

Response to the Comments of Referees

RH and O₃ concentration as two prerequisites for sulfate formation

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We thank the referees for the critical comments, which are very helpful in improving the quality of the manuscript. We have made major revision based on the critical comments and suggestions of the referees. Our point-by-point responses to the comments are listed in the following.

Anonymous Referee #1

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Comment NO.1: *The manuscript by Fang et al. provides a nice year-long dataset of PM_{2.5} along with chemical composition and some important precursors, which would be of interest in improving the understanding of pollution evolution in Beijing. Throughout the manuscript, the authors focused mostly on the observed relationships between SOR and O₃/RH, and made conclusions that O₃ and RH are two “prerequisites” of sulfate formation. These conclusions, however, are predictable. RH and O₃ together provide almost all the necessary conditions for sulfate formation: for gas phase oxidation, they are sources of OH, and for aqueous phase or heterogeneous phase oxidations, water and oxidants (O₃, H₂O₂ (O₃ was a precursor of H₂O₂)).*

This is saying, that the authors focused on the relationship between SOR and O₃/RH and concluded on multi-phase reaction by H₂O₂ oxidation dominate (or major) sulfate formation is over concluded, or more like a speculation, especially given the absence of H₂O₂ data.

In addition, there should be seasonal difference on the formation route, for example, in summer, pollution was the lowest and SOR was the highest, given the data presented, one cannot judge that multi-phase reaction by H₂O₂ oxidation should be responsible for sulfate formation: won't the gas-phase oxidation also enhanced in summer? In fact,

for multiphase reactions, AWC might be a better indicator, however, as shown in Figure 7, SOR is not well correlated with AWC but better with RH. This for me is a good if not strong indicator that gas-phase oxidation (promoted by high O₃ + RH + insulation) is important for at least summer high SOR.

Response:

We are grateful to the reviewer for the positive and encouraging comments on the dataset and the scientific contribution of our manuscript to understanding sulfate formation.

1) We would like to first summarize the main contribution of our manuscript here. Our manuscript is the first to introduce the idea that there are some threshold values (or turning points), above which the SOR increases rapidly, for both RH and O₃, based on year-long observations. We presented clear observational evidence for these thresholds, best seen in the plot of SOR versus RH and O₃ data (Fig. 5 in the revised manuscript, Page 20). The thresholds at roughly 35 ppb O₃ and 45% RH are observed. Although such turning point possibly varies in different seasons and locations, such thresholds immediately indicate that both RH and O₃ are two “prerequisites” for the multiphase formation of sulfate. In the case of the RH threshold, this is consistent with current understanding in the dependence of the multiphase sulfate formation on aerosol water, since RH threshold relates to the semisolid-to-liquid phase transition of atmospheric aerosols. Correlation analysis between SOR and AWC further backs this point up (Fig. R1 in this response, which has been added to the revised SI as Fig. S3, Page 6). In the case of O₃ concentration threshold, this is consistent with the consumption of liquid oxidants in multiphase sulfate formation.

2) We agree with the referee that lack of H₂O₂ measurement is a weakness in the discussion of possible role of H₂O₂ in sulfate formation mechanisms. To add more confidence in such discussion, a proxy measurement of H₂O₂ is included in the revised manuscript. Taking the advice of referee #1 (comment NO.4), that H₂O₂ was non-linearly correlated with temperature (Fu, 2014). H₂O₂ was estimated from temperature, by assuming the same relationship applicable to our measurements in the full year of

2012–2013. As shown in Fig.S2 in this response (added in the revised SI as Fig. S6, Page 9), maximum concentration of H_2O_2 in summer is expected and confirmed, which is in line with the fastest sulfate formation in summer all over the year. SOR was further plotted against H_2O_2 and positive correlation was found between them (Fig. R3 in this response, which has been added in the revised SI as Fig.S7, Page 9. Please also refer to comment NO.4). In addition, coincident increases in the concentration of H_2O_2 and $\text{PM}_{2.5}$ in winter of Beijing also lead to an important role of the H_2O_2 route in sulfate formation (Ye et al., 2018). These discussions were added up to our previous analysis in the original manuscript, i.e., O_3 and H_2O_2 are proposed to be the major oxidants in multiphase sulfate formation based on the above threshold analysis. Since O_3 was excluded as a major oxidant in multiphase sulfate formation, for that the high aerosol acidity in urban environments limits its reaction rate, H_2O_2 remains the only possible liquid phase oxidant (Page 7 lines 14–24 in the revised manuscript). Based on all the above discussions, we carefully proposed in the revised manuscript that H_2O_2 might be an important oxidant of sulfate formation.

3) As reminded by referee #1, we double-checked the relationship between SOR and AWC (Fig. R1 in this response, which has been added in the revised SI as Fig. S3, Page 6), and positive correlation between them was found, which further supports that the multiphase reactions, rather than gas phase reactions, are responsible for sulfate formation.

4) The possible role of gas phase reactions was further discussed in the revised manuscript. First, the thresholds of O_3 and RH are suggestive of multiphase reactions, as stated above, rather than gas phase reactions, to account for sulfate formation. Second, coincident increases in SOR with aerosol loading (Fig.11 in the revised manuscript, Page 26), with concomitant suppression of photochemistry due to light shielding by aerosols (Wang et al., 2017) and NO-titration of O_3 (Page 6 line 19 in the revised manuscript), excludes gas phase reactions as a major route of sulfate formation in Beijing. Last but not the least, gas phase reactions may contribute but are not the major route of sulfate formation, either in Beijing or globally, due to the relatively slow reaction of SO_2 with OH. For example, the lifetime of SO_2 with respect to OH oxidation

is about 3–4 days, assuming a 24-h average OH concentration of 1×10^6 molecules cm^{-3} and a pseudo-secondary-order rate constant of 10^{-12} cm^3 molecules $^{-1}$ s $^{-1}$ (Brothers et al., 2010). However, the overall oxidation lifetime of SO₂ is on the order of hours (Berglen et al., 2004; He et al., 2018). Hence, that gas phase reactions contribute but are not the major route of sulfate formation is a well-accepted point in the literature (Finlayson-Pitts and Pitts, 2000; He et al., 2018).

However, we agree with the reviewer that gas phase reactions cannot be neglected and that the gas phase reaction competes with multiphase reactions in sulfate formation. For example, both O₃ and RH/water vapor concentration increased in summer with pollution accumulation. As the precursors of OH radicals, the increasing trends of both O₃ and water vapor might indicate increasing concentration of OH, and hence reaction rate of SO₂ and OH. A discussion of the possible role of gas phase reactions has been added to Page 9 lines 14–20 in the revised manuscript.

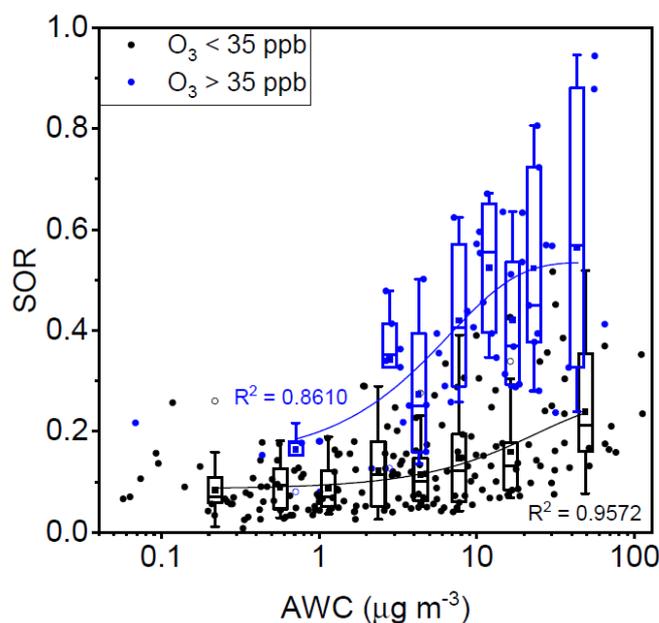


Figure R1. Plot of the sulfur oxidation ratio (SOR) against aerosol water content (AWC) (note log scale), grouped by O₃ concentration. The solid blue circles represent O₃ > 35 ppb and the solid black circles represent O₃ < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin, which were also separated according to the 35 ppb O₃ concentration threshold; the bin widths were set such that there were an approximately equal number of data points in each bin. The whiskers, solid squares, and open circles represent 1.5 times the interquartile range (IQR), mean values, and outlier data points, respectively. The lines are best fits to the mean values based on a sigmoid function. Data for days with rain or snow were excluded from this plot.

Changes in Manuscript: As for the discussion on H₂O₂ oxidation, please refer to the revised manuscript, Page 5 lines 25–27 and Page 7 lines 12–24. For the discussion on gas reaction, please refer to the revised manuscript, Page 9 lines 14–20.

Comment NO.2: *The fact of no correlation between SOR and NO₂ could make a good argument on the role of NO₂ in sulfate formation, I suggest to emphasize this point. In addition, comparing SOR, NO₂ and NH₄⁺ (it would be better if NH₃ is available), and see if there is any clue on the role of NH₃ in aerosol pH and the promoted NO₂ oxidation route as proposed by earlier studies.?*

Response:

We took the advice and further discussed the possible role of NO₂+O₂ route in the revised manuscript based on the following two points. First, no correlation between the SOR and NO₂ was found. Secondly, although in our study, NH₃ measurements were not available, previous studies have reported a mean aerosol pH value of 4.2 with a low limit of 3.0 in Beijing (Ding et al., 2019; Liu et al., 2017), which suggests that several pH-sensitive routes of sulfate formation, such as NO₂ + O₂, TMI_s + O₂, O₃ etc., are highly suppressed. Therefore, we proposed that NO₂+O₂ might not be a major mechanism of sulfate formation.

Changes in Manuscript: Please refer to the revised manuscript, Page 7 lines 30–32 and Page 8 lines 1–3.

Comment NO.3: *It looks the authors dealt with SOR as a sole local phenomenon (local emission and local oxidation), but how about the difference in the regional transport of SO₂ and SO₄²⁻? What would this do to SOR?*

Response:

Yes, regional transport or intrusion of SO₂ and SO₄²⁻ into Beijing has been evidenced in the literature (Lang et al., 2013; Li et al., 2016), and would contribute to SOR. However, our analysis was based on stationary measurements and regional transport could not be considered based on the data we have. Even though, strong relationships between SORs and RH/O₃ were still found, revealing the dominant role of Local

multiphase reactions in sulfate formation. Further chemical-transport model study in the future is encouraged to more accurately evaluate the contribution of local chemical formation to sulfate.

Changes in Manuscript: Uncertainty analysis introduced from neglecting regional transport has been added to the revised manuscript, Page 2 lines 23–25.

Comment NO.4: *There is observational data on the relationship of H₂O₂ concentration and temperature in Beijing (Fu, A.: Study on peroxides concentration and its influencing factors in the urban atmosphere, master of engineering, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou, China, 56 pp., 2014 (in Chinese)), the authors can derive the H₂O₂ concentration from the temperature data to better constrain the role of H₂O₂ by comparisons with O₃ and SOR data.*

Response: Accepted

According to Fu (2014), H₂O₂ was non-linearly correlated with temperature. By assuming the same relationship applicable to our measurements in the full year of 2012–2013, H₂O₂ was estimated from temperature and shown in Fig. R2 in this response (added to the revised SI as Fig. S6, Page 9). Maximum concentration of H₂O₂ in summer is expected and confirmed, which is in line with the fastest sulfate formation in summer all over the year.

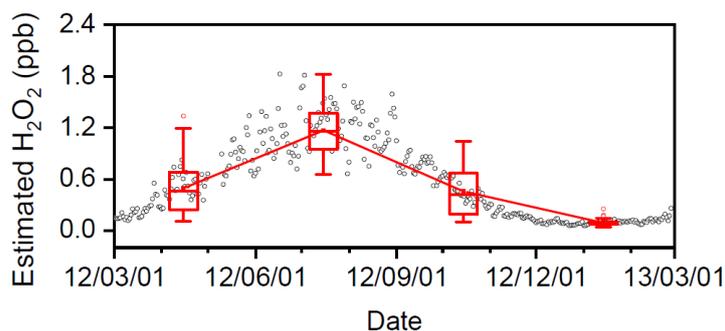


Figure R2. Time series of estimated H₂O₂ from from March 12012 to February 28 2013 (open black circles). H₂O₂ was estimated from temperature (T) based on the fitting function $H_2O_2 = 0.1155e^{0.0846T}$ according to Fu (2014). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles for each season. The whiskers, solid red squares, and open red circles represent 1.5 times the interquartile range (IQR), seasonal mean values, and outlier data points, respectively.

SOR was further plotted against H₂O₂ and positive correlation was found between them

(Fig. R3 in this response, which has been added to the revised SI as Fig. S7, Page 9), provides more confidence in our discussion of possible role of H₂O₂ oxidation in sulfate formation.

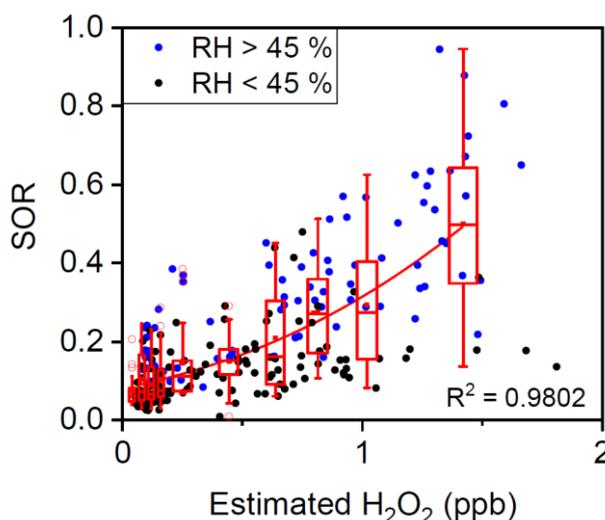


Figure R3. Plot of the SOR against estimated H₂O₂ grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths were set such that there were an approximately equal number of data points in each bin. The whiskers, solid squares, and open circles represent 1.5 times the IQR, mean values, and outlier data points, respectively. The line are best fits to the mean values based on an exponential function. Data for days with rain were excluded from this plot.

Changes in Manuscript: The proxy measurement of H₂O₂ and further discussion have been added into our revised manuscript, Page 7 lines 14–24.

Comment NO.5: *Atmospheric oxidation capacity is a rather vague (or big) definition when related to specific oxidation route of chemicals. Try to avoid*

Response: Accepted.

Changes in Manuscript: Atmospheric oxidative capacity was replaced by the appropriate oxidants. Please refer to the revised manuscript, Page 6 line 16, Page 8 line 31, Page 9 lines 23–24, and Page 10 line 8.

Comment NO.6: *The manuscript need a little bit more tuned, e.g., line 31-32: what is “a given RH threshold”?*

Response: Accepted.

A given RH threshold” refers to RH threshold of around 45% observed in our study.

Changes in Manuscript: We have rewrite the sentence to “when RH was above a threshold of 45%”, please refer to the revised manuscript, Page 5 line 24.

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