

Reply to Anonymous Referee #1

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

Liu et al. presented a regional modeling study about the effects of stabilized Criegee Intermediates (sCI) on sulfate formation during the summertime in Beijing-Tianjin-Hebei, China. They found that the heterogeneous uptake involving aerosol water and gas-phase OH oxidation of SO₂ were the two important source of sulfate, while sCI oxidation pathway could be insignificant in the actual case. This study calls for the attention of a better-constrained evaluation of the role of sCI in sulfate formation in regional and global models. This manuscript is overall well-written and the discussion is sound. I recommend for publication after considering the following points:

General comments:

1. About heterogeneous oxidation: It is better to show some more details about this reaction pathway since it is the most important contribution but only one parameter (γ) is involved. For example, how much is the aerosol-phase liquid water content in the model during this period? What is the total surface area of particles? What are the fractions that POA and SOA contributing to heterogeneous oxidation of SO₂? How about the sensitivity test of γ to sCI contribution?

Response: We have clarified in Section 2.2: *“The aerosol hygroscopic growth is directly predicted by ISORROPIA in the model, and the aerosol water surface area is scaled from the calculated wet aerosol surface area using the third-moment of aerosol species.”*

We have clarified in Section 3.3: *“It is worth noting that the uncertainty in HR_SO₂, as the most important sulfate source, also influences the sulfate contribution of sCI_SO₂. Several factors influence the heterogeneous reactions of SO₂ on aerosol*

surfaces, including aerosol water surface area, aerosol acidity, organic coating, et al. In the B-case, the predicted average aerosol liquid water and wet surface area are $18.8 \mu\text{g m}^{-3}$ and $2.4 \times 10^{-4} \text{ m}^2 \text{ m}^{-3}$ in the BTH during the episode, and the uptake coefficient of SO_2 by aerosols (γ) is assumed as 0.5×10^{-4} . To investigate the sensitivity of $s\text{CI}_{\text{SO}_2}$ sulfate contributions to uncertainties in HR_{SO_2} , we perform sensitivity simulations with γ of 0.25×10^{-4} and 1.0×10^{-4} . The sulfate concentration of HR_{SO_2} is affected considerably by the variation of γ , with the average change of -18.3% and 25.6% in BTH during the episode when the γ is assumed as 0.25×10^{-4} and 1.0×10^{-4} , respectively. However, effects of the γ change to sulfate contributions of $s\text{CI}_{\text{SO}_2}$ is not significant, with the change of -4.4% and 3.9% when the γ is assumed as 0.25×10^{-4} and 1.0×10^{-4} , respectively.”

2. About sCI profile: The authors only showed the sCI effect of SO_2 . What are the temporal profiles of sCIs? How about the fates of them in the atmosphere, especially for different sCI types? Is H_2O always the predominant sink of sCIs?

Response: We have clarified in Section 3.3: “Figure 10 shows the diurnal profiles of $s\text{CI}_1$, $s\text{CI}_2$ and $s\text{CI}_3$ concentrations in BTH from 04 to 15 July 2015. The average concentration of $s\text{CI}_1$, $s\text{CI}_2$ and $s\text{CI}_3$ is 1.8×10^4 , 2.0×10^4 and 1.9×10^4 molecules cm^{-3} , respectively. Novelli et al. (2017) have estimated the concentration of sCI in the lower troposphere based on the observation in a boreal forest in Finland and in rural southern Germany. The results show that the average concentration of sCI is about 5.0×10^4 molecules cm^{-3} , with an order of magnitude uncertainty, generally consistent with our study. Dominant sCI peaks frequently occur during nighttime, mainly caused by the low PBL facilitating accumulation of alkenes and sCI and low reaction rates of sCI with other species (Smith et al., 2015; Stone et al., 2014; Taatjes et al., 2017). It is worth noting that sCI are predominantly quenched by reactions with water vapor in the atmosphere.”

Specific comments:

1. Page 2 Line 62: "Basing on" should be "based on"

Response: We have changed “Basing on” to “Based on” in the sentence.

2. Page 11 Line 282: "worth nothing..." should be "worth noting"

Response: We have revised “worth nothing” to “worth noting” in the sentence.

3. Figure 4: the legend for wind speed is too small

Response: We have revised the legend of wind speed in Figure 4.

4. Figure 9: what could be the potential reasons for the dominant peak of sulfate temporal profile in S1 and S2 cases around July 10, while in other time periods much smoother and lower compared with the base case?

Response: We have clarified in Section 3.3: *“In the S1-case and S2-case, there is a dominant peak of sulfate concentrations on July 10, which might be caused by the reaction rate constants used in the two cases. We have performed an additional sensitivity study (S3-case), in which the reported κ_{sCI+SO_2} ($3.42 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and κ_{sCI+H_2O} ($7.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) suggested by Stone et al. (2014) and Smith et al. (2015) are used. The results show that the average sulfate contribution of sCI_SO_2 becomes more insignificant, about $0.06 \mu\text{g m}^{-3}$ or less than 0.6%. However, there is no obvious peak around July 10 (Figure 11), indicating that the large uncertainty in contributions of sCI_SO_2 to sulfate mass is due to the different value of κ_{sCI+SO_2} and κ_{sCI+H_2O} used in the sensitivity studies.”*

References:

- Novelli, A., Hens, K., Tatum Ernest, C., Martinez, M., Nölscher, A. C., Sinha, V., Paasonen, P., Petäjä, T., Sipilä, M., Elste, T., Plass-Dülmer, C., Phillips, G. J., Kubistin, D., Williams, J., Vereecken, L., Lelieveld, J., and Harder, H.: Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument, *Atmos. Chem. Phys.*, 17, 7807–7826, <https://doi.org/10.5194/acp-17-7807-2017>, 2017.
- Smith, M., Chang, C-H., Chao, W., Lin, L-C., Takahashi, K., Boering, K., and Lin, J. J-M: Strong negative temperature dependence of the simplest Criegee Intermediate CH_2OO reaction with water dimer, *J. Phys. Chem. Lett.*, 6(14), 2708–2713, <https://doi.org/10.1021/acs.jpcclett.5b01109>, 2015.

- Stone, D., Blitz, M., Daubney, L., Howes, N., and Seakins, P.: Kinetics of CH₂OO reactions with SO₂, NO₂, NO, H₂O and CH₃CHO as a function of pressure, *Phys. Chem. Chem. Phys.*, 16, 1139–1149, <https://doi.org/10.1039/c3cp54391a>, 2014.
- Taatjes, C. A.: Criegee intermediates: What direct production and detection can teach us about reactions of carbonyl oxides, *Annu. Rev. Phys. Chem.* 2017. 68:183–207, <https://doi.org/10.1146/annurev-physchem-052516-050739>, 2017.

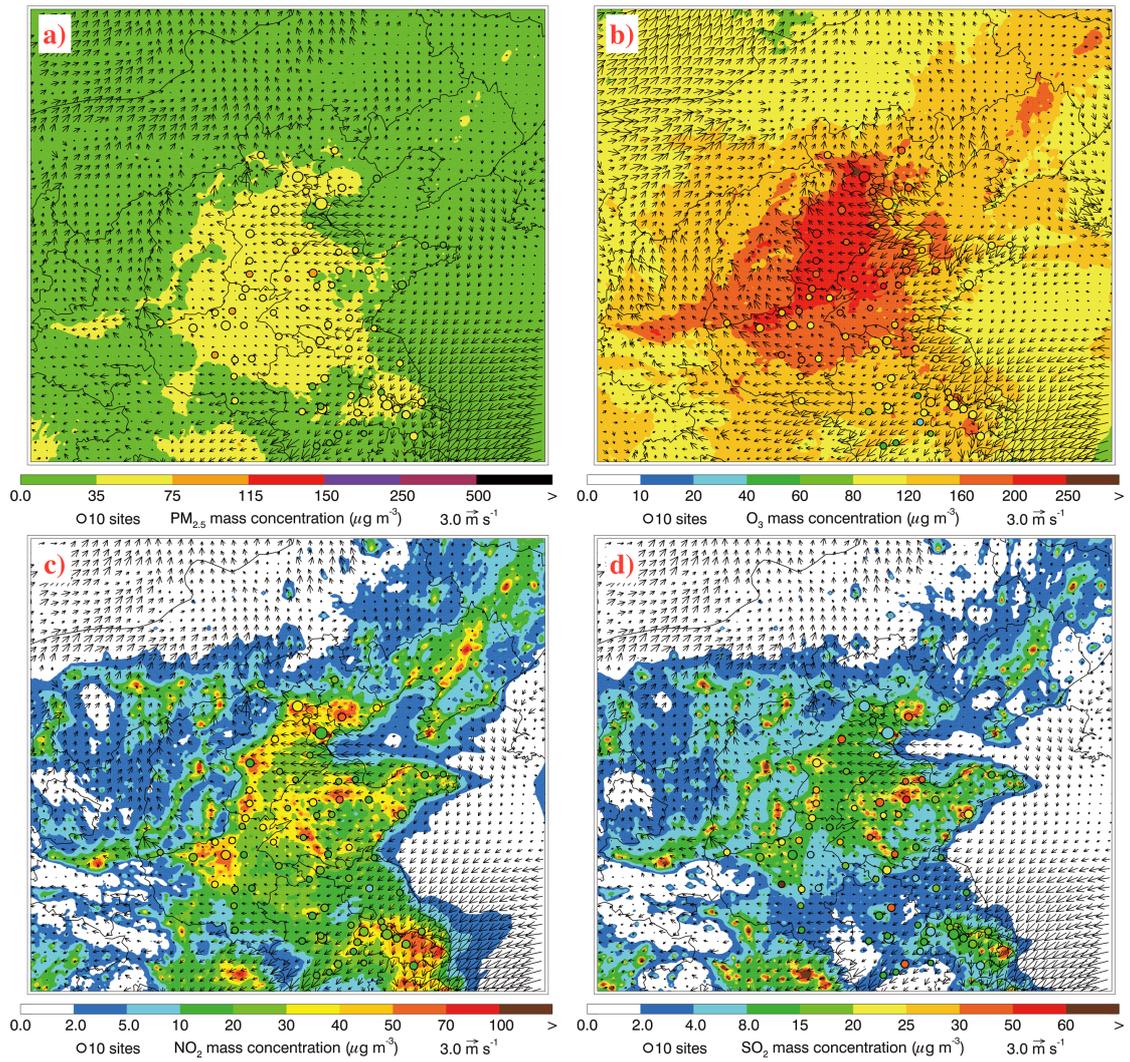


Figure 4 Spatial distributions of average (a) PM_{2.5}, (b) peak O₃, (c) NO₂, and (d) SO₂ mass concentrations from 04 to 15 July 2015. Colored dots, colored contour, and black arrows are observations and simulations of air pollutants, and simulated surface winds, respectively.

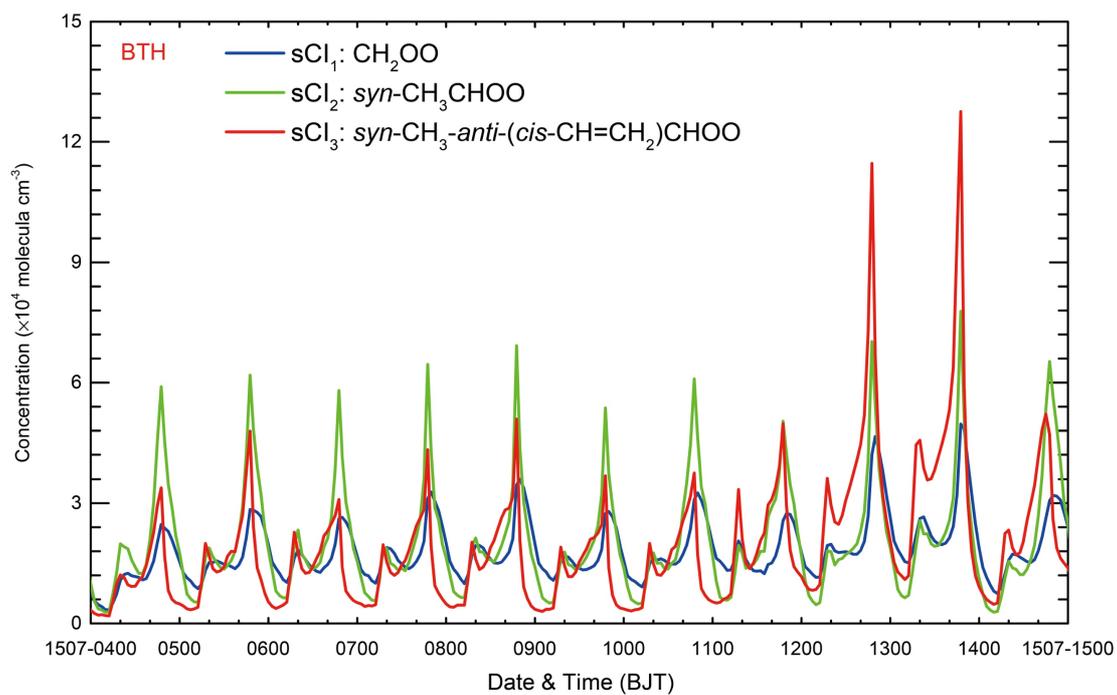


Figure 10 Temporal variations of the average simulated concentration of different sCI (Blue line: sCI₁; Green line: sCI₂; Red line: sCI₃) in BTH from 04 to 15 July 2015.

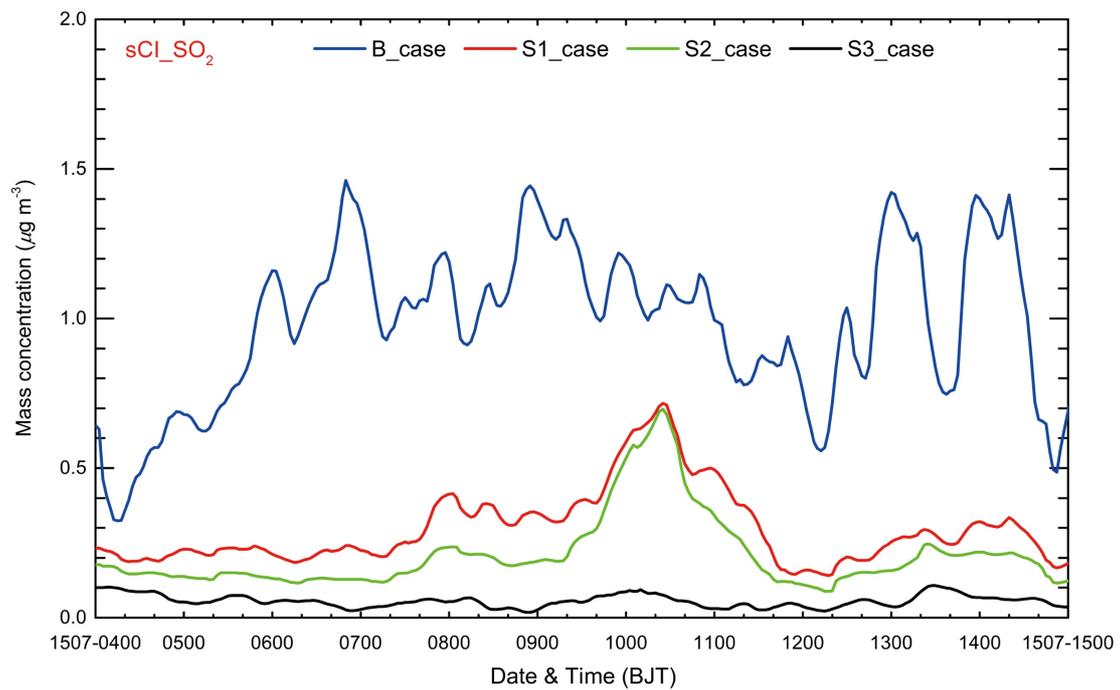


Figure 11 Temporal variations of the simulated average sulfate concentration contributed by the sCl_SO₂ (Blue line: B-case; Red line: S1-case; Green line: S2-case; Black line: S3-case) in BTH from 04 to 15 July 2015.