Response to the Comments of Referees

RH and O_3 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 #2

Received and published: 29 April 2019

Comment NO.1: *The paper deals with the mass concentration and chemical composition of $PM_{2.5}$ in Beijing during 1 year from filter samples and its correlation with pollution classes (clear days, slight, light, medium and heavy pollution). Most of the paper is devoted to the two prerequisites for sulfate formation based discussion. This is certainly a positive feature of the paper. Although the article has a clear logical structure, I strongly recommend to make the text more concise, to clarify statements, and to delete redundancies.*

Response: Accepted.

We deleted redundancies and clarified several statements based on the referee's suggestions to make the text more concisely.

Changes in Manuscript: We have deleted redundancies in abstract and section 3.1, please refer to the revised manuscript, Page 1 lines 14–28 and Page 5 lines 8–15. We have replaced the atmospheric oxidation capacity to appropriate oxidant, please refer to the revised manuscript, Page 6 line 16, Page 8 line 31, Page 9 lines 23–24, and Page 10 line 8. Please also refer to the comments NO.5, NO.9, and NO.12.

Comment NO.2: *Most importantly, in the absence of data on hydrogen peroxide, all*

speculation seems weak. The main idea of the article is still in the cognition of previous studies, and no more innovative conclusions have been put forward. In a word, this article is full of paradoxical conclusions and cannot provide a powerful help to the scientific community. Therefore, I don't recommend the publication in ACP journal in current status.

Response: We have made major revision of our manuscript, concerning the following two point:

1) We would like to first summary 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 O_3, based on year-long observations. We presented clear observational evidence for these thresholds, best seen in the plot of SOR versus RH and O_3 data (Fig. 5 in the revised manuscript, Page 20). The thresholds at roughly 35 ppb O_3 and 45% RH are observed. Although such turning point possible varies in different seasons and locations, such thresholds immediately indicate that both RH and O_3 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 O_3 concentration threshold, this is consistent with the consumption of liquid oxidants in multiphase sulfate formation.

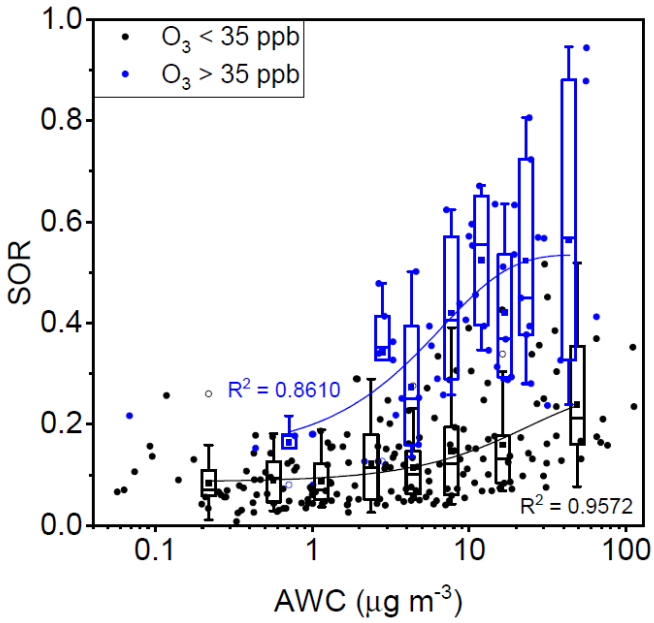

Figure R1. Plot of the sulfur oxidation ratio (SOR) against aerosol water content (AWC) (note log scale), grouped by O_3 concentration. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin, which were also separated according to the 35 ppb O_3 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.

2) We agree with the referee that lack of H_2O_2 measurement is a weakness in the discussion of possible role of H_2O_2 in sulfate formation mechanisms. To add more confidence in such discussion, a proxy measurement of H_2O_2 is included in the revised manuscript. Taking the advice of referee #1, that H_2O_2 was non-linearly correlated with temperature (Fu, 2014). H_2O_2 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.). In addition, coincident increases in the concentration of H_2O_2 and $PM_{2.5}$ 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.

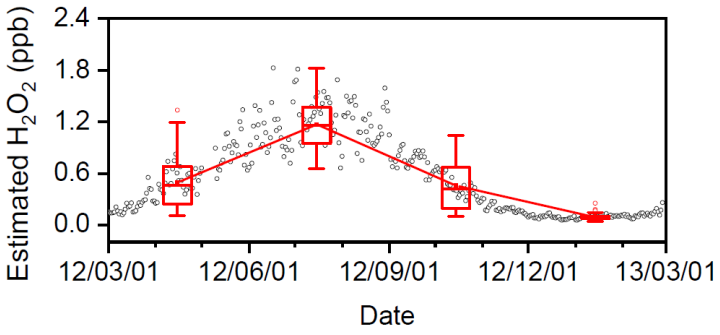

Figure R2. Time series of estimated H_2O_2 from from March 12012 to February 28 2013 (open black circles). H_2O_2 was estimated from temperature (T) based on the fitting function $H_2O_2 = 0.1155e^{0.0846T}$ according to Fu (2014). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles 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.

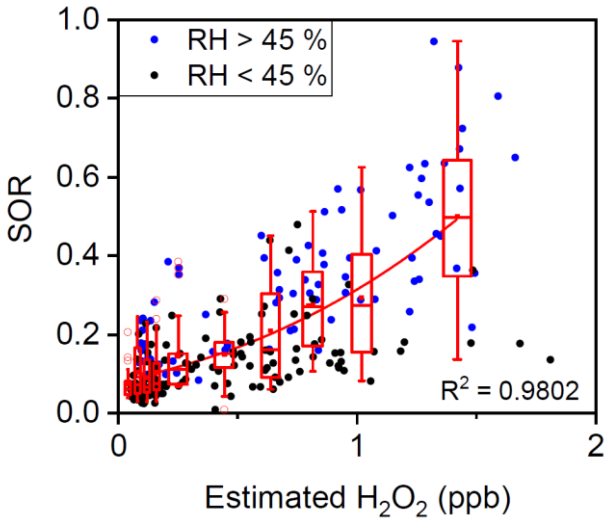

Figure R3. Plot of the SOR against estimated H_2O_2 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths were set such that there were an approximately 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: A summary of our scientific contribution has been revised in the abstract and in the text, please refer to the revised manuscript, Page 1 lines 13–19 and Page 5 lines 25–26. Further discussions on the role of H_2O_2 has also been added to the revised manuscript, Page 7 lines 14–24.

Comment NO.3: *The author name should be Weili Lin.*

Response: Accepted.

Changes in Manuscript: We have made a correction, please refer to the revised manuscript, Page 1 line 2.

Comment NO.4: *"threshold of RH and ozone" Where is this statement coming from? Is it a definition/estimate of the authors? If the threshold changed with different locations and seasons? What is the effect of these thresholds?*

Response:

1) "Thresholds of RH and ozone" are obtained based our measurement in the full year of 2012-2013 that above some turning points of RH and O_3 concentration, SORs increase rapidly. This is best seen in the plot of SOR versus RH and O_3 data (Fig. 5 in the original manuscript, Page 20). Our interpretation of this is that there are thresholds or turning points in RH and O_3 concentration that must be exceeded to allow for the fast formation of sulfate. Although such turning point possible varies in different seasons and locations, such thresholds immediately indicate that both RH and O_3 are two "prerequisites" for the multiphase formation of sulfate.
2) It is also the authors' interpretation that the threshold of RH is around 45 % and the threshold of O_3 is around 35 ppb. There could be some uncertainty attached with such inferred values. For example, one could argue that the threshold of O_3 concentration is any value between 30–40 ppb. Also, the daily average RH and O_3 data used in our analyses are not the best to evaluate the thresholds. For example, the observed RH threshold is proposed to be determined by the phase transition RH.

However, the timescale of the phase transition in ambient air is on the order of seconds (Liu et al., 2008), in comparison to RH changes on timescales of hours to days, and thus the daily average RH is not an accurate estimate of the phase transition RH. This explains why the apparent RH threshold of 45 % observed in Fig. 5 is somewhat below the *in situ* phase transition RH of 50–60 % (Liu et al., 2017b).

3) The thresholds might change with locations and seasons. For instance, Fig. R4 in this response (added to the revised manuscript as Fig. 6, Page 21) suggests that the RH threshold is roughly around 45 % during all four seasons in Beijing. The turning point varied within 40%- 50% in different sampling location of Beijing (Liu et al., 2015; Xu et al., 2017; Yang et al., 2015; Zheng et al., 2015). However, similar analyses must be performed using high time resolution data to confirm the trends observed based on our daily average data.

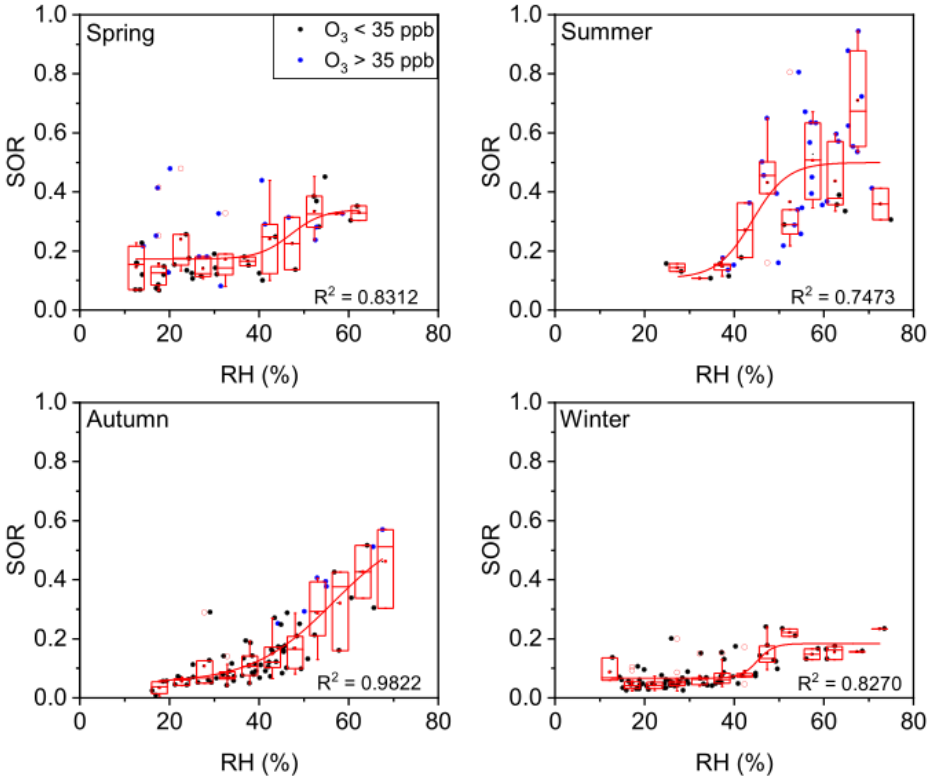

Figure R4. Plots of SORs against RH, grouped by O_3 concentration in four seasons. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin (ΔRH = 5 %). The whiskers, solid red squares, and open red circles represent 1.5 times the IQR, mean values, and outlier data points, respectively. The red lines are best fits to mean values based on sigmoid function. Data for days with rain or snow were excluded from these plots.

4) As stated above, above the thresholds of RH and O_3 concentration, sulfate formation could be enhanced (Please also refer to the response of comment NO.2).

Changes in the Manuscript: A discussion on the possible seasonal variations in the thresholds were added in our revised manuscript, please refer to the revised manuscript, Page 6 lines 32–34 and Page 7 lines 1–7.

Comment NO.5: *Redundancy: Page 1 line 15-16 and line 24-25. Line 13-14 and Line 17-18.*

Response: Accepted.

Changes in the Manuscript: We have rewritten the abstract and deleted the redundant sentences in the revised manuscript. Please refer to the revised manuscript, Page 1 lines 14–28.

Comment NO.6: *Section 2.1.2. Please add the steps of weighing after sampling.*

Response:

The steps of weighting after sampling have been provided in the original manuscript. Please refer to the revised manuscript, Page 4 lines 3–5 (highlighted).

Comment NO.7: *Page 4, line 27. Should be annual standard*

Response: Accepted.

Changes in Manuscript: We have changed the phrase to "Chinese National Ambient Air Standard annual mean concentration of ", please refer to the revised manuscript, Page 5 line 5.

Comment NO.8: *Page 5, line 2. The method to calculate POM should be introduced in previous section.*

Response:

The method to calculate POM was provided in the original SI. The discussion on source appointment, including POM, has been deleted in the revised manuscript and SI.

Comment NO.9: *Overall, section 3.1 is not necessary, because it has nothing to do*

with the main idea. If this section is deleted in the main article, it will not affect the presentation of the article. For example, the authors described the measurements of ions, organics and metal. However, ions except SNA, organics and metals except Fe didn't help the discussion of your topic. Therefore, the method and results section should to be streamlined.

Response: Accepted

Changes in Manuscript: Sect 3.1 has been reduced so that a general description of data is presented, and that variations in $PM_{2.5}$ and its main components are introduced. Please refer to the revised manuscript, Page 5 lines 3–18.

Comment NO.10: *Section 3.2. I strongly recommend the authors discussing the relationship between sulfate and RH/ozone in different seasons. The threshold should be changed with seasons.*

Response: Accepted

Changes in Manuscript: The seasonal variations are discussed now in the revised manuscript (also refer to response to comment NO.4). Please refer to the revised manuscript, Page 6 lines 32–34 and Page 7 lines 1–7.

Comment NO.11: *Page 7, line 12-16 repeats the previous statement.*

Response:

We intended to summarise our major findings and discuss their implications in this section.

Changes in Manuscript: We have rewritten the sentences, please refer to the revised manuscript, Page 7 lines 12–24.

Comment NO.12: *Page 7, line 14. What is the atmospheric oxidative capacity? From your statement, does ozone concentration correspond to this? Is it correct? Do you have some references to support your opinion? The authors should clarify this question because the same definition is also used in Page 9, line 20.*

Response: Accepted.

Atmospheric oxidative capacity relates to the concentrations of major oxidants such as OH radicals, O_3, etc. (Murray et al., 2009). Since O_3 is a major oxidant and a precursor to other major oxidants, including OH radicals, to a certain degree, O_3 can be used as a proxy for atmospheric oxidative capacity. To improve clarity, atmospheric oxidative capacity was replaced by the appropriate oxidant in each context in the revised manuscript.

Changes in Manuscript: Atmospheric oxidative capacity was replaced by the appropriate oxidant. 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.13: *Page 7, Line 23-24. Since you couldn't exclude NO_2-based reactions as major route of sulfate formation, the analysis of the relationship between SOR and NO_2 is not necessary.*

Response:

We took the advice of referee #1 and further discussed the possible role of NO_2+O_2 route in the revised manuscript based on two points. First, no correlation between the SOR and NO_2 was found. Secondly, although in our study, NH_3 measurements were not available, previous studies has 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., 2017a), which suggests that several routes of sulfate formation, such as NO_2 + O_2, TMIs + O_2, O_3 etc., are suppressed. Therefore, we proposed that NO_2+O_2 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.14: *Page 9, line 2-3. The authors described on page 7, line 7-10 that the self-catalytic nature is beyond the scope of your study. However, you illustrate the importance of the self–catalytic in this paragraph. I think it's self-contradictory.*

Response:

To clarify, our manuscript states that the self-constrained nature, i.e., sulfate formation increases the acidity of aerosols, which suppresses sulfate formation via several routes, such the O_3 oxidation and TMIs + O_2 routes. The self-catalytic nature of sulfate formation is best seen from the perspective that sulfate formation adds up the aerosol volume/surface density which helps with further sulfate formation. Those two mechanisms compete in determining the sulfate formation as pollution accumulation. In our manuscript, the self-constrained nature of sulfate formation is not discussed in detail due to the lack of direct or proxy measurements of aerosol acidity in our measurements.

Comment NO.15: *Page 10, line 21. Should be Zhejiang University.*

Response: Accepted.

Changes in Manuscript: We have made the correction. Please refer to the revised manuscript, Page 11 lines 18–19.

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