

Dear Anonymous Referee,

Thank you for your thorough review of the manuscript. We have read the editor's and the reviewer's comments carefully, taken all of the reviewer's comments into consideration and revised the manuscript accordingly. All the changes have been highlighted in the revised manuscript. Our detailed responses, including a point-by-point response to the reviews and a list of all relevant changes, are as follows:

**Responds to the comments from Anonymous Reviewer 2:**

**Q1: This manuscript presents the assess of the contributions of cloud chemistry to the SO<sub>2</sub> and sulfate levels in typical regions in China using a WRF/CUACE model.**

**Evaluating the cloud chemistry scheme in WRF/CUACE by the in-situ cloud chemistry observations at Mount Tai in summers of 2015 and 2018 in case-1; Quantifying the contributions of cloud chemistry to the SO<sub>2</sub> and sulfate changes in a typical winter pollution month of December 2016 in case-2.**

A: Thanks for your careful review. We have carefully read all your comments and suggestions and answered and revised the article accordingly for all the points raised in the review.

**First, the authors stated in Lines 59-61 that few models have assessed the contribution of cloud chemistry to sulfate formation in polluted regions in China. This is not true. A lot of previous studies have demonstrated that cloud chemistry is insufficient to explain sulfate formation in polluted regions in China. The improvement of the WRF/CUACE model used in this study compared to previous models is not well justified. What is the advantage to use WRF/CUACE model?**

A: We agreed that previous studies have studied the cloud chemistry and its impacts on sulfate formation in polluted regions in China and pointed out the impacts were insufficient to explain the sulfate pollution. We have added the most resent researches related with pollution evaluated in liquid and cloud state and traditional together with new multiphase oxidation pathways in very heavy pollution episode in China into the introduction of the manuscript:

“Several regional and global models have tried to include only two, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, in-cloud oxidant in cloud chemistry mechanisms, (Park et al., 2004; Tie et al., 2005; Salzen et al., 2000; Chapman et al., 2009; Leighton and Ivanova, 2008). A very few models can simulate the pathway of NO<sub>2</sub>, TMIs of Fe or Mn ions (Ge et al., 2021; Binkowski and Roselle, 2003; Chang et al., 1987; Terrenoire et al., 2015; Menut et al., 2013).”

and:

“WRF/CUACE is an online coupled chemical numerical model that considers chemical and aerosol feedbacks to meteorology and is able to accurately describe the concentrations of

seven atmospheric aerosol components by 12 size-bin distributions (Gong et al., 2003 ), with an explicit aerosol-cloud activation scheme (Zhou et al., 2012, 2016, 2021), which facilitates more accurate cloud chemistry calculations by more accurate simulations of cloud distribution ranges and ambient liquid water content concentrations and distributions. A complete heterogeneous chemistry module has been built in CUAC for nine gas-to-particle heterogeneous reactions including SO<sub>2</sub> to sulfate in CUACE (Zhou et al., 2021, Zhang et al., 2021), which supports the initiation of the cloud chemistry module. The cloud chemistry mechanism in CUACE considers the pathways of multiphase oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> in both stratocumulus and convective clouds (Gong et al., 2003; Von Salzen et al., 2000). CUACE's cloud chemistry occurs in an environment containing cloud water and fog water, which is closely related to the ambient liquid water content and can also present the contribution of cloud chemistry in hazy days.”

Together with more 10 literatures added into the reference list:

1. Binkowski, F. S., and Roselle, S. J.: Models - 3 Community Multiscale Air Quality (CMAQ) model aerosol component 1. Model description, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2001jd001409>, 2003.
2. Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R., and Walcek, C. J.: A three-dimensional eulerian acid deposition model physical concepts and formulation, *journal of geophysical research*, 92, 14,681-614,700, <https://doi.org/10.1029/jd092id12p14681>, 1987.
3. Chapman, E. G., Gustafson, W. I., Easter, R. C., Barnard, J. C., and Fast, J. D.: Coupling aerosol-cloud-radiative processes in the WRF-Chem model: Investigating the radiative impact of elevated point sources, *Atmos. Chem. Phys.*, 9, 945–964, <https://doi.org/10.5194/acp-9-945-2009>, 2009.
4. Dovrou, E., Rivera-Rios, J. C., Bates, K. H., and Keutsch, F. N.: Sulfate Formation via Cloud Processing from Isoprene Hydroxyl Hydroperoxides (ISOPOOH), *Environ Sci Technol*, 53, 12476-12484, <https://doi.org/10.1021/acs.est.9b04645>, 2019.
5. Leighton, H. G., and Ivanova, I. T.: Aerosol–Cloud Interactions in a Mesoscale Model. Part I: Sensitivity to Activation and Collision–Coalescence, *Journal of the Atmospheric Sciences*, 65, 289-308, <https://doi.org/10.1175/2007jas2207.1>, 2008.
6. Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Colette, A., Coll, I., Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J. L., Pison, I., Turquety, S., Valari, M., Vautard, R., and Vivanco, M. G.: Regional atmospheric composition modeling with CHIMERE, *Geoscientific Model Development*, 6, 981–1028, <https://doi.org/10.5194/gmdd-6-203-2013>, 2013.
7. Park, R. J., and Jacob, D. J.: Sources of carbonaceous aerosols over the United States and implications for natural visibility, *Journal of Geophysical Research*, 108, <https://doi.org/10.1029/2002jd003190>, 2003.
8. Terrenoire, E., Bessagnet, B., Rouïl, L., Tognet, F., Pirovano, G., Létinois, L., Beauchamp, M., Colette, A., Thunis, P., Amann, M., and Menut, L.: High-resolution air quality simulation over Europe with the chemistry transport model CHIMERE, *Geoscientific Model Development*, 8, 21-42, <https://doi.org/10.5194/gmd-8-21-2015>, 2015.

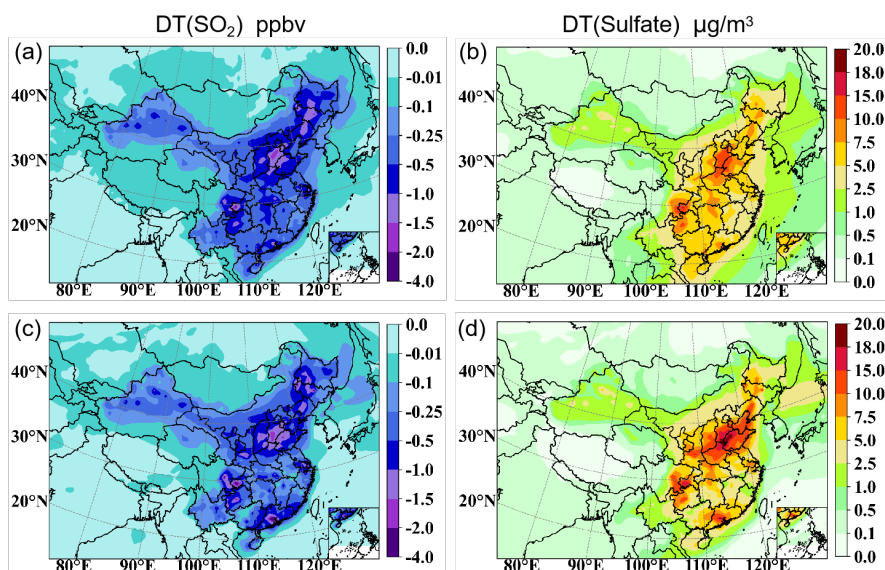
9. Tie, X.: Assessment of the global impact of aerosols on tropospheric oxidants, *Journal of Geophysical Research*, 110, <https://doi.org/10.1029/2004jd005359>, 2005.
10. Zhou Y., Gong S., Zhou C., Zhang L., He J., Wang Y., Ji D., Feng J., Mo J., Ke H.: A new parameterization of uptake coefficients for heterogeneous reactions on multi-component atmospheric aerosols, *Science of the Total Environment*, 781, <https://doi.org/10.1016/j.scitotenv.2021.146372>, 2021.

This is true as we all realized the complex formation scheme of sulfate aerosol by many factors, i.e., emission, nucleation, heterogeneous chemistry, cloud chemistry, meteorology etc., which all contributes to the sulfate formation. As the ambient conditions vary greatly from region to region in China, the relative importance of each factor may change a lot depending on the geographic locations of the concerns. This paper is intended to quantify the relative contributions of cloud chemistry to the SO<sub>2</sub> depletion and sulfate formation in different regions of China as compared to other processes. We fully agree with the reviewer's point that the cloud chemistry was not fully responsible for the heavy pollution of sulfate. This study presents the characteristics of the contribution of cloud chemistry in different regions of China for four seasons and finds that the average contribution to be greater than the monthly average contribution during heavy pollution. Cloud chemistry processes consuming SO<sub>2</sub> are well assessed, and more analysis for sulfate are added as followed third replies.

**Second, Lines 111-112: Henry's law constant of SO<sub>2</sub> was corrected from 1.23 to 1.23×10<sup>-3</sup> M/atm in the model. However, the correct value should be 1.23 M/atm (Seinfeld and Pandis, 2016). Are all the model results in this study based on an incorrect Henry's law constant of SO<sub>2</sub> ?**

A: The Henry's law constant for SO<sub>2</sub> is 1.23 M/atm as used in Von et al (2000), but the Henry's law constant for SO<sub>2</sub> in Leighton et al (1990) is 1.23×10<sup>-3</sup> M/atm. According to Rolf Sander's compilation (R. Sander: Compilation of Henry's law constants (version 4.0) for water as solvent, *Atmos. Chem. Phys.*, 15, 4399-4981 (2015), [doi:10.5194/acp-15-4399-2015](https://doi.org/10.5194/acp-15-4399-2015)), the Henry's law constant for SO<sub>2</sub> is around 1.2 (mol/(kg\*bar)). To convert to the unit of M/atm, it is around 1.23×10<sup>-3</sup>. This was also validated by our the test experiments which show that the oxidation rate of SO<sub>2</sub> by CUACE cloud chemistry is too high when using 1.23 M/atm as the Henry's law constant for SO<sub>2</sub>, which is close to 100% and deviates from the observed experiments. In this paper, to reduce the oxidation rate of SO<sub>2</sub> in cloud chemistry, the SO<sub>2</sub> conversion equation is multiplied by 10<sup>-3</sup>. After adjusting the SO<sub>2</sub> oxidation rate, the simulation results are more approximate to the observed results as shown in Tables 3 and 5.

Figure S1 shows the difference between SO<sub>2</sub> and sulfate concentrations when using 1.23 and 1.23×10<sup>-3</sup> M/atm as the Henry's law constant for SO<sub>2</sub>. The difference in SO<sub>2</sub> concentration in most of eastern China is 0.1-1 ppb, and in the high value areas of NCP, SCB, YRD and PRD the difference in SO<sub>2</sub> concentration is 1-2 ppb. The difference in sulfate concentration in most of eastern China is 1-7.5 μg/m<sup>3</sup>, and the difference in sulfate concentration is 7.5-20 μg/m<sup>3</sup> in the high value areas of NCP, SCB and PRD, and 5-10 μg/m<sup>3</sup> in YRD.



**Figure S1. The average difference between SO<sub>2</sub> and sulfate concentrations when using 1.23 and  $1.23 \times 10^{-3}$  M/atm as the Henry's law constant for SO<sub>2</sub>. (a), (b) for the whole month of December, (c), (d) for Dec. 16-21.**

**Third, Regarding the validation of WRF/CUACE, only the modeled hourly SO<sub>2</sub> and oxidants concentrations are compared to measurements in Figure 2. Are the sulfate concentrations comparable? This is key information for evaluating the performance of this model. Also, the observed and modeled sulfate concentrations should be compared in Tables 5 and 6.**

A: The statistics of correlation coefficients (R), relative average deviation (RAD), and normalized mean deviation (NMB) between hourly simulated and observed SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and sulfate are shown in Table 3. Figure 5 shows the scatter plots of simulated versus observed. It is also found that when cloud chemistry occurs, SO<sub>2</sub> concentration values range from 0-3 ppbv, mostly less than 1 ppbv, O<sub>3</sub> in the range of 25-125 ppbv, and H<sub>2</sub>O<sub>2</sub> in the range of 0-100 µM (Fig. 2), and sulfate in the range of 0-50 µg/m<sup>3</sup>. All four species are agreed within a factor two of observed concentrations, while the sulfate is underestimated. The model underestimates the sulfate concentration with the NMB of -65.5% and -58.2% and R of 0.3 and 0.45, for the CP1 and CP2 respectively. This shows that even though the model can simulate the trend of sulfate concentration, the concrete concentration is much lower than the observation. For the two important oxidants, O<sub>3</sub> is mostly over consumed while H<sub>2</sub>O<sub>2</sub> not. So the underestimation of sulfate may be due to the incomplete of other cloud chemistry mechanisms and the complex liquid water content from cloud physics of the model.

The model is good for SO<sub>2</sub> and both oxidants, and can simulate the concentration trends and average states. Therefore, the current cloud chemistry mechanism of CUACE can also be used to assess the contribution of cloud chemistry to SO<sub>2</sub> and sulfate.

PM<sub>2.5</sub> concentrations are compared in Tables 5 and 6 due to the lack of sulfate observations at multiple site surface stations in the four major pollution areas. The validation of PM<sub>2.5</sub> simulations with and without cloud chemistry during the heavy pollution periods and monthly in Dec. is compared in Tables 5. The results show that with the addition of cloud chemistry simulations, the PM<sub>2.5</sub> simulations do not improve significantly during the heavy pollution periods, and only effectively simulate in PRD, but become worse in NCP. Statistical analysis of PM<sub>2.5</sub> cloud chemical simulation and PM<sub>2.5</sub> observation is compared in Table 6, and the results show that the mean PM<sub>2.5</sub> is closer to the observation with cloud chemistry simulation, and the R improves from 0.65 to 0.73, and the deviation is slightly overestimated by 5% from the original underestimation of 45%.

Table 1. Statistics for SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and sulfate in cloud chemistry at Mount Tai site.

		Obs	Mod	R	RAD	NMB(%)
CP-1	SO <sub>2</sub> (ppbv)	2.16	2.54	0.77	-0.08	17.4%
	O <sub>3</sub> (ppbv)	97.79	61.70	0.49	0.23	-36.9%
	H <sub>2</sub> O <sub>2</sub> (uM)	26.52	49.11	0.72	-0.30	85.2%
	Sulfate( $\mu\text{g}/\text{m}^3$ )	26.76	9.23	0.30	0.49	-65.5%
CP-2	SO <sub>2</sub> (ppbv)	0.56	0.81	0.49	-0.18	44.9%
	O <sub>3</sub> (ppbv)	60.68	49.36	0.46	0.10	-18.7%
	H <sub>2</sub> O <sub>2</sub> (uM)	46.92	49.32	0.03	-0.02	5.1%
	Sulfate( $\mu\text{g}/\text{m}^3$ )	17.73	7.41	0.45	0.41	-58.2%

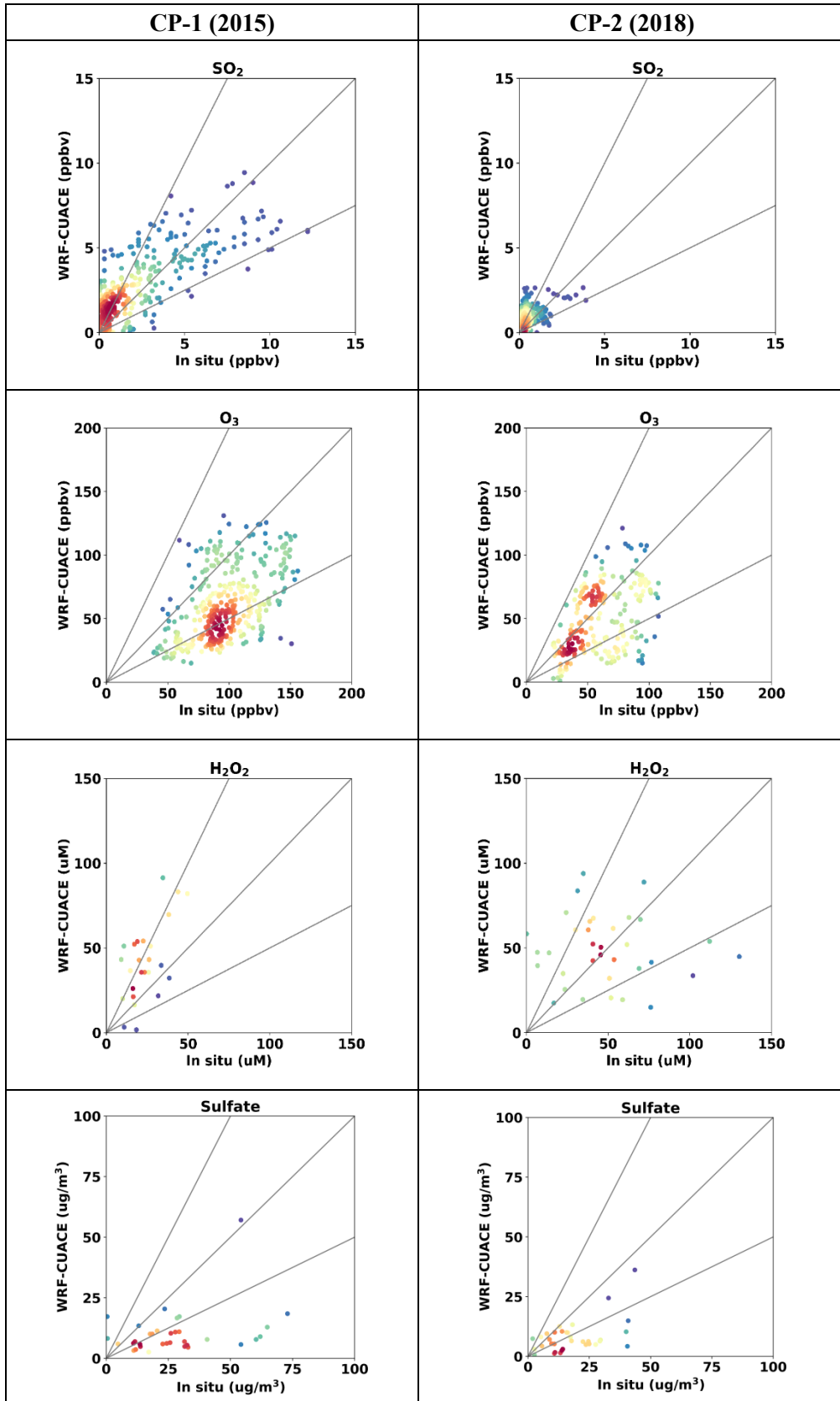


Figure 1. Scatter plots of hourly SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and sulfate concentrations between WRF/CUACE and in situ observations at Mount Tai.