA.”

6. Lines 342-349, Add: “This is well supported by the time-series variations in the concentrations of acetic acid at different SO_2 concentrations measured by the HR-ToF-PTRMS (Fig. S15a), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−56 ppbv). These results were in good agreement with those reported by Liggio et al. (2005) and Liu et al. (2010), who observed that that the uptake of organic compounds under acidic conditions would be enhanced significantly. Recently, Huang et al. (2016) have also reported that acetic acid is present in SOA formed via α-pinene ozonolysis and its uptake would increase in the presence of seed particles.”

7. Line 361, Add: “(i.e., shorten induction period)”

8. Lines 385-390, Add: “As shown in Figs. S12b and S12c, compared to $(NH_4)_2SO_4$ seed particles, the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ were obtained with NaCl seed particles, consequently resulting in higher OS_C of SOA. The time-series evolution of O/C, H/C, and N/C ratios is shown in Figs. S16 and S17, which indicate that O/C ratio with NaCl seed particles is higher than that with $(NH_4)_2SO_4$ seed particles.”

9. Lines 405-409, Add: “As shown in Fig. S15, the concentration of acetic acid in the gas phase with NaCl seed particles was lower than that with $(NH_4)_2SO_4$ seed particles.

It suggests that the uptake of acetic acid on NaCl seed particles might be higher than that on $(NH_4)_2SO_4$ seed particles under the similar experimental conditions (i.e., NO_x and guaiacol concentrations, temperature, and RH)."

10. Lines 431-435, Add: "The decays of guaiacol, NO_x, and SO_2 are shown in Fig. S5, Fig. S6, and Fig. S7, respectively, which have the similar changing trends for different experiments. Fig. S19 shows the time-series evolution in the sulfate concentration in the presence of different SO_2 concentrations and seed particles, which indicates that sulfate concentration is dependent on SO_2 concentration."

11. Lines 437-438, Add: "but had an ignorable impact on the induction period"

12. Lines 451-455, Add: "which was well supported by the time-series variations in H/C, O/C, and N/C ratios at different SO_2 concentrations with NaCl and $(NH_4)_2SO_4$ as seed particles, shown in Figs. S16 and S17. In addition, as shown in Figs. S12b and S12c, the higher fraction of CHO^+_{gt1} and lower fraction of CH^+ were obtained at higher SO_2 concentration, consequently resulting in higher OS_C of SOA."

13. Line 467-471, Add: "This hypothesis could be supported by the variations in acetic acid concentration in the presence of different seed particles and SO_2 concentrations (Fig. S15), which shows that acetic acid concentration decreased with the increase of SO_2 concentration (0−54 ppbv)."

Comment 2: Error bars on the comparison plots (Figs 2, 4, 5, and 7) would really help with interpretation. Were replicate experiments at some of the same initial conditions run? How much variation was observed?

Response to comment 2: Error bars in the Figures 2, 4, 5, and 7 in the original manuscript have been added, which are determined by HR-ToF-AMS analysis. In addition, the uncertainties of SOA yields, M_o, and OS_C have been added in the revised manuscript, which have been pointed out in the responses to the Referee #2's Comment 4. Thus, these revisions were not listed as follows.

Comment 3: What is the motivation for the PMF analysis? The difference between the two factors appears to be dominated by the intensity difference for CO_2^+. Do you expect a difference in chemical formation/aging when SO_2 is added? It looks like there is a difference in the chemical properties of the aerosol as a function of time for the different systems (Figure S4). Is this due to different chemistry or differences in partitioning of condensable vapors to the particles? Please also include more information on how the PMF analysis was carried out in the supplemental.

Response to comment 3: In order to further identify the effect of SO_2 on the chemical properties of SOA, positive matrix factorization (PMF) analysis for all AMS data obtained at different SO_2 concentrations over the course of experiments was carried out. The PMF analysis has been added in the Supplement. The detailed revisions about PMF analysis have been pointed out in the response to the Referee #2's Comment 2, thus these revisions were not listed.

In this work, we compared the effect of sulfate formed via SO_2 oxidation on SOA formation with/without seed particles. The results showed that the physical and chemical factors could be both helpful to enhance SOA yield, but their contributions were very difficult to quantify. It is well known that sulfate formed via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008), increase the surface areas and change the composition of particles (Xu et al., 2016). All of these factors are favorable to partition more SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields. Therefore, the average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) over the course of experiment and the vapor wall-loss timescale ($\tau_{\text{g-w}}$) under different experimental conditions were estimated and discussed in the revised manuscript. Based on $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio, the underestimation of SOA yield caused by vapor wall loss could be determined. The detailed revisions of the discussion about $\overline{\tau}_{\text{g-p}}$ and $\tau_{\text{g-w}}$ have been pointed out in the response to the Referee #1's Comment 1, thus these revisions were not listed.

Comment 4: You claim that oligomerization reactions will decrease the oxidation state of the SOA (page 12, line 236). How does this occur (please either explain or provide references)? Oligomerization should lead to an increase in carbon number but little change in the net O/C or H/C values for the oligomer.

Response to comment 4: According to your valuable suggestion, this sentence has been rewritten in the revised manuscript.

Revision in the manuscript:

Line 316, Change "the oxidation state of SOA will decrease" **To** "the carbon number of oligomers will increase but their net O/C or H/C values have little change, consequently resulting in little change in the oxidation state of SOA (Chen et al., 2011)."

Comment 5: How are the spectra in Figures S5, S9, and S10 normalized? Are they normalized to the max intensity or to the sum of the intensities? It looks like there is very little negative ion intensity in many of the figures which I would not expect if these are normalized to the sum. When are these mass spectra taken from in terms of experiment time? Are they the average over the whole or the end only? Please also increase the size of this figure, it is very difficult to read which m/z values are negative.

Response to comment 5: All the spectra shown in Figures are the average spectra over the course of the experiment, which are normalized to the sum of the intensities. The little negative ions in the figures might be caused by the functionalization and oligomerization reactions, which were both enhanced in the presence of SO_2. But, we observed that increasing SO_2 concentration was in favor of improving the carbon oxidation state (OS_C) of SOA, indicating that the functionalization reaction should be more dominant than oligomerization reaction in this work. In addition, the size of these figures has been increased in the Supplement.

Comment 6: Please briefly outline how organosulfate concentration was calculated (page 13, line 251). In figure S6, what is the system being shown? Is this methyl sulfate alone or is it a mixture? If it is methyl sulfate alone, why are there so many oxidized and reduced nitrogen peaks fit under the curve? When fitting AMS data, it is best to use the smallest number of ions to fit the curve as you can always improve the fit by adding more ions.

Response to comment 6: Figure S6 in the original Supplement is taken from smog chamber experiment. In order to describe accurately, its caption has been revised in the revised Supplement and the experiment which the figure is taken from has been added in the suitable position in the revised manuscript. In addition, the calculation of organosulfate concentration has been added in the Supplement. The detailed revisions about the calculation of organosulfate concentration were pointed out in the response to the Referee #2's Comment 6, thus these revisions were not listed.

We agree that it is best to use the smallest number of ions to fit the curve. However, we found that if the N-containing peaks were not included during the fitting AMS data process, the fit result was not satisfactory. Thus, the N-containing peaks were taken into account during the fitting process. In addition, the significant N/C ratios were observed in this work, suggesting that organic N-containing compounds were produced via guaiacol photooxidation in the presence of NO_x.

Revisions in the manuscript:

1. Line 339, Add: "(Exp. 3 in Table 2)"

2. Caption of Figure S14, Change "Fitted peaks of average W-mode mass spectrum of methyl sulfate obtained at 56 ppb SO_2 without seed particles." **To** "Fitted peaks of average W-mode mass spectrum of methyl sulfate obtained from smog chamber experiment with 56 ppbv SO_2 and no seed particles."

Comment 7: You note on line 267, page 13 that you do not see evidence of H_2SO_4 formation. Is this conclusion drawn from a lack of the ion(s) observed in the AMS? Have you run acidified ammonium sulfate particles? How do the mass spectra of the sulfate peaks from acidified ammonium sulfate measured in your AMS compare to the sulfate peaks observed here?

In Table 2 you note that the sulfate concentration formed via SO_2 oxidation increases with more SO_2 in the chamber (~10-20 ug/m^3). You also note that the organosulfate concentration was in the range of 2.1-4.3 ng/m^3 (page 13, line 250). What is the identity of the remaining sulfate in the particles (ammonium sulfate, sulfuric acid)? Going back to the first question, what does its time trace look like?

Response to comment 7: In the original manuscript, we wanted to express that new particle formation by H_2SO_4 was not observed using a SMPS. However, we observed the significant formation of sulfate by AMS, and the time-series changes in the sulfate concentration with different seed particles are shown in Figure R14. Since it is difficult to completely remove trace NH_3 in the zero air, thus the formed sulfate should be the mixture of H_2SO_4 and $(NH_4)_2SO_4$. The time-series changes in the concentration of ammonium salt at different SO_2 concentrations are shown in Figure R2. Its concentration increases obviously with increasing SO_2 concentration, suggesting that the more amounts of $(NH_4)_2SO_4$ are produced. In our study, SOA is rapidly formed via guaiacol photooxidation when UV lamps are turned on, thus the new particle formation attributed to sulfuric acid formed via SO_2 oxidation was not observed by the SMPS during experimental process. In order to describe accurately, some revisions have been made in the revised manuscript.

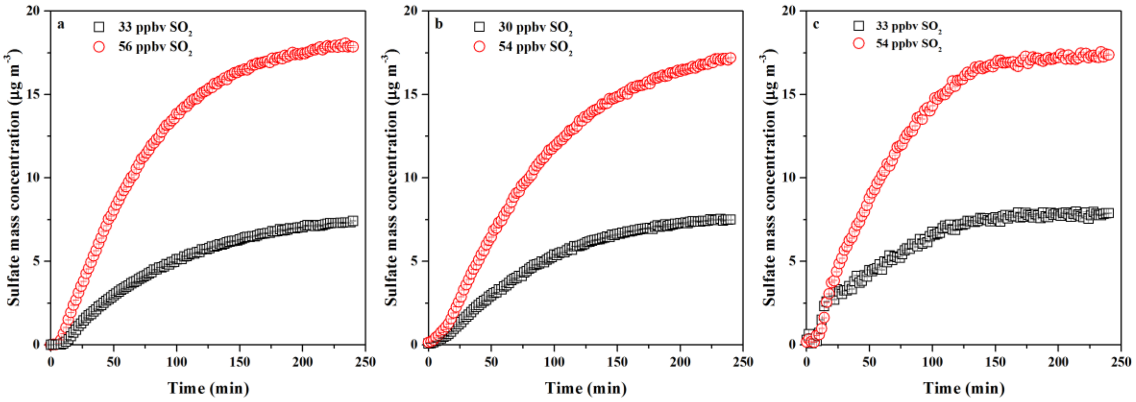

Figure R14. Variations in the concentrations of sulfate as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$). The sulfate concentrations shown in Figure R1c is the net concentrations formed via SO_2 oxidation, e.g., do not include the $(NH_4)_2SO_4$ concentration added in the smog chamber.

Revisions in the manuscript:

1. Figure R14 has been added in the Supplement.

2. Lines 266-274, Add: "Nevertheless, the particle peak attributed to sulfate formed via SO_2 oxidation was not observed by the SMPS during experimental process due to the quick particle growth in the presence of organic vapors. In this work, it is difficult to completely remove trace NH_3 from zero air, thus the formed sulfate should be the mixture of H_2SO_4 and $(NH_4)_2SO_4$. The time-series changes in the concentration of ammonium salt at different SO_2 concentrations are shown in Fig. S8. Its concentration increased obviously with increasing SO_2 concentration, suggesting that the more amounts of $(NH_4)_2SO_4$ was produced. The similar results have also been reported recently by Chu et al. (2016)."

Comment 8: Even if the surface area of the aerosol particles is much smaller than that of the smog chamber (page 14 line 276) I would still expect that small increases in the surface area of particles for condensation would have an effect on SOA yield. Your data for surface area and SOA yield appears to follow a relatively linear trend. Can you run an experiment with the same initial surface area with and without SO_2? (i.e. start with higher initial seed in the experiment without SO_2). This will help interpret the influence of SO_2 on SOA yield.

Response to comment 8: Thank you very much for your constructive suggestion, the increase in the surface area of particles for SOA-forming vapor condensation is discussed in the revised manuscript according to the ratios of $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$. The results show that $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio decreases from 0.82 to 0.71 and 0.61 when SO_2 concentration increases from 0 to 33 and 56 ppbv. These suggest that more SOA-forming vapors are in favor of partitioning onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields.

Revisions in the manuscript:

1. Lines 259-264, Add: "As shown in Fig. 3, $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio decreased from 0.82 to 0.71 and 0.61 when SO_2 concentration increased from 0 to 33 and 56 ppbv. It suggests that the formed sulfate via SO_2 oxidation could serve as seed particles (Jaoui et al., 2008) and increase the surface areas of particles (Xu et al., 2016). These roles are favorable to partition more SOA-forming vapors onto particle phase (Zhang et al., 2014), consequently enhancing SOA yields."

2. Lines 445-448, Add: "As shown in Fig. 3, $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio had a decreasing trend when increasing SO_2 concentration in the presence of seed particles, suggesting that the underestimation of SOA yields caused by vapor wall loss was weakened significantly because of the additional sulfate formed from SO_2 oxidation."

Comment 9: In Figure 6, the intensity of CO^+ does not match the intensity of CO_2^+. What frag tables are being used to calculate the CO^+ ion? Usually, that is set at the same value as CO_2^+ because of interference from atmospheric N_2^+. When (during the experiment) are these mass spectra collected? Are they an average over the whole or the end of the experiments? How reproducible are these differences? Is the difference spectra shown in Figure 6c observed for all the combinations of NaCl and ammonium sulfate seeds (at the same SO_2 concentrations)?

Response to comment 9: Figure 6 in the original manuscript shows the average mass spectra over the course of experiments. The difference spectrum shown in Figure 6c is obtained without SO_2. We are very sorry to make a mistake about the wrong expression in Figure 6 and Figure S8 in the original versions. We double checked the MS data. The intensities of m/z 44 shown in Figure 6 and Figure S8 were obtained by selecting the "Sum to UMR" during the output process of mass spectra, which were the total intensities of all fragments at m/z from 43.981 to 44.026. Thus, the intensities of CO^+ and CO_2^+ do not match in our original figures. The corrected figures have been added in the revised manuscript and Supplement, as shown in Figures R15 and R16. The detailed revisions were listed as follows.

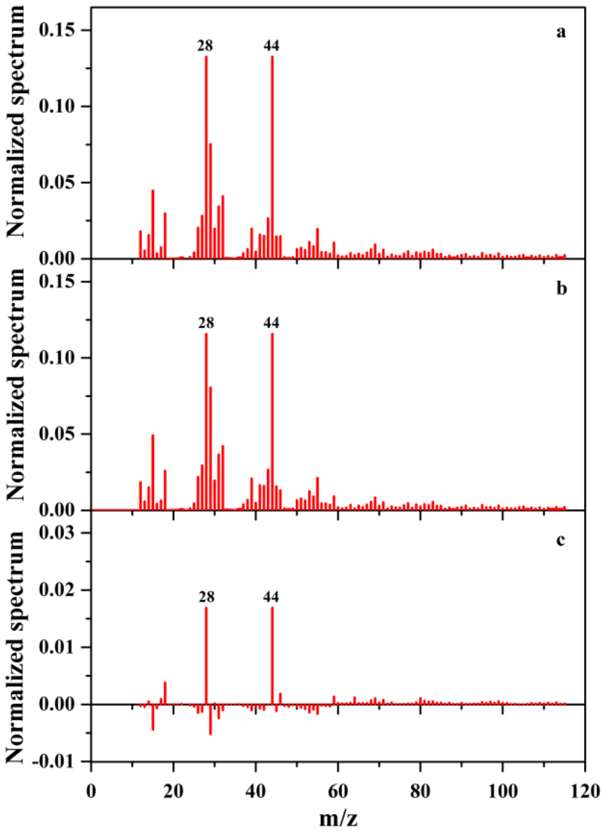

Figure R15. Mass spectra of SOA with NaCl (a) and $(NH_4)_2SO_4$ (b) as seed particles obtained by HR-ToF-AMS, as well as their difference mass spectrum (c) obtained by a minus b.

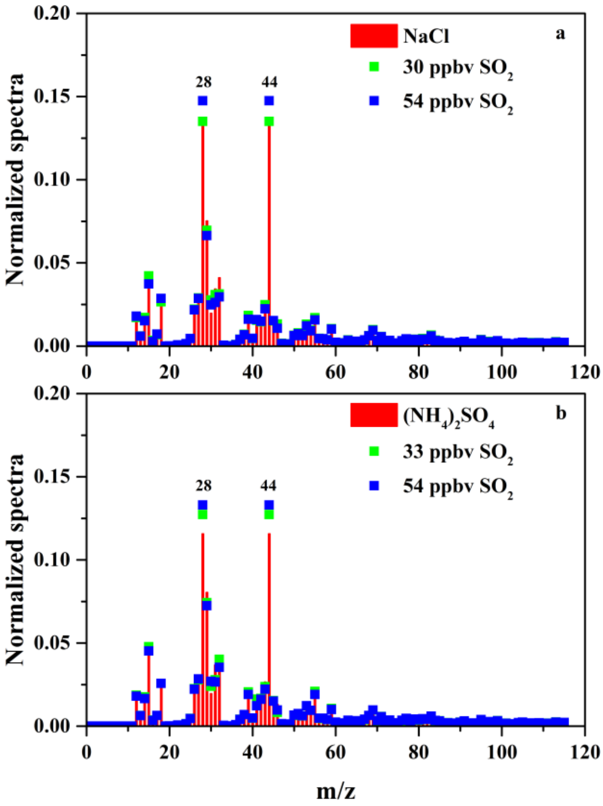

Figure R16. Mass spectra of SOA with NaCl (a) and $(NH_4)_2SO_4$ (b) as seed particles obtained by HR-ToF-AMS at different SO_2 concentration (red bars: without SO_2; olive markers: 30 ppbv SO_2 for a and 33 ppbv SO_2 for b; blue markers: 54 ppbv SO_2).

Revisions in the manuscript:

Figure S15 has been added in the revised manuscript (Figure 7).

Figure R16 has been added in the revised Supplement (Figure S20).

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