Reply to Anonymous Referee #2

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

This manuscript presents a heterogeneous formation mechanism of sulfate in which gaseous SO_2 is proposed to be oxidized by O_2 on the aerosol water surface with Fe^{3+} serving as the catalyst. The parameterized mechanism is implemented in WRF-Chem and is evaluated through two heavy haze episodes in the China urban environments. Model simulations show that the proposed mechanism can reproduce the observed sulfate concentrations and improve the $PM_{2.5}$ simulations. This study provides valuable information on improving our understanding of the SO_2 oxidation and sulfate formation in the atmosphere. It is well written and is suitable for publication with minor revisions.

Specific comments

(1) Comment: There are two possible pathways for the heterogeneous SO_2 oxidation catalyzed by Fe^{3+} involving aerosol water—aqueous reactions in cloud water or fog, and heterogeneous reactions on aerosol surfaces (e.g., lines 47-48 and lines 164-165). Does the proposed mechanism in this study consider both and only the latter? If it considers the latter only, would there still be some overlaps in the parameterization presented? And would the sulfate concentrations be possibly overestimated if both pathways are included? Are there any connections or relations between these two pathways?

Response: We have highlighted in Section 3.1: "*There are two possible pathways for the sulfate formation: bulk aqueous-phase oxidation of SO_2 in aerosol water and heterogeneous reaction of SO_2 on aerosol surfaces involving aerosol water.*", and further clarified in Section 3.1: "*We propose here a SO_2 heterogeneous reaction parameterization in which the SO_2 oxidation in aerosol water by O_2 catalyzed by Fe^{3+} is limited by mass transfer resistances in the gas-phase and the gas-particle interface.*". So, The proposed mechanism considers both the aqueous-phase oxidation of SO_2 in aerosol water and heterogeneous reaction of SO_2 on aerosol surfaces involving aerosol water.

The Fe^{3+} catalytic reaction occurring in the two SO_2 oxidation pathways is the same, but under different circumstances. The sulfate concentrations are not possibly overestimated when the both pathways are included.

(2) Comment: Line-208, How is the aerosol water surface area calculated? Since the SO_2 oxidation is highly sensitive to RH, it is critical to treat the aerosol hygroscopic growth, which is closely relevant to the aerosol chemical composition, in the model. How is the aerosol hygroscopic growth treated in the model?

Response: We have clarified in Section 3.1: "*The aerosol hygroscopic growth is directly predicted by ISORROPIA (Version 1.7) 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.*". Considering that the SO_2 heterogeneous oxidation is highly sensitive to RH, we have further evaluated evaluations of the RH simulations (Please found in Comment 5).

(3) Comment: Lines 104-106, The two haze events need to be elaborated.

Response: We have added the description of the two haze events in Section 2.1 as follows: "*A very severe haze episode occurred in GZB during the period from December 16 to 27, 2013, with an average $PM_{2.5}$ concentration of 325.6 μg m^{-3}. The maximum of the average $PM_{2.5}$ concentration in GZB even exceeded 500 μg m^{-3} during the episode. The average temperature and relative humidity in Xi'an was 3.7 ℃ and 72% during the episode, respectively, and the average wind speed was around 3.7 m s^{-1}. The average $PM_{2.5}$ concentration from January 13 to 21, 2014 in BTH was 195.3 μg m^{-3}, with a maximum of 363.9 μg m^{-3}. The average temperature and relative humidity in Beijing during the episode was -0.5 ℃ and 42%, respectively, and the average wind speed was about 7.4 m s^{-1}.*"

(4) Comment: Lines 140-155, It would be helpful to provide quantitative contributions of the gas-phase oxidations by OH (and sCI if possible) to the sulfate formation.

Response: We have included the discussion in Section 3.2: "*It is worthy to note that during the two episodes, the SO_2 oxidation by OH to the sulfate formation is not important. We have performed additional sensitivity simulations in which only the direct emissions of sulfate are considered. Comparisons of the sensitivity simulation with the B-case show that the SO_2 oxidation by OH can explain about 5.1% and 11.7% of the observed sulfate concentrations in Xi'an and Beijing on average, respectively.*"

(5) Comment: Section 3.2, Given the evidence of the importance of RH in the SO_2 oxidation, it would be helpful to add the evaluation of the RH simulations and discussions of the effects of possible simulated RH biases.

Response: We have added Figure 13 in the Section 3.2 and clarified as follows:

" *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.*"

(6) Comment: Section 3.2, The authors attribute all modeled biases of sulfate concentrations to long range transport and/or meteorological factors. There may be other factors that also contribute to the biases (such as other oxidation mechanisms). Among the meteorology, RH could be a factor too.

Response: We have removed the speculative sentences in Section 3.2 due to lack of comparisons of simulated wind fields with observations and included the discussion about the effect of the simulated RH biases on the sulfate simulations.

(7) Comment: Lines 244-350, It would be helpful to include percentage contributions of the $HRSO_2$ mechanism for the two episodes.

Response: We have classified in Section 3.2 as follows:

"*The difference of the simulated [NO_2] in the B-case and E-case is minor, and the average [NO_2] is increased by 0.69% in GZB and decreased by 0.1% in BTH in the E-case compared to the B-case, showing that the impact of the $HRSO_2$ parameterization on NO_2 simulations is not significant in GZB and BTH.*"

"*On average, inclusion of the $HRSO_2$ parameterization decreases the [SO_2] by 15.9% and 3.4% in GZB and BTH on average, respectively.*"

"*However, in the E-case, the WRF-CHEM model generally yields the observed sulfate variations during the 11-day episode, with a MB of -17.0 μg m^{-3} and an IOA of 0.89, and the average sulfate concentration is enhanced by 172% compared to the B-case.*"

"*The average sulfate concentration is enhanced by 58.4% in the E-case compared to the B-case in Beijing.*"

"*The inclusion of the $HRSO_2$ parameterization deceases the simulated nitrate concentration by 15.3% and 19.5% in Xi'an and Beijing, respectively, on average.*"

"*The average ammonium concentration is enhanced by 36.8% in Xi'an and 7.2% in Beijing by the inclusion of the $HRSO_2$ parameterization.*"

"*Inclusion of the $HRSO_2$ parameterization in the E-case improves the ability of the model to reproduce the $PM_{2.5}$ measurements in GZB and BTH. In GZB, due to very humid conditions which facilitate the heterogeneous sulfate formation during the episode, the simulated $PM_{2.5}$ mass concentrations are increased by more than 40 μg m^{-3} in the E-case compared to the B-case with an average increase of 12.3%, and more consistent with the measurements. The $HRSO_2$ parameterization also improves the $PM_{2.5}$ simulations in BTH,* *with an average increase of less than 3.0%, reducing the underestimation from around -13.3 to -5.1 μg* m^{-3}.”

Technical comments

Comment: Line 21, Should switch the order of develop and evaluate.

Response: The relationships obtained from observed sulfate with PM2.5, iron, and relative humidity are first used to evaluate the proposed mechanism and further, based on the mechanism to develop a sulfate heterogeneous parameterization.

Comment: Line 66, “model oxides”?

Response: We have changed the “model oxides” as “*oxides*” in the manuscript.

Comment: Line 186, “showing considerable background contributions”, of what, irons? $PM_{2.5}$?

Response: We have revised the sentence in Section 3.1 as “*showing considerable background iron contributions*”.