

Response to Anonymous Referee #1

Understanding the relative importance of sulfate formation pathways is essential for mitigation of haze pollution in China. However, there are a lot of debates on this topic. This manuscript presents a very comprehensive examination of aerosol pH and the relative importance of sulfate formation pathways during winter haze in the North China Plain. The results elucidate the dynamic changes in both pH and chemical regimes of sulfate formation. The scientific importance and presentation are of high quality, but some details need to be added before being published. The specific comments are listed below:

We thank the reviewer for the very valuable and constructive comments, which help us to improve the study and manuscript. Please find our point-by-point response (black) and the corresponding revisions (blue and *Italic*) below.

1. Page 4, line 1: in the North China Plain

Response:

Thanks. We have revised it accordingly:

“regimes for sulfate formation may indeed co-exist in the North China Plain”

2. Page 4, line 18: Sulfate is used in other places, use sulfurous instead of sulphurous to keep consistent.

Response:

Thanks. We have replaced the “sulphurous” by the “sulfurous” throughout the manuscript.

3. Page 5, lines 5-8: This is heterogeneous uptake of NO₂ on surface of fine particles, not aqueous phase chemistry. Is there any reason to include it? The purpose is not clear.

Response:

Thanks for pointing out this issue. In this study, we focus on the aerosol pH as well as detailed mechanisms for the sulfate formation (the relevant reactions rates highly depend on aerosol pH) in aerosol water. In order to better predict aerosol pH, it is necessary to reproduce the observed aerosol loadings for sulfate, nitrate and other components. And we have tested that if the heterogeneous formation of nitrate was ignored, nitrate concentrations would be underestimated. Considering that the explicit mechanisms for the aqueous phase production of nitrate are very complicated (Herrmann et al., 1999; Herrmann et al., 2005), and beyond the scope of our current study, we have adopted a parameterization scheme to simulate the heterogeneous formation of nitrate (Zheng et al., 2015; Chen et al., 2016). We have clarified this issue in the third paragraph of Section 2.2 in the revised manuscript:

“The CTRL scenario is expected to reproduce the observed fine particle compositions (including sulfate, nitrate, ammonium, chloride and crustal components) and gas phase pollutants, and thus more reliably predict the spatio-temporal distribution of pH, AWC and sulfate production.”

4. Page 7, lines 14-17: Is there any observation of dissolved Fe³⁺ or Mn²⁺ to adjust FSFE³⁺ and FSMN²⁺. In Wang et al. (2016), observations of Fe and Mn are provided. It is not very convincing to adjust FSFE³⁺ and FSMN²⁺ based on sulfate observation here.

<https://www.pnas.org/content/113/48/13630>

Response:

Very good suggestion, thanks. Soluble Fe/Mn concentrations are often measured and reported in studies focusing on dust events (e.g., Takahashi et al., 2011; Shi et al., 2012; Schroth et al., 2009; Ravelo-Perez et

al., 2016). However, during the urban haze episodes, the concentrations as well as sources for Fe/Mn ions in aerosol water remain not well constrained and understood, although the observed concentrations of total Fe/Mn elements in urban PM_{2.5} have been reported in some previous studies (e.g., Sun et al., 2006; Wang et al., 2006; Chen et al., 2017). Validation of the simulated Fe³⁺/Mn²⁺ ions in aerosol water is indeed limited by the lack of observations in our study. Nonetheless, we have compared the simulated soluble Fe/Mn concentrations with the observed data reported in Wang et al. (2016). As shown in Table R1, the simulated concentrations for Fe³⁺/Mn²⁺ at the Beijing TSU site and the Yan'an city are at the same or similar order of magnitude as the observations at a Xi'an urban site (note that the Xi'an site is outside of our simulated domain, and inside the simulated domain, Yan'an city is the nearest city to Xi'an).

Table R1. Comparison of the soluble Fe/Mn concentrations in aerosol water

	This study	This study	Wang et al. (2016)
Time	January 2013	January 2013	November-December 2012
Site location	Beijing	Yan'an	Xi'an
Soluble Fe (ng/m ³)	/	/	1.5-16
Soluble Mn (ng/m ³)	/	/	10-41
Fe ³⁺ (ng/m ³)	3.2	0.6	/
Mn ²⁺ (ng/m ³)	3.6	3.3	/

In this study, we have adopted 7% and 40% for FS_{FE3+} and FS_{MN2+}, respectively. The observed values for FS_{FE} and FS_{MN} both show a large variability (1-10% and 20-60%, respectively), depending on dust mineralogy and atmospheric aging (Journet et al., 2008; Schroth et al., 2009; Johnson et al., 2010; Shi et al., 2012; Claquin et al., 1999; Meskhidze et al., 2003; Takahashi et al., 2011; Duvall et al., 2008; Baker et al., 2006; Hsu et al., 2010). Our adopted values are within these ranges. We have also investigated the potential changes in predicted aerosol pH and sulfate production relevant with the uncertainties in TMI concentrations. Sensitivity tests indicate that sulfate formation is rather sensitive to the availability of TMI species, and TMI concentrations need to be better constrained in future observational and modeling studies. We have further clarified this issue in the third paragraph of the Discussion Section:

“Our results indicate that sulfate production is rather sensitive to the availability of TMI species. Unfortunately, the concentrations as well as sources for TMI species in aerosol water during haze episodes remain not well constrained and understood. The simulated mean concentration for Fe³⁺ and Mn²⁺ in PM_{2.5} at the Beijing TSU site is 3.2 and 3.6 ng/m³, respectively, and are smaller than the observed concentrations for soluble Fe and Mn (1.5-16 and 10-41 ng/m³, respectively) in PM_{2.5} at a Xi'an site (Wang et al., 2016). Note that Fe³⁺/Mn²⁺ ions also have an anthropogenic source, and were estimated to account for 10-30% in Beijing (Shao et al., 2019). Furthermore, the soluble Fe/Mn speciation (including Fe³⁺-Fe²⁺, Mn²⁺-Mn³⁺-Mn⁴⁺ cycling) depends on dust mineralogy, particle acidity and heterogeneous redox reactions (Takahashi et al., 2011; Schroth et al., 2009), and is very difficult to be explicitly treated. Also the activity coefficients for Fe³⁺/Mn²⁺ ions under the high ionic strength environment might differ (Cheng et al., 2016). The treatment of TMI pathway should be further improved in future studies.”

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