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 #3

Received and published: 12 May 2019

Comment NO.1: *General points: This study provides long-term continuous filter sampling and composition analysis data of PM$_{2.5}$. Many previous studies usually conducted such kind of observation intermittent for a short period, but such long-term uninterrupted observations are quite scarce. Thus, the data is of scientific value for analysis of variation characteristics of PM$_{2.5}$ compositions and model validation. Moreover, this paper focus on identifying the possible factors on sulfate formation, which is helpful for understanding of mechanism of sulfate formation. If the general and specific points below are addressed, I recommend this paper for publication.*

The authors investigate the relationship of SOR and RH/O$_3$, and conclude that RH and O$_3$ are two "prerequisite" for sulfate formation. But the further speculation of "H$_2$O$_2$ oxidation was proposed to be the major route" seems lack of sufficient evidence without the H$_2$O$_2$ data and laboratory experiment results support. The refs. (Sievering et al. 2004; Alexander et al., 2005) are also not solid enough to back your speculation.

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.

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.S1 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. R2 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.
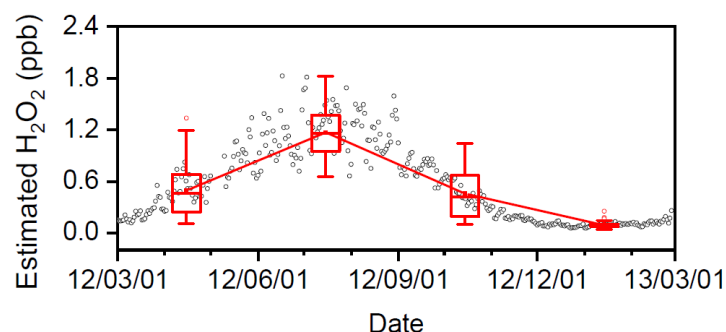

Figure R1. Time series of estimated H_2O_2 from from March 12012 to February 28 2013 (open black circles). H_2O_2 was estimated from temperature (T) based on the fitting function $H_2O_2 = 0.1155e^{0.0846T}$ according to Fu (2014). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles 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.
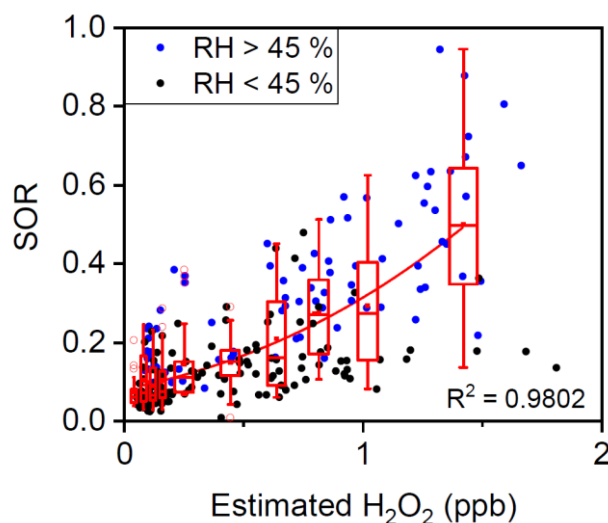

Figure R2. Plot of the SOR against estimated H_2O_2 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths were set such that there were an approximately 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: Discussions on the role of H_2O_2 has also been added to the revised manuscript, Page 7 lines 14–24.

Comment NO.2: *The authors should adjust the structures of the paper to make more clear and concise statement. Although the overview of the data is needed for the readers, the discussion in Sect3.1 is concentrated on the source appointment of $PM_{2.5}$, which is abundant and deviate away from the theme. I suggest this Sect. discuss the variations of the components concentrations and contribution ratios using the classification method based on season or pollution levels. Sulfate can be focused on.*

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.3: *The order of the figures and tables in the main text and SI is confusing, the authors should rearrange the figures and tables according to the main text.*

Response: Accepted

Changes in Manuscript: We have rearranged the figures. Please refer to the revised manuscript, Pages 18–19 Figs 3–4.

Comment NO.4: *The authors should carefully go through the whole manuscript to avoid mistakes. Specific points: 1. Avoid duplicated sentences and definitions. E.g. Page1, line18- 20 vs Page 2, line 1-2; Page 1, line 25-26 vs Page2, line 23-26, and the definition of "self-catalytic" is vague.*

Response: Accepted

1) Duplicated sentences deleted in the revised manuscript.

2) We need to better define the term "self-catalytic" as referee #2 has also suggested. We have therefore defined it consistently in both the abstract and introduction. The definition has changed to: "the formation of hydrophilic sulfate aerosols under high RH conditions results in an increase in aerosol water content, which results in greater particle volume for further multiphase sulfate formation".

Changes in Manuscript: The definition has been clarified, please refer to the revised manuscript, Page 1 lines 25–27 and Page 2 lines 16–18.

Comment NO.5: *Page 2, line 14, what is "various parameters" refer to*

Response: oxidants, catalysts, meteorological conditions, etc.

Changes in Manuscript: We have clarified the parameters as "exactly how do various parameters (oxidants, catalysts, meteorological conditions, etc.) influence sulfate formation" in the revised manuscript, Page 2 line 10.

Comment NO.6: *Page 4, line 6, Figure 1 should be "Fig. 1"; Page 4, line 15, give the location information (lat, long) of the site; Page 5, line 4-10, rewrite the first sentence "The chemical. . … . (TEOs)." There actually 8 categories including "others" and the category is not according to the source type. Why you start with Fig. S2 not S1? Page 6 why you put Fig. 4 before Fig.3 in your text. Check the orders as mentioned in general points 3.*

Response: Accepted.

Changes in Manuscript:

1) Figure 1 has been changed to Fig. 1. Please refer to the revised manuscript, Page 3 line 22.

2) The lat/long of the Beijing Meteorological Observatory Station (116.47° E, 39.81° N) has been added. Please refer to the revised manuscript, Page 3 line 29.

3) The sentence the reviewer mentions has been rewritten to: "The chemical components of $PM_{2.5}$ were divided into eight categories: sulfate, nitrate, ammonium, organic matter (OM), EC, minerals, trace element oxides (TEOs), and others." Please refer to the revised manuscript, Page 4 lines 14–15.

4) We have rearranged the order of Figs. Please refer to the revised manuscript, Page 4 lines 17–18 and Pages 18–19 Figs. 3–4.

Comment NO.7: *Sect. 3.2 How do you give the definition of threshold? The SOR or ΔSOR exceed certain value? The authors also compared the results with previous studies in this Sect., what is the reason for the difference in these studies?*

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, the thresholds might change with locations and seasons. 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., 2017).

Comment NO.8: *Page 9, line 5-8 and Page 9, line 12-14 the sentences are contradictory*

Response:

The sentences on Page 9, lines 5–8 explain that the self-catalytic nature of sulfate formation accounts for the increased SOR as pollution accumulates. The sentences on page 9, lines 12–14 summarise our conclusion about the thresholds of O_3 and RH.

Comment NO.9: *Use "clear", "formation", "evolution" etc. to represent different pollution level is improper, because you do not conduct case or course study in the paper.*

Response: Accepted.

Changes in Manuscript: The definitions have been changed to: clean, moderate pollution, heavy pollution, and severe pollution in the revised manuscript. Please refer to the revised manuscript, Page 9 line4, Page 25 Fig. 10, and Page 26 Fig.11. These still represent each quartile of $PM_{2.5}$ levels.

Comment NO.10: *How about other factors such as wind speed and wind direction impact on SOR except RH and O_3?*

Response:

Wind speed and wind direction are not assumed to be influencing parameters of sulfate formation according to the mechanism summarised in the introduction section and hence were not discussed in our manuscript. However, it is clear that high SORs and high $PM_{2.5}$ were commonly found at low to medium wind speeds (Fig. R3 in this

response), which might be related to the increasing SORs as aerosol pollution accumulated. Hotspots of SOR at high wind speed with northwest sector and south sector are also found, which might be related to regional transport of sulfate. The uncertainty concerning regional transport has been discussed in the response to referee #1 comment NO.3.
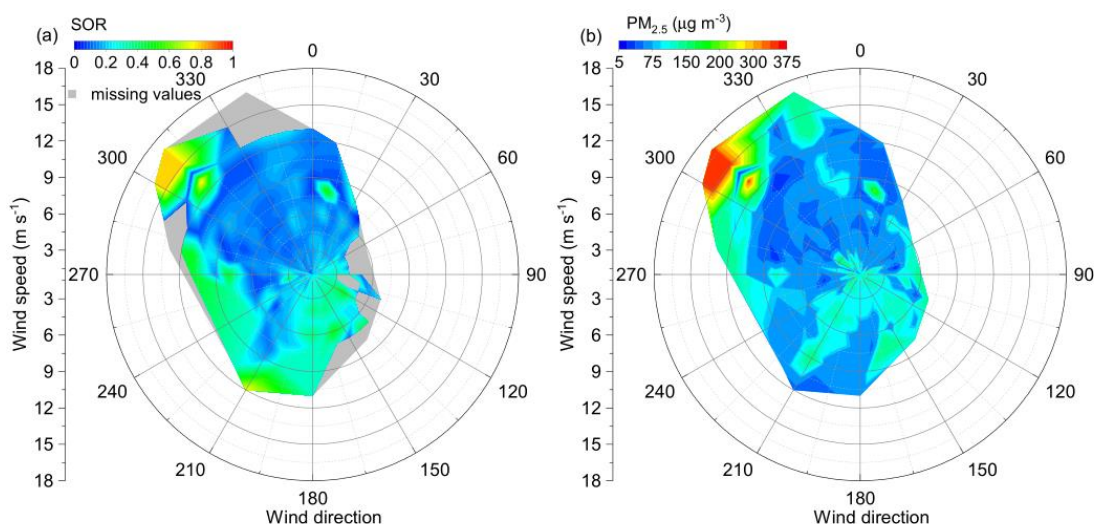

Figure R3. Bivariate polar plots for (a) SOR and (b) PM$_{2.5}$. The grey shading indicates lack of data. Wind speed and wind direction were download from the National Climate Data Center (www.ncdc.noaa.gov), which were measured at a station located in the Beijing Capital International Airport.

Comment NO.11: *Is all the data in this paper daily data? Please give make it clear in the paper.*

Response:

Yes, all the data used in this manuscript are daily averages and this has been clarified in the method section of the revised manuscript (Page 3, lines 29–30 in the revised manuscript).

To be more specific, daily PM$_{2.5}$ filter samples were collected for 23.5 h, from 9:30 am to 9:00 am the next day; thus, PM$_{2.5}$ and its components were daily averaged data. Gaseous pollutants (SO$_2$, O$_3$, NO$_x$, etc.) and RH with a time resolution of mins were averaged according to the filter sampling time period. Daily solar radiation data was used as it is.

Comment NO.12: *SOR is the conversion ratio of SO$_2$, I doubt whether it can indicate the conversion rate (or speed) as you mentioned in your paper (e.g. Page 1, line 21,*

Page 10, line 14 etc.) What is the relationship of O₃ and atmospheric oxidative capacity? AWC and RH? Please reconsider in your statement and discussions? (Page 8, line 10, Page 9, line 10-11 etc.).

Response:

1) We agree with the referee that SOR is defined as the ratio of sulfate to total sulfur and it is not the SO_2-sulfate conversion rate. However, due to the long chemical lifetime of sulfate, sulfate is tend to accumulate with chemical production within at least 24 hrs, which could be best reflected in SOR, the ratio of sulfate to total sulfur. SOR has been widely used as an indicator of SO_2-to-sulfate conversion in numbers of references (Sun et al., 2014; Zheng et al., 2015), where a high SOR reflects a high SO_2-to-sulfate conversion rate on average during the measurement period.

2) 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.

3) The AWC calculated using the ISORROPIA-II thermodynamic model (http://isorropia.eas.gatech.edu). Please also refer to the revised SI (Page 3 lines 14–16). In brief, AWC is a function of aerosol mass concentration, aerosol chemical composition, RH, etc.

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.13: *The fitting methods were used in this paper (Fig. 5 and Fig. S5), please give the evaluation parameters (such as p-value and R) of the fitting method to prove the validity and accuracy of the fitting. Also in Fig 5b, the last 2 box bins only have 1-2 points, does the results make sense?*

Response: Accepted

1) R^2 has been added to Fig. 5 in the revised manuscript (Page 20).

2) In Fig. 5 (Page 20 in the revised manuscript), O_3 concentrations were grouped by 5 ppb intervals and RH by 5 % intervals. There were only a few data points on the right-hand sides of these figures because there were only a few days with daily average O_3 (RH) above 70 ppb (70 %). However, the shapes of the fits are not much different when we group them by the number of data points in each bin, as show in Fig. R4 in this response. O_3 in Fig. R4a was the original method that grouped by 5 ppb intervals, while O_3 in Fig. R4b were grouped with an approximately equal number of data points (15-16) in each bin, which shows the robustness of our fitting.
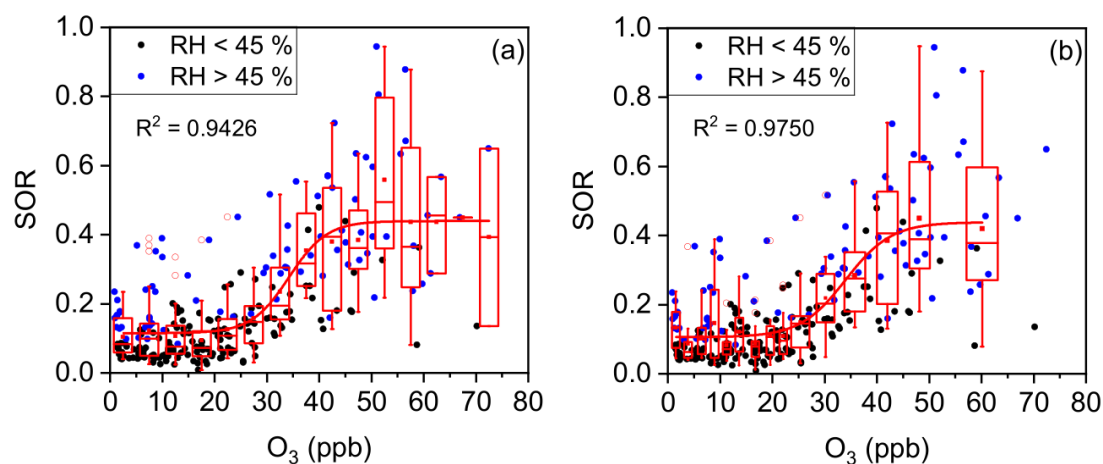

Figure R4. Plots of the SOR against O_3, grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin ((a) ΔO_3 = 5 ppb, (b) variable ΔO_3, 15–16 data points in each bin). The whiskers, solid red squares, and open red circles represent 1.5 times IQR, mean values, and outlier data points, respectively. The red lines are best fits to the mean values based on a sigmoid function. Data for days with rain or snow were excluded from these plots.

Changes in Manuscript: R_2 has been added to the plots that containing fitting lines. Please refer to the revised manuscript, Page 20 Fig. 5, Page 21 Fig. 6, Page 22 Fig. 7. Please also refer to the revised SI, Page 6 Fig. S3, and Page 9 Fig. S7.

Comment NO.14: *Give the right form of the author's name in Page 1 and Page 12. There should be a space between units and the quantity.*

Response: Accepted.

Changes in Manuscript:

1) The right form of the author's name has been given. Please refer to the revised manuscript, Page 1 line 2.

2) Space has been added between number and % or number between °C, Please refer to the revised manuscript, Page 1 line13, Page 4 lines 6 and 29, Page 5 lines 5, 14, 16, 23, 24, 26, and 29, Page 6 lines 28–29, Page 8 lines 21–22 and 29, Page 9 lines 3–4 and 32, Page 20 lines 4–5 and legend of Fig. 5b, Page 24 line 5, and Page 26 line 6.

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