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## **A comprehensive analysis of sulfate formation**

Anonymous Referee #1

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Referee comment on "A comprehensive observation-based multiphase chemical model analysis of sulfur dioxide oxidations in both summer and winter" by Huan Song et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-377-RC1>, 2021

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This paper focuses on evaluating various pathways for conversion of SO<sub>2</sub> to PM<sub>2.5</sub> sulfate over the North China Plane, a topic that has generated a large number of published papers in the last 2 years or so. The modeling work here is likely the most comprehensive analysis comparing all current mechanisms. Whether the results are accurate or not is hard to assess, but this work does provide valuable new insights by contrasting all the possible (main) mechanisms. The paper is appropriate for publication in this journal; however, it could be improved by careful editing focusing on grammar and clearer explanations. Additional broad and specific comments are provided below.

Broad Comments:

It would be worthwhile stating somewhere (maybe include in Table 1) what fraction of the PM<sub>2.5</sub> mass is sulfate; ie, how important is this problem.

These authors find that the most important route involves transition metal ions, however the concentration of these species seem to be very uncertain since in this work only the total (elemental) concentration was measured and the actual TMI species concentrations

had to be estimated based on estimated solubilities (which can vary over a large range). This substantial uncertainty needs to be addressed. For example, maybe the authors should provide a range in predicted sulfate formation rates for the TMI route, include this in the plots (say something similar to Fig 2, if possible) and discuss the implications (does it change the findings).

The concentration of the TMIs (mainly Fe(II)+Fe(III)) and Mn involved in the surface reaction chemistry determines how fast sulfate is formed (line 97 notes that the TMI concentration is crucial...). But what are the TMI concentrations, only total metals measured by XRF are given? What is unique about these region that makes these metal ions a major route? The authors point to the haze reducing photochemistry (during pollution events the PM2.5 mass is very high compared to many other regions globally), high RH, moderate particle pH, but what about the concentration of TMI? My rough analysis suggests that the mass ratio of TMI to sulfate is much higher in this region than many others, which would also be an important reason why this route may be important in this specific region. It would also support the conclusions of the paper, that emissions of these metals should be reduced (although as I note below, I believe more details are needed on the sources of the TMI, I don't think it is solely coal combustion based on the cited paper). I think the authors should assess this question; are TMI a uniquely large fraction of the PM2.5 or (TMI/sulfate ratio) in this region? At the very least, please provide some form of assessment of TMI mass concentrations, (this could include for example the sum of the various forms since the speciation is highly variable, eg, Fe(II)+Fe(III), etc), relative to PM2.5 or sulfate, ie, maybe in Table 1.

Finally, throughout the paper it should be clarified that all particle concentrations reported are PM2.5.

Specific Comments

Abstract line 11, change hindes to hinders.

Line 83, can you provide plots of Fe and Mn vs PM2.5 mass? This would also help address one of the major points raised above?

Table 1 Description (above the table) is incomplete. There are also aerosol particle metal species data but not noted, etc. Is the aerosol data PM2.5, please specify?

Table 1. Why not add the PM2.5 mass ranges for each pollution level to the table? Or put in the Table caption.

Lines 99-100. Is it really true that the main source (on a mass basis) for Fe, Cu and Mn is combustion? Is there a reference? Seems like road dust/tire and brake wear would be important as well as mineral dust. A more comprehensive assessment of the source of PM2.5 TMI in this study would also be useful given the conclusions (lines 277-285). Is coal fly ash really the main source for PM2.5 TMI in this region?

What are the units for data in table S9?

Fig 1 caption needs work; does plot (c) really show diurnal trends, keep same scale for

SO<sub>4</sub> in (c) and (d), and define SOR and indicate it is the line in plots (e and (f).

Line 150-151, correlation is not causation, reword to say the correlation is consistent with....

Line 153, what does  $n(\text{SO}_2)$ ... mean?

It should be stated that Eq(1) is simply the conversion of sulfate formation rate in the aerosol water (ie, per mL water) to sulfate formation per m<sup>3</sup> of air. There is nothing special about this.

Line 186-187 and on is not clear. Is the point that the equilibrium amount of H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and NO<sub>2</sub> in units of mass/m<sup>3</sup> air is controlled by the amount of ALW, ie there is equilibrium between gas and particle water for these oxidants formed in the gas phase. Is the idea that TMI is a primary aerosol (that is not likely really true, it may be true for the total elements, Fe, or Mn, but not the ions) so does not depend on ALW? So the idea is that ALW does not affect TMI levels in solution by affecting the solubility of the overall metal form of the specific species (ie, fig 3 shows insensitivity of pH to ALW, which has been pointed out in other papers (eg, Wong,et al., 2020, Env Sci Tech, 54: 7088-96.)

What does PM<sub>2.5</sub> represent in Fig 3, the total mass including particle water?

Line 199-200. What does transition metal mass will not increase mean? The mass concentration of TMI in air or the liquid concentration? Care must be taken in this whole section on what concentration (in air or in ALW) is being discussed.

Line 200-201. This is not clear and Fig S7 is not clear how it supports this idea of a dilution effect. Define Ft in Fig S7.

Line 203, it is not clear how the results of Sholkovitz apply here as they are looking at regions largely influenced by mineral dust and some combustion, here the authors state that the metals are from combustion. There is an inconsistency.

Line 204, I do not understand the statement, the importance of aqTMI and Mn-surface contributions were lowered. Why is it lowered, pH in Fig 3 changes very little at ALWC ? 150 ug/m<sup>3</sup>. This whole section on the effect of water is very confusing. Can the authors give a physical explanation on what the effect of liquid water is on the ambient air concentration of transition metal ions in PM<sub>2.5</sub>

Fig 4 should have plots labeled (a) and (b)

Line 253 to 255 is not clear (While as mentioned above, .....

Line 260-261 reword, not clear.

Line 324, state-state?