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.

General comments

In this study, the authors attempted to implement a SO_2 heterogeneous reaction parameterization into chemical transportation models to improve simulation of the sulfate rapid growth during haze pollution periods. The proposed parameterization focused on the treatment of the Fe^{3+}- catalyzed oxidation of SO_2 by O_2 in aerosol water. Simulations using WRF-CHEM model were conducted on haze episodes at two cities in China to evaluate the performance of the new parameterization. The authors found that the new parameterization could improve the representation of sulfate heterogeneous formation in WRF-CHEM model since the simulations with the parameterization could reproduce the observed rapid growth of sulfate aerosol and diurnal variations. Given that current models still underestimate the conversion of SO_2 to sulfate, the SO_2 heterogeneous reaction parameterization proposed here to improve sulfate simulation would be interesting to the readerships of the ACP journal. However, some issues related to the clarity of discussions and latest refs need to be addressed before its publication.

Specific comments:

(1) Comment: In the abstract and a statement on p. 3 lines 80-82, it appeared that the observed filter measurements in Xi'an, China since 2003 was used to develop SO_2 heterogeneous reaction parameterization, but how to apply these filter measurements to parameterize SO_2 heterogeneous reaction was not clearly explained. According to the parameterization section (section 3.1), it was more like that the filter measurements was only used to illustrate the relationships between sulfate, iron, humidity and $PM_{2.5}$. None of values for the parameters in parameterization equation (line 208) was derived based on the filter measurements.

Response: We have clarified in the abstract: "*The relationships based on the observed sulfate with $PM_{2.5}$, iron, and relative humidity in Xi'an, China have been employed to evaluate the mechanism and to develop a parameterization of the sulfate heterogeneous formation involving aerosol water for incorporation into atmospheric chemical transport models.*".

(2) Comment: At several places (e.g., p. 7, lines 166-175; p. 9, lines 210-213) the authors stated that oxidation of sulfite by NO_2 in aerosol water was proposed to contribute considerably to the sulfate production when NH_3 concentrations were high. A very recent paper (Wang et al., PNAS, 2016, 113, 13630–13635) has provided the elucidation of this specific mechanism for sulfite- sulfate conversion. In addition, this work also pointed out the critical role of sulfate formation in haze development in China, including promoting the formation of SOA (Zhao et al., Environ. Sci. Technol. 40, 7682, 2006) and nitrate (Zhang et al., Geophys. Res. Lett. 22, 1493, 1995). Those references should be discussed when discussing the aerosol chemistry.

Response: We have clarified in Section 3.1 as follows: "*Recently, Wang et al., (2016) have also elucidated a specific mechanism for the sulfite-sulfate conversion, in which oxidation of sulfite by NO_2 in aerosol water in case of high NH_3 concentrations contributes considerably to the sulfate production. They have also pointed out the critical role of the sulfate formation in haze formation in China through further promoting the formation of SOA and nitrate due to the enhanced hygroscopicity. Zhang et al. (1995) have reported that the high concentration of nitrate is attributed to an efficient heterogeneous conversion of NO_x to HNO_3 due to the hydrolysis of N_2O_5 on sulfate aerosols. Zhao et al. (2006) have investigated the heterogeneous chemistry of methylglyoxal with liquid H_2SO_4, showing that the hydration and oligomerization reactions of methylglyoxal are enhanced by sulfate formation due to the high dependence of these reactions on particle hygroscopicity. Therefore, future studies need to be performed to incorporate the specific mechanism into CTMs to improve sulfate, nitrate, and SOA simulations.*"

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy, Z. M., Hu, M., Lin, Y., Peng, J., Guo, S., and Meng, J.: Persistent sulfate formation from London Fog to Chinese haze,

Proceedings of the National Academy of Sciences of the United States of America, 113, 13630, 2016.

Zhang, R., Leu, M. T., and Keyser, L. F.: Hydrolysis of N_2O_5 and $ClONO_2$ on the $H_2SO_4/HNO_3/H_2O$ ternary solutions under stratospheric conditions, Geophysical Research Letters, 22, 1493-1496, 1995.

Zhao, J., Levitt, N. P., Zhang, R., and Chen, J.: Heterogeneous reactions of methylglyoxal in acidic media: implications for secondary organic aerosol formation, Environmental Science & Technology, 40, 7682-7687, 2006.

(3) Comment: Some statements regarding to the discrepancies between simulation and observation were confused and speculative. For example, in both lines 293 and 314, it was stated that the model had difficulties in reproducing the long-range transport of pollutants like sulfate and nitrate. My concern was that the long-range transport contribution to pollutants could be negligible in this case since Guanzhong Basin was under the control of stagnation condition based on wind fields shown in Fig. 7. Therefore, the long-range transport may be not the reason why the simulated concentrations differ from the observations. Also in lines 302-307, the discrepancies between simulated and observed sulfate mass was attributed to inaccurate simulations of wind fields, but there was no direct comparison between simulated and observed wind fields to demonstrate this point.

Response: We have removed the speculative sentences in both lines 293 and 314, and lines 302-307 due to lack of comparisons of simulated wind fields with observations. We have also included a paragraph about the evaluation of RH in Xi'an and Beijing and the impact of the simulated RH uncertainties on the sulfate simulations:

" *Considering the importance of RH in the SO_2 heterogeneous oxidation, Figure 13 shows the simulated and observed RH in Xi'an from December 16 to 27, 2013 and in Beijing from January 13 to 21, 2014. The model generally performs reasonably well in simulating the observed RH, with IOAs of 0.80 for Xi'an and 0.76 for Beijing. Overall, the model is subject to overestimate the RH, especially in Beijing, but well captures the observed peaks of the RH in Beijing and Xi'an. The RH biases considerably affect the sulfate simulations. The underestimation of the high RH generally corresponds the underestimation of the sulfate*

concentration, i.e., during nighttime on January 15 and 16, 2014 in Beijing, and in the morning from December 23 to 25, 2013 in Xian.".

(4) Comment: To be consistent with Figs. 11 and 12, how about adding one panel for time series of NH_3 (in gas phase) to Figs. 9 and 10 to evaluate the model performance on NH_3?

Response: We do not have the NH_3 measurement from 16 to 27 December 2013 in GZB and from 13 to 21 January 2014 in BTH. We have clarified in Section 3.2: "*Due to lack of routine measurements of NH_3 in GZB and BTH, the evaluation of the model performance on NH_3 is not provided in the present study. Future studies are imperative to be performed to evaluate the model performance on NH_3 which plays an important role in the sulfate formation (Wang et al., 2017).*"

Technical corrections

Comment: On p. 5 in the equation for defining IOA, $|P_i\text{-}\overline{O}|$in the denominator should be $|P_i - \overline{P}|$

Response: The equation of IOA in the manuscript is right, please reference the website "http://www.rforge.net/doc/packages/hydroGOF/d.html".

Comment: Line 321: "sulfate aerosols play a more important role" than what? Nitrate aerosol?

Response: We have revised the sentence as "*sulfate aerosols play an important role*" in Section 3.2.