Response to the comments of referee #2

The manuscript entitled “A Comprehensive Observational Based Multiphase Chemical Model Analysis of the Sulfur Dioxide Oxidations in both Summer and Winter” by Song et al. presents the comprehensive evaluation of the contribution of different sulfate production pathways in both summer and winter by their self-developed multiphase box model (PKU-MARK). The model includes nearly all the established sulfate production pathways, providing valuable insights into the sulfate formation evaluation. Overall, I have some concerns that need the authors to clarify before that I can recommend publication in Atmospheric Chemistry and Physics.

We thank the reviewer for the helpful comments. The referee’s comments are first given in black type, followed by our response to each in turn in blue type. Any changes to the manuscript in response to the comments are then given in quotation marks in red type.

1 The concentration of TMIs is vital in this work since the two dominant sulfate production pathways the authors proposed are aqTMI and Mn-surface. An online monitor measured the Fe and Cu concentrations. Due to the lack of Mn data, the authors propose a fixed ratio of Fe/Mn to stimulate the concentration of Mn. So how about the uncertainty of this method? It is better to compare the concentration of Mn with literature results in the same region.

Under the assumption of fixed Fe/Mn air $PM_{2.5}$ mass concentration ratio as 28, the air mass concentrations of Mn were calculated and shown in Table 1. Mn averaged mass concentration range from 12.4±9.4 ng/m^3 in clean situation to 46.5±10.3 ng/m^3 in highly polluted situation in PKU-17 observation. Compared to measurement results of Mn in the same region reviewed in the Table S9 (27.9 - 92.3 ng/m^3), values were slightly lower. While in the measurements of Cui et al. (2019) in 2016.6 to 2017.5 which is the closest measurement time, averaged Mn concentration was 32±25 ng/m^3 in non-heating periods and 35±36 ng/m^3 in heating periods. The results were in consist with our estimation. However, fixed ratio of Fe/Mn leads to uncertainties of effective aqueous TMI concentration when evaluating the sulfate formation. We have revised the MS to supplement the sensitivity analysis on the concentration of aqueous TMI. Please refer to the response below.

2 The authors state that the average soluble percentage of Fe and Mn in winter polluted conditions was 0.79% and 19.83%. However, the water-soluble fraction of Fe and Mn may change a lot in different regions, as stated in the manuscript. Also, the solubility may change under clean conditions and polluted conditions. It is better to add some discussion about the sensitivity of the solubility of Fe and Mn to the model results.

We added the following discussion of transition metal sensitivity on sulfate formation in PKU-17 winter field campaign in the revised SI Text S4, Figure S9 and Table S10.

Water soluble fraction of Fe, Mn and Cu can vary over a large range. A large part of the soluble metals is in the form of soluble organic complexes or hydroxides rather than ions in aerosol particles. There are evidences that the existence of various aerosol water soluble organic acids (oxalate, malonate, tartrate and humic acid) cause an enhancement of Fe, Cu and Mn solubility and the formation of metal-organic complex (Paris and Desboeufs, 2013; Wozniak et al., 2015; Tapparo et al., 2020). What's more, the dissolution of Fe and Mn is highly influenced by aerosol pH. Circumneutral pH leads to a supersaturated soluble Fe (III), which then precipitates out of the solution. For these reasons, the promotion of metal solubility may have non-proportional influences on the aqueous concentration TMI. We conducted the sensitivity analysis for the solubility of Fe from 1% to 15% (Scenario one with fixed aqueous Mn and Cu concentration consist with the base run in the MS, Scenario two with fixed ratio of soluble Fe/Mn and Fe/Cu mass, ie, Mn solubility in the range of 10% to 100%, Cu in 5% to 75%, as shown in Table S10). Other aerosol component concentration, ionic strength, ALWC, observed meteorological parameters and trace gases concentrations stay consistent with the base run.

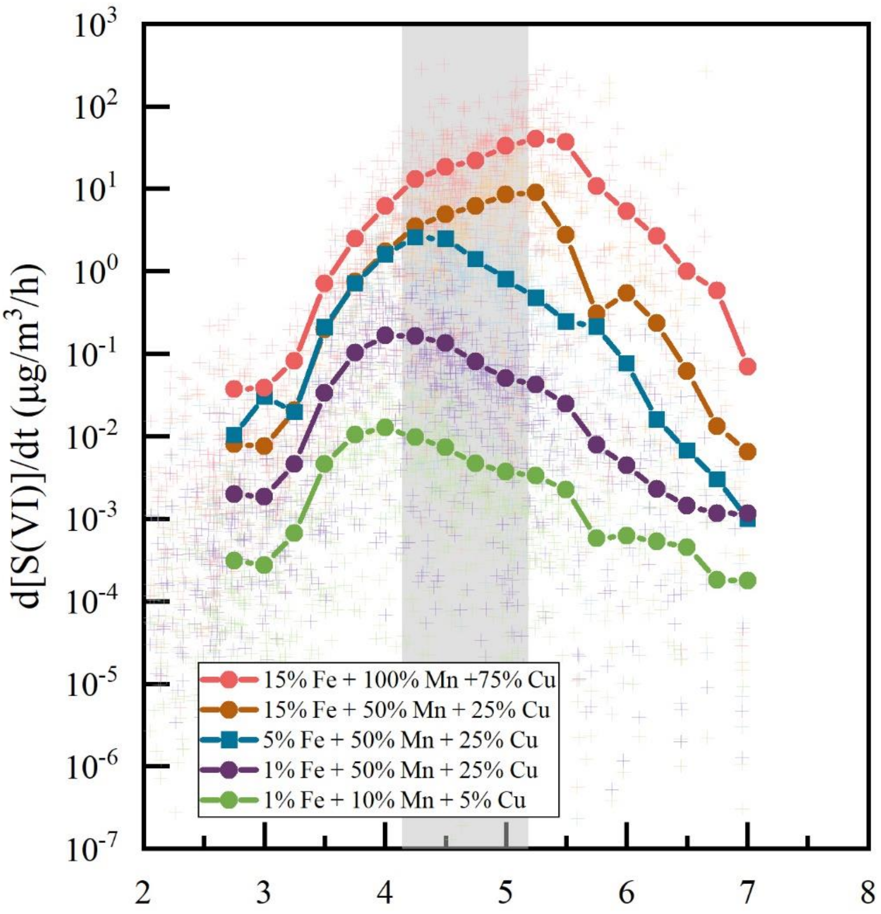

Figure S.9 Sensitivity analysis of transition metal including Fe, Mn and Cu solubility influences on the averaged sulfate formation rates in PKU-17 field observation. Dotted lines in the figure show the cluster averaged results with a pH span of 0.5 under actual ambient conditions with different transition metal solubilities.

Table S10. Base run and scenarios of the solubility sensitivity analysis.

Sensitivity Analysis	Solubility of transition metals	Sulfate formation contribution in haze pH range (4.2-5.2) ($\mu g/m^3/h$)
Base Run	5% Fe + 50% Mn + 25% Cu	0.80 - 2.58
Scenario 1	15% Fe + 50% Mn + 25% Cu 1% Fe + 50% Mn + 25% Cu	3.49 - 8.57 0.05 - 0.16
Scenario 2	15% Fe + 100% Mn + 75% Cu 1% Fe + 10% Mn + 5% Cu	12.97 - 32.87 0.009 - 0.004

As shown in Figure S.9, In the range of winter haze periods pH (4.2-5.2), averaged sulfate formation rates in PKU-17 field observation is non-proportional to the initial transition metal solubility. Fe solubility increasing from 1% to 5% will cause d[S(VI)]/dt to increase over an order of magnitude, and increasing to 15% cause no obvious effect when pH smaller than 4.2, while obvious effect the pH ranging from 4.2 to 6. This phenomenon may be due to the piecewise calculation equations of TMI-catalysis oxidizing SO_2 as mentioned in the SI and following. In the presence of TMI organic complexes and redox reactions, this equation may need to be further verified, but verification is not within the scope of this study. It is obvious that the d[S(VI)]/dt changes caused by the proportional expansion of the solubility of the three transition metals (Scenario 2) is more significant especially when the solubility is reduced to 1%+10%+5%. Increasing of solubility to 15%Fe+100%Mn+75%Cu can increase sulfate formation rate to 5-84 times higher than in base run during haze periods pH as 4.2-5.2. This can explain to a certain extent that excessive TMI concentrations will not cause a sharp increase in d[S(VI)]/dt, which may be due to the buffering effect caused by the formation of organic complexes.

Part of Table S2. Aqueous-phase reaction rate expressions, rate constants (k) and influence of ionic strength (Is) on k for sulfate production in aerosol particle condensed phase.

Oxidants	The reaction rate expressions ($R_{S(IV)+oxi}$), constants (k) and influence of I_s (in unit of M) on k [a]	Notes	References
$TMI+O_2$ [f]	$k_6[H^+]^{-0.74}[S(IV)][Mn(II)][Fe(III)]$ (pH $\leq$ 4.2) $k_6 = 3.72\times10^7\times e^{(-8431.6\times(1/T-1/297))}$ M^{-2} s^{-1} $k_7[H^+]^{0.67}[S(IV)][Mn(II)][Fe(III)]$ (pH > 4.2) $k_7 = 2.51\times10^{13}\times e^{(-8431.6\times(1/T-1/297))}$ M^{-2} s^{-1}		Ibusuki and Takeuchi (1987)
	$\log_{10}(\frac{k}{k^{I_s=0}}) = \frac{b_4\sqrt{I_s}}{1+\sqrt{I_s}}$ [g] b_4 is in range of –4 to –2	$I_{s,\ max}$ = 2 M	Martin and Hill (1987, 1967)

3 The authors declare that their result is consistent with the result of the WRF-CHEM study. However, in the cited work, the ionic strength inhibition effect was not included. More discussion about the results is needed.

In the latest WRF-CHEM study of Tao et al. (2020), the concentrations of Fe and Mn were modeled as the minimum of the solubility of metals regardless of the acidity of aerosol water and ion equilibrium depending on pH. The ionic strength inhibition effect was not included. Using the same Fe/Mn concentration calculation method and considering the ionic strength, Wang et al. (2021) pointed out in the latest research results that aqTMI catalysis only accounts for less than 1% of sulfate formation. Our rough analysis suggests that the calculation method of Fe/Mn may underestimate the actual TMI concentration due to the promotion of metal solubility by organic acid associated with aqTMI concentrations which needs further evaluation and verification. In the revised MS, we deleted the reference of Tao et al. (2020). The influence of ionic strength on the reaction rates were shown in the SI Fig.S1 and discussed in Section 2.1 in the original MS.

4 It is important that the model has considered the activity coefficient values and reactions about oxalate and Fe. So how about the concentration of oxalate used in the model?

Due to the lack of direct measurements in the mentioned field observation campaign, we calculated the aerosol oxalate concentration according to Tao and Murphy (2019) which indicated a mechanisms responsible for the interactions among oxalate, pH, and Fe dissolution in $PM_{2.5}$ based on a long term records in urban and rural areas. The linear regression between monthly average oxalate ($nmol/m^3_{air}$) and water-soluble Fe ($nmol/m^3_{air}$) concentration in $PM_{2.5}$ was fitted as $y=2.89x+0.27$ with R^2 as 0.68. Averaged oxalate aqueous concentration in winter field campaign were 0.55±0.42 in clean period, 0.82±0.48 in slightly polluted period, 0.38±0.29 in polluted period and 0.15±0.16 in highly polluted period with the Fe solubility as 5% in $PM_{2.5}$. We also added the above paragraph in the revised SI Section Text S2.

Other minor comments:

5 Line 11, the wording of sulfate should be better consistent, “sulphate” or “sulfate”.

We changed all word “sulphate” to “sulfate” in the revised MS.

6 Line 13, the statement of “observed concentrations of transition metal ions” is not appropriate from my perspective, given the authors only measured the total concentration of Fe and Cu.

We deleted the words “ions (TMI)” in the revised MS abstract as “…using a state-ofart multiphase model constrained to the observed concentrations of transition metal, nitrogen dioxide, ozone, …"

7 Line 22, "…affect the environmental quality and human health", references to support this conclusion are lacking.

We added the references in the revised MS as "Secondary sulfate aerosol is an important component of fine particles in severe haze periods (Zheng et al., 2015; Huang et al., 2014; Guo et al., 2014), which adversely affect the environmental quality and human health (Lippmann and Thurston, 1996; Fang et al., 2017; Shang et al., 2020)."

8 Line 149, "Obvious correlations between alpha-Fe (III) and sulfate…", The author may better calculate the R^2 of alpha-Fe (III) and sulfate.

In four haze periods mentioned in the PKU-17 field campaign, the correlation coefficient R^2 was 0.71, and in WD-14 field campaign haze periods, the coefficient was 0.63 indicating the obvious correlations between aqueous TMI and sulfate formation rates.

In section 2.2 in the revised MS:

"Obvious correlations between αFe (III) and sulfate concentration shown in **Fig. 1 (c) and (d)** were observed in the haze periods both in summer (R^2=0.63) and winter (R^2=0.71) and the correlation is consistent with the important contributions from aqTMI pathway to the sulfate formation."

9 Line 380, in Fig. 1(d), the modeled sulfate concentration line is missing.

We added the modeled sulfate concentration line in the Figure 1 panel (d). Because of the higher boundary layer height and more active lateral boundary conditions in summer, the simulations of secondary sulfate were not in line with observed sulfate concentration. In the section Method 4, we clarified the uncertainties of summer simulated sulfate concentration.

"Due to the higher and more dramatically diurnal changing BLH in summer (Lou et al., 2019), and the lack of relevant data in WD-14 field campaign, we could not get the modelled results of sulfate concentrations in summer haze periods. Direct emissions and transport of sulfate were not considered in the calculation because secondary sulfate is the predominant source in winter haze periods. Dilution was not considered either because the atmosphere is relatively homogeneous during winter haze episodes. Since haze events are normally accompanied by a low boundary layer height (Ht), Ht was set at 300 m at night-time and 450 m at noon (Xue et al., 2016). At other times, Ht was estimated using a polynomial (n = 2) regression as recommended in previous study (Xue et al., 2016). The diurnal trends of sulfate concentrations of the winter haze period using the deposition velocity of 1.5 cm/s and of 2 cm/s in summer are shown in Fig. 1 (c) and (d). Model results had the same trend with the observed values and could explain the missing source of sulfate aerosol to some extent in winter while with high uncertainties in summer condition."

And Figure 1 in the revised MS:

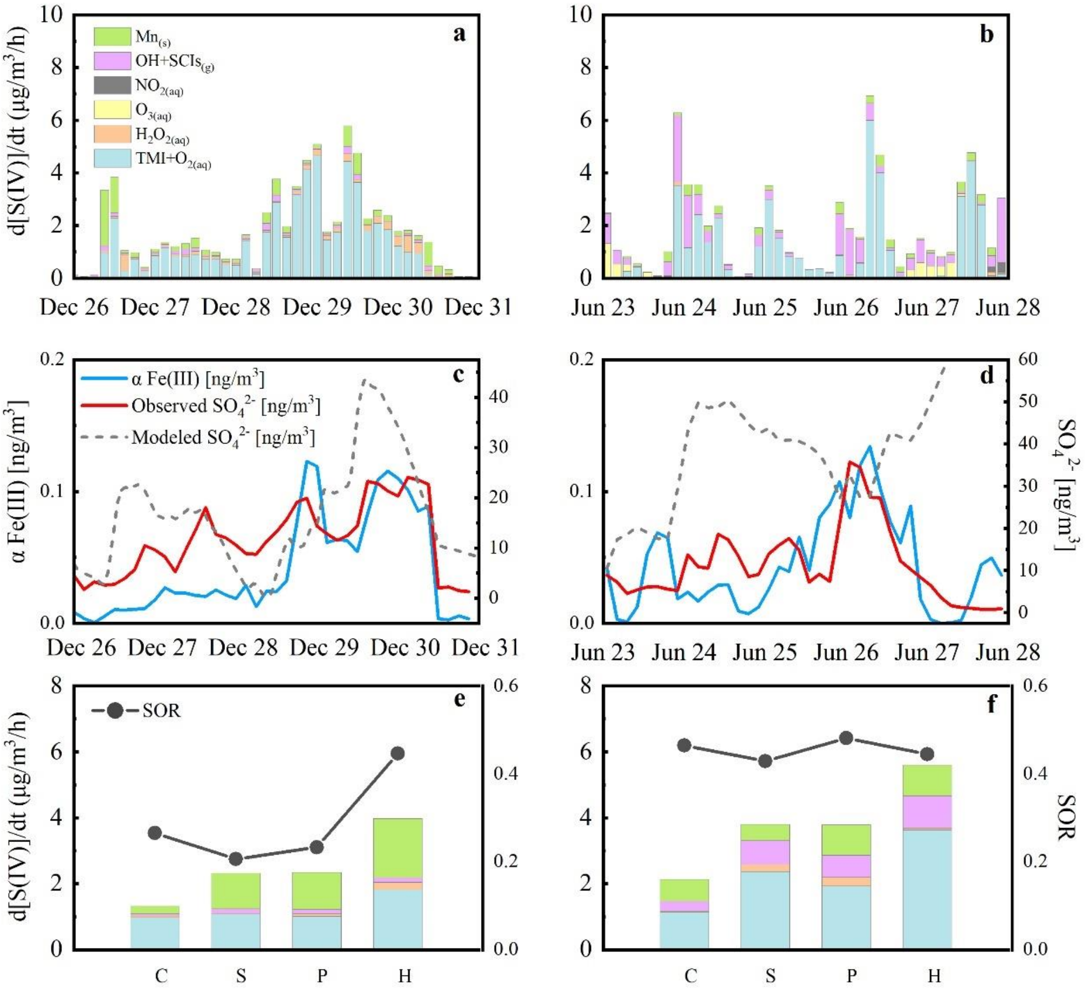

Figure 1. Three-hour average sulfate formation rates during haze periods in winter and summer (a)&(b), corresponding effective Fe (III) concentrations and sulfate concentrations (c)&(d), sulfate formation rates (the histogram) and SOR (the dotted lines) in different pollution levels in two field campaigns (e)&(f).

Reference:

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