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.

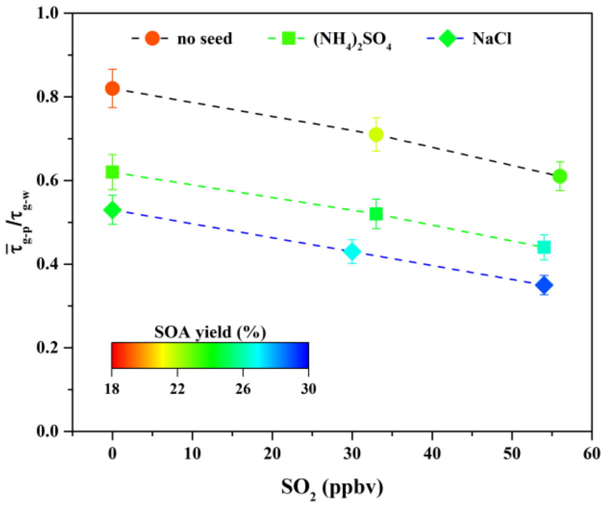

Figure R1. Variations in $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ ratio in the presence of various seed particles as a function of SO_2 concentration.

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.

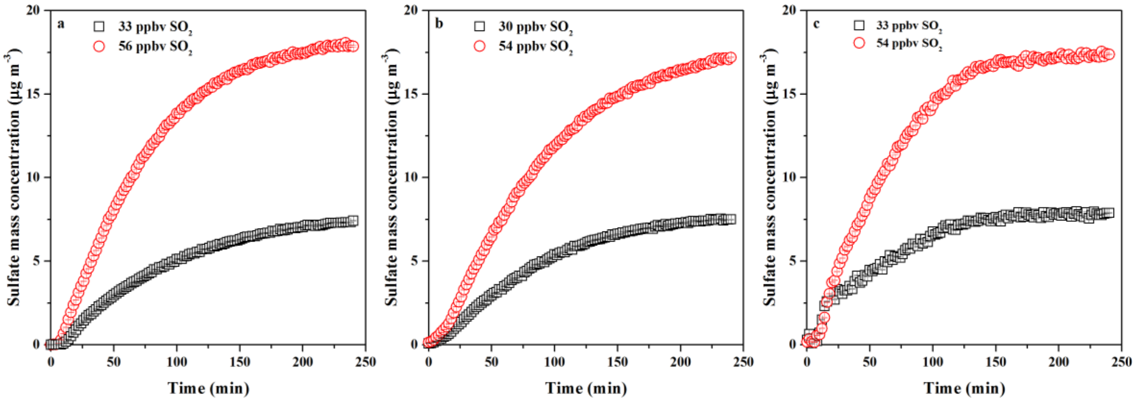

Figure R2. Variations in the concentrations of sulfate as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$). The sulfate concentrations shown in Figure R1c is the net concentrations formed via SO_2 oxidation, e.g., 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.

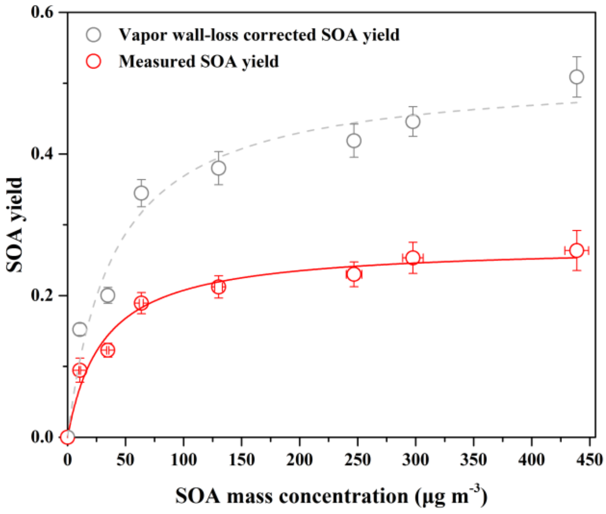

Figure R3. SOA yield as a function of SOA mass concentration (M_0) for guaiacol photooxidation in the presence of NO_x at different guaiacol concentrations. The solid lines was fit to the experimental data using a one-product model. Values of α and $K_{om,i}$ used to generate the solid line were (0.27 ± 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, $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ 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."

8. Lines 370-374, Add: “As shown in Fig. 3, $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ 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, $\overline{\tau}_{\text{g-p}} / \tau_{\text{g-w}}$ 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.”

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

11. Lines 495-497, 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.”

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

3 Timescale calculation

The average gas-particle partitioning timescale ($\overline{\tau}_{\text{g-p}}$) 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).

$$\overline{\tau}_{\text{g-p}} = \frac{1}{2\pi \overline{N}_{\text{p}} \overline{D}_{\text{p}} D_{\text{gas}} F_{\text{FS}}} \qquad \text{(S1)}$$

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

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

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:

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

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).

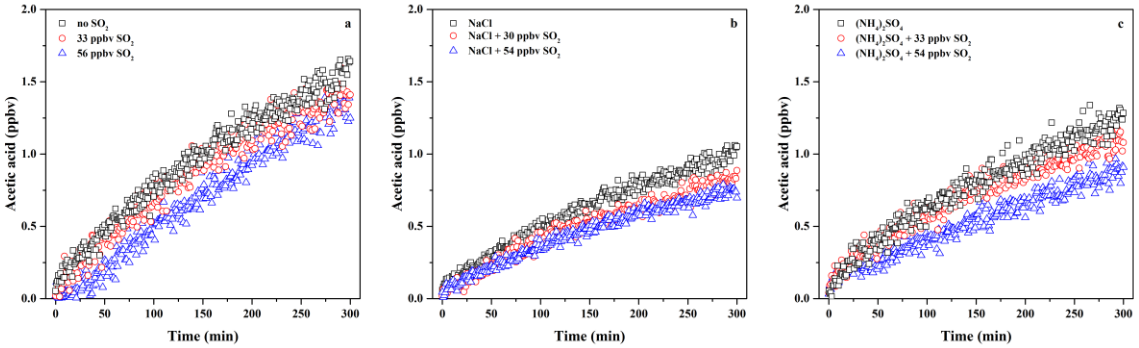

Figure R4. Variations in the gas-phase concentrations of acetic acid as function of irradiation time in the presence of various seed particles and SO_2 concentrations (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$).

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.

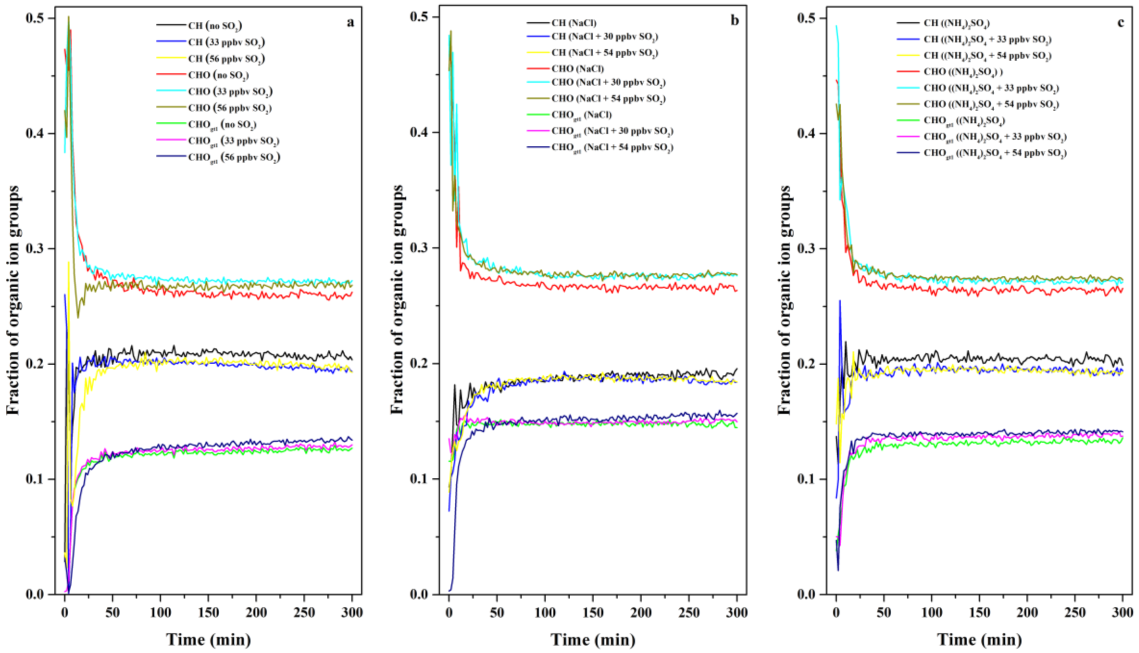

Figure R5. Variations in the fraction of organic ion groups as a function of irradiation time in the presence of different SO_2 concentrations and seed particles (a: no seed, b: NaCl, c: $(NH_4)_2SO_4$).

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)."

References

Liggio, J., Li, S.-M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, J. Geophys. Res.-Atmos., 110, doi:10.1029/2004JD005113, 2005.

Liu, Z., Ge, M., Yin, S., and Wang, W.: Uptake and reaction kinetics of α-pinene and β-pinene with sulfuric acid solutions, Chem. Phys. Lett., 491, 146-150, doi: 10.1016/j.cplett.2010.04.004, 2010.

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