Response to the Comments of Referees

RH and O_3 concentration as two prerequisites for sulfate formation

Yanhua Fang and Chunxiang Ye, Junxia Wang, Yusheng Wu, Min Hu, Weili Lin, Fanfan Xu, Tong Zhu

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

Received and published: 9 May 2019

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 O_3/RH, and made conclusions that O_3 and RH are two "prerequisites" of sulfate formation. These conclusions, however, are predictable. RH and O_3 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 (O_3, H_2O_2 (O_3 was a precursor of H_2O_2).*

This is saying, that the authors focused on the relationship between SOR and O_3/RH and concluded on multi-phase reaction by H_2O_2 oxidation dominate (or major) sulfate formation is over concluded, or more like a speculation, especially given the absence of H_2O_2 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 H_2O_2 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 O_3 + 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 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 25). 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 37). In the case of O_3 concentration threshold, this is consistent with the consumption of liquid oxidants in multiphase sulfate formation.
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 (comment NO.4), 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. R2 in the response to Referee #1 comment 4 (added in the revised SI as Fig. S6, Page 39), 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 (in the response to Referee #1 comment 4, added in the revised SI as Fig.S7, Page 40). 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. 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, added in the revised SI as Fig. S3, Page 37), 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 31), with concomitant suppression of photochemistry due to light shielding by aerosols (Wang et al., 2017) and NO-titration of O_3 (Page 8 line 201 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 SO_2 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 O_3 and RH/water vapor concentration increased in summer with pollution accumulation. As the precursors of OH radicals, the increasing trends of both O_3 and water vapor might indicate increasing concentration of OH, and hence reaction rate of SO_2 and OH. A discussion of the possible role of gas phase reactions has been added to Page 11 lines 311–319 in the revised manuscript.

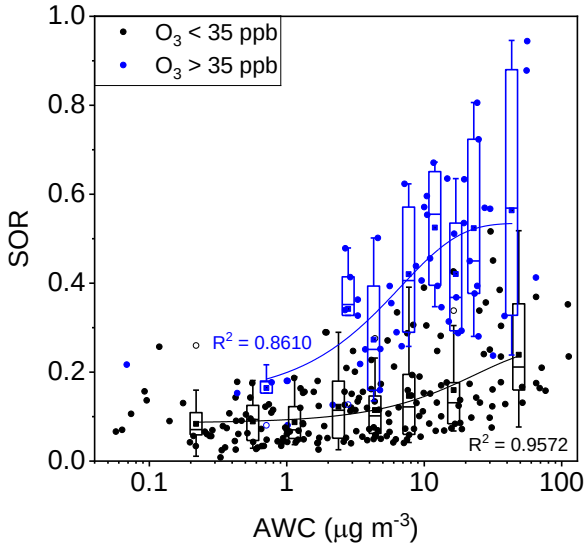

Figure R1. Plot of the sulfur oxidation ratio (SOR) against aerosol water content (AWC) (note log scale), grouped by O_3 concentration. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles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

Changes in Manuscript: As for the discussion on H_2O_2 oxidation, please refer to the revised manuscript, Page 6 lines 169–170 and Page 9 lines 230–245. For the discussion on gas reaction, please refer to the revised manuscript, Page 11 lines 311–319.

Comment NO.2: *The fact of no correlation between SOR and NO_2 could make a good argument on the role of NO_2 in sulfate formation, I suggest to emphases this point. In addition, comparing SOR, NO_2 and NH_4^+ (it would be better if NH_3 is available), and see if there is any clue on the role of NH_3 in aerosol pH and the promoted NO_2 oxidation route as proposed by earlier studies.?*

Response:

We took the advice and further discussed the possible role of NO_2+O_2 route in the revised manuscript based on the following 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 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., 2017a), which suggests that several pH-sensitive routes of sulfate formation, such as NO_2 + O_2, TMIs + O_2, O_3 etc., are highly 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 9 lines 245–259 and Page 10 lines 260–261.

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 SO_2 and SO_4^{2-}? What would this do to SOR?*

Response:

Yes, regional transport or intrusion of SO_2 and SO_4^{2-} into Beijing has been evidenced in the literature (Lang et al., 2013; Li et al., 2016), and would contributes 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/O_3 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 3 lines 60–63.

Comment NO.4: *There is observational data on the relationship of H_2O_2 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 H_2O_2 concentration from the temperature data to better constrain the role of H_2O_2 by comparisons with O_3 and SOR data.*

Response: Accepted

According to Fu (2014), H_2O_2 was non-linearly correlated with temperature. By assuming the same relationship applicable to our measurements in the full year of 2012–2013, H_2O_2 was estimated from temperature and shown in Fig. R2 in this response (added to the revised SI as Fig. S6, Page 39). 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.

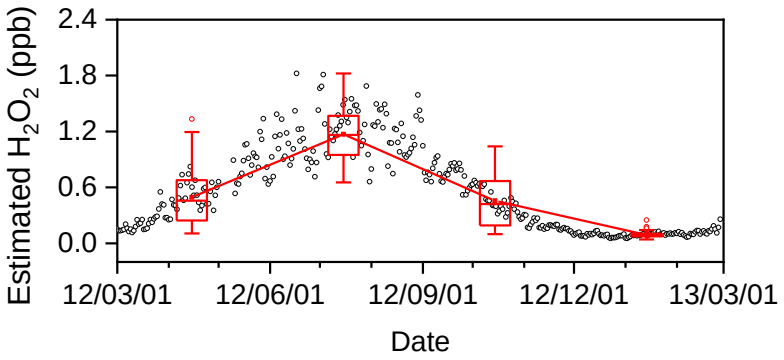

Figure R2. Time series of estimated H_2O_2 from March 1 2012 to February 28 2013 (open black circles). H_2O_2 was estimated from temperature (T) based on the fitting function $H_2O_2 = 0.1155e^{0.0846T}$ according to Fu (2014). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles 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.

SOR was further plotted against H_2O_2 and positive correlation was found between them (Fig. R3 in this response, added to the revised SI as Fig. S7, Page 40), provides more confidence in our discussion of possible role of H_2O_2 oxidation in sulfate formation.

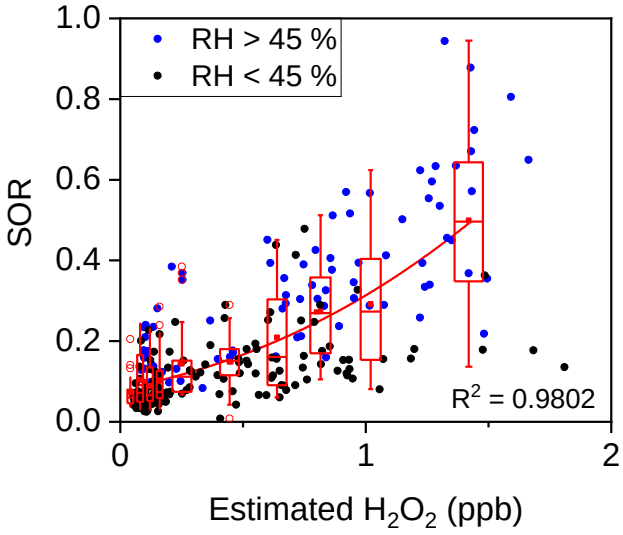

Figure R3. Plot of the SOR against estimated H_2O_2 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths were set such that there were an approximately 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: The proxy measurement of H_2O_2 and further discussion have been added into our revised manuscript, Page 9 lines 230–245.

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 7 line 197, Page 11 line 291, Page 12 lines 323 and 342.

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 6 line 168.

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 15–29 and Page 6 lines 149–158. We have replaced the atmospheric oxidation capacity to appropriate oxidant, please refer to the revised manuscript, Page 7 line 197, Page 11 line 291, Page 12 lines 323 and 342. Please also refer to the comments NO.5, NO.9, and NO.12 below.

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 points:

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 25). 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 the response to Referee # 1 comment NO.1, added to the revised SI as Fig. S3, Page 37). In the case of O_3 concentration threshold, this is consistent with the consumption of liquid oxidants in multiphase sulfate formation.
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 (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. R2 (in the response to Referee # 1 comment NO.4, added in the revised SI as Fig. S6, Page 39), 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 the response to Referee # 1 comment NO.4, added in the revised SI as Fig.S7, Page 40.). 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. 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.

Changes in Manuscript: A summary of our scientific contribution has been revised in the abstract, please refer to the revised manuscript, Page 1 lines 14–29. Further discussions on the role of H_2O_2 has also been added to the revised manuscript, Page 9 lines 230–245.

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 revised manuscript, Page 25). 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 (Page 25 in the revised manuscript) 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 26) 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.

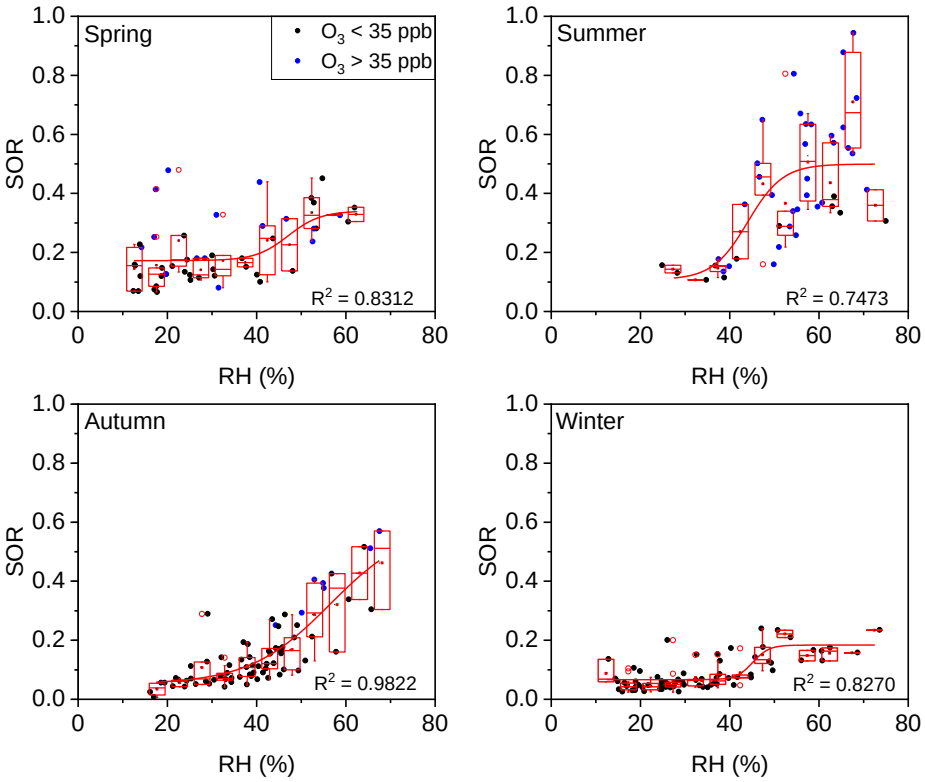

Figure R4. Plots of SORs against RH, grouped by O_3 concentration in four seasons. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin (ΔRH = 5 %). The whiskers, solid 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 to Referee #2 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 8 lines 215–223.

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 14–29.

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 also refer to the revised manuscript, Page 4 lines 109–110 (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 6 line 147.

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 6 lines 144–161.

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. Please refer to the revised manuscript, Page 8 lines 215–223.

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 9 lines 230–232.

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 7 line 197, Page 11 line 291, Page 12 lines 323 and 342.

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 9 lines 247–259 and Page 10 lines 260–261.

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 14 lines 388.

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_2O_2 oxidation was proposed to be the major route" seems lack of sufficient evidence without the H_2O_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 (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. R2 (in the response to Referee # 1 comment NO.4, added in the revised SI as Fig. S6, Page 39), 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 the response to Referee # 1 comment NO.4, added in the revised SI as Fig.S7, Page 40.). 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. 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.

Changes in Manuscript: Discussions on the role of H_2O_2 has also been added to the revised manuscript,

Page 9 lines 230–245.

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 6 lines 144–161.

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 23–24 Figs 3 and 4. Please also refer to the revised SI, Pages 34–35 Figs. S1and S2.

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, Pages 1–2 lines 30–32 and Page 2 lines 52–54.

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 43–44.

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 4 line 96.
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 4 line 104.
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 5 lines 121–122.
4) We have rearranged the order of figures. Please refer to the revised manuscript, Pages 5 lines 125–125 and Pages 23–24 Figs 3 and 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 revised manuscript, Page 25). 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 (Page 25 in the revised manuscript) is somewhat below the *in situ* phase transition RH of 50–60 % (Liu et al., 2017b).

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 11 lines 299–300, Page 30 lines 606–607, and Page 31 lines 609–610. 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. R5 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.

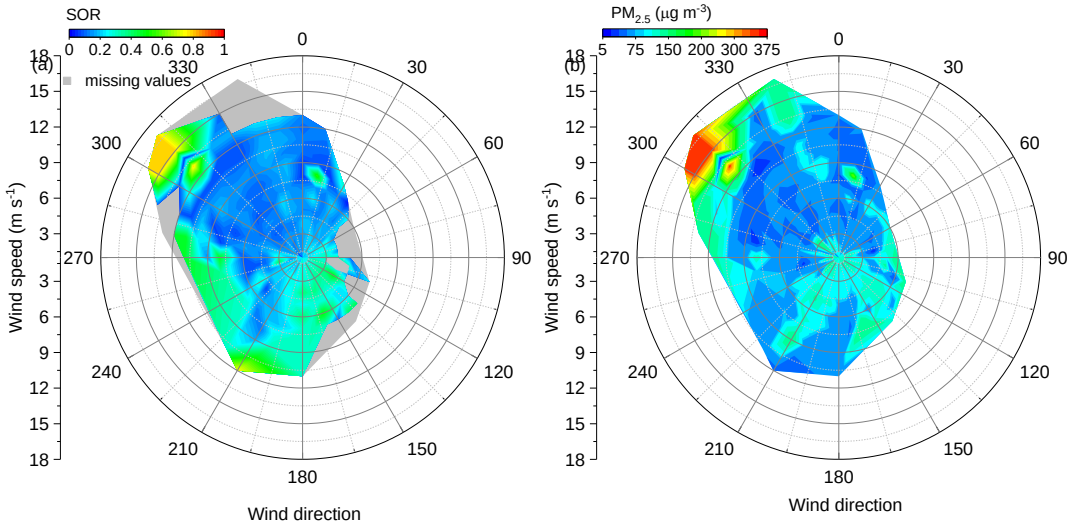

Figure R5. Bivariate polar plots for (a) SOR and (b) $PM_{2.5}$. The grey shading indicates lack of data. Wind speed and wind direction were download from the National Climate Data Center (www.ncdc.noaa.gov), which were measured at a station located in the Beijing Capital International Airport.

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 4 line105).

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.), RH and temperature 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 O_3 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 35 lines 661–663). 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 7 line 197, Page 11 line 291, Page 12 lines 323 and 342.

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 25).
2) In Fig. 5 (Page 25 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. R6 in this response. O_3 in Fig. R6a was the original method that grouped by 5 ppb intervals, while O_3 in Fig. R6b were grouped with an approximately equal number of data points (15–16) in each bin, which shows the robustness of our fitting.

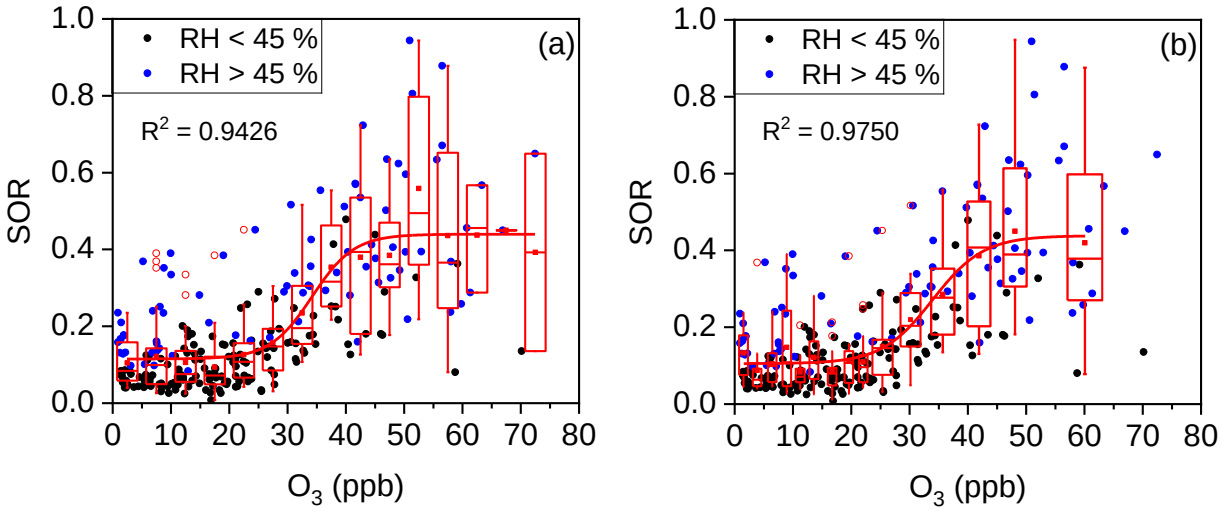

Figure R6. Plots of the SOR against O_3, grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin ((a) ΔO_3 = 5 ppb, (b) variable ΔO_3, 15–16 data points in each 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 25 Fig. 5, Page 26 Fig. 6, Page 27 Fig. 7. Please also refer to the revised SI, Page 37 Fig. S3, and Page 40 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 line 15, Page 4 lines 111 and 112, Page 5 line 139, Page 6 lines 147, 157, 159, 166, and 168, Page 7 lines 171 and173, Page 8 lines 211 and 216, Page 9 line 235, Page 10 lines 279, 281, and 288, Page 11 line 299, Page 12 line 332, Page 25 lines 579 and 580, Page 26 line 586, Page 27 lines 590 and 591, Page 29 line 602, and Page 31 line 613.

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RH and O_3 concentration as two prerequisites for sulfate formation

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Abstract. Sulfate formation mechanisms have been discussed extensively but are still disputed. In this work, a year-long particulate matter ($PM_{2.5}$) sampling campaign was conducted together with measurements of gaseous pollutant concentrations and meteorological parameters in Beijing, China, from March 2012 to February 2013. The sulfur oxidation ratio (SOR), an indicator of secondary sulfate formation, displayed a clear summer peak and winter valley, even though no obvious seasonal variations in sulfate mass concentration were observed. A rapid rise in the SOR was found at a RH threshold of ~45 % or an O_3 concentration threshold of ~35 ppb, allowing us to first introduce the idea that RH and O_3 concentrations are two prerequisites for rapid sulfate formation via multiphase reactions. In the case of the RH threshold, this is consistent with current understanding of the multiphase formation of sulfate, since it relates to the semisolid-to-liquid phase transition of atmospheric aerosols. Correlation analysis between SOR and AWC further backed this up. In the case of the O_3 concentration threshold, this is consistent with the consumption of liquid oxidants in multiphase sulfate formation. The thresholds introduced here lead us to better understanding of the sulfate formation mechanism and sulfate formation variations. H_2O_2 might be the major oxidant of sulfate formation, since another liquid phase oxidant, O_3, has previously been shown to be unimportant. The seasonal variations in sulfate formation could be accounted for by variations in the RH and O_3 prerequisites. For example, over the year-long study, the fastest SO_2-to-sulfate conversion occurred in summer, which was associated with the highest values of O_3 (and also H_2O_2) concentration and RH. The SOR also displayed variations with pollution levels, i.e., the SOR increased with $PM_{2.5}$ in all seasons. Such variations were primarily associated with a transition from the slow gas phase formation of sulfate to rapid multiphase reactions, since RH increased higher than its prerequisite value of around 45% as pollution evolved. In addition, the self-catalytic nature of sulfate formation (i.e., 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) also contributed to variations among the pollution scenarios.

1 Introduction

Beijing, the capital of China, suffers from serious air pollution due to its rapid economic growth and urbanisation (Hu et al., 2015). The chemical composition and sources of fine particulate matter ($PM_{2.5}$) in Beijing have been studied extensively (Han et al., 2015; Lv et al., 2016; Zhang et al., 2013; Zheng et al., 2005). Secondary components, especially sulfate, nitrate, and ammonium (SNA), are the main contributors to $PM_{2.5}$ (Huang et al., 2014a). On the most severely polluted days, SNA account for more than half of total $PM_{2.5}$ mass concentrations and play a more important role than on clean days (Quan et al., 2014; Wang et al., 2014b; Zheng et al., 2015b).

The kinetics and mechanisms of the formation of sulfate, a major component of SNA, are complex and remain unclear (Ervens, 2015; Harris et al., 2013; Warneck, 2018). For example, two key questions concerning sulfate formation are: (1) exactly how do various parameters (oxidants, catalysts, meteorological conditions, etc.) influence sulfate formation, and (2) how do multiple formation routes compete and contribute together to sulfate formation under ambient conditions. In general, sulfate is produced from SO_2 via gas phase oxidation reactions involving the hydroxide radical (OH) and Criegee intermediates (Gleason et al., 1987; Sarwar et al., 2014; Vereecken et al., 2012), heterogeneous reactions (mainly on dust aerosols), and multiphase transformations with O_3, H_2O_2, or O_2 (catalysed by transition metal ions (TMIs) (i.e., TMIs + O_2) and NO_2 (NO_2 + O_2)) as liquid phase oxidants, which occur mainly in clouds but also in aerosol droplets near the ground (Zhu et al., 2011).

Due to the major role of multiphase transformations, sulfate production is presumed to be self-catalysed, i.e., the formation of hydrophilic sulfate aerosols under high relative humidity (RH) conditions results in an increase in aerosol water content (AWC), which results in greater particle volume for further multiphase sulfate formation (Cheng et al., 2016; Pan et al., 2009; Xu et al., 2017). Analyses of the correlation of sulfate formation with RH and AWC have been conducted to test this hypothesis, using the concept of the sulfur oxidation ratio (SOR), defined as the molar ratio of sulfate to total sulfur (= sulfate + SO_2). It is used to indicate the magnitude of the secondary formation of sulfate and expressed as (Wang et al., 2005):

$$SOR = \frac{n_{SO_4^{2-}}}{n_{SO_4^{2-}} + n_{SO_2}}, \quad \text{(Eq. 1)}$$

where $n_{SO_4^{2-}}$ and n_{SO_2} represent the molar concentrations of sulfate and SO_2, respectively. Even though regional transport or intrusion of SO_2 or sulfate (or local sulfate emissions) would modify the SOR, it has still often been a relatively good proxy of secondary sulfate formation (i.e., local SO_2-to-sulfate conversion). For example, Sun et al. (2014; 2013) found positive correlations between the SOR and RH, and observed rapid increases in SORs at elevated RH levels. Xu et al. (2017) found positive correlations of the SOR with both RH and AWC. Multiphase transformation routes, including O_3 oxidation, TMIs + O_2, and NO_2 + O_2, are pH-sensitive and suppressed at low pH (Seinfeld and Pandis, 2006). Sulfate production raises the acidity of aerosols and therefore the multiphase transformations of sulfate are presumed to be self-constrained (Cheng et al., 2016). For example, a significant contribution from the O_3 oxidation route can only be expected under alkaline conditions (e.g., sea-salt), otherwise, O_3 oxidation is a minor pathway for sulfate formation (Alexander et al., 2005; Sievering et al., 2004). How the self-constraining nature of sulfate formation influences the relative significance of the TMIs + O_2 and NO_2 + O_2 routes is still under debate. Cheng et al. (2016) proposed that the NO_2 + O_2 route is important during severe haze events under neutral pH conditions (He et al., 2018; Wang et al., 2016). Guo et al. (2017) suggested that aerosols are acidic in Beijing (except for during the limited cases of dust or sea-salt events), casting doubt on the importance of the NO_2 + O_2 route in sulfate formation (Liu et al., 2017a). According to laboratory-based Raman spectroscopy studies, sulfate can be produced via the aqueous oxidation of SO_2 by NO_2 + O_2, with an SO_2 reactive uptake coefficient of 10^{-5}, which represents an atmospherically relevant value (Yu et al., 2018), whereas others have suggested that this route is of minor importance in the atmosphere (Li et al., 2018; Zhao et al., 2018). In addition, Xie et al. (2015) proposed that NO_2 could enhance the formation of sulfate in certain cases, for example, in biomass burning plumes or dust storms (He et al., 2014). Evaluation of the contribution of TMIs + O_2 reactions appears to be more complex since it depends on aerosol acidity, solubility, oxidation state, and the synergistic effects of different TMIs (Deguillaume et al., 2005; Warneck, 2018).

The compensating effects among AWC, aerosol acidity, and the concentrations of precursors and catalysts show that the kinetics and mechanisms of sulfate formation are highly complex. It can be inferred that there is competition between the various routes, with dependences on atmospheric conditions (e.g., seasonal and pollution level variations) likely, but this has not received much research attention previously.

Here, daily $PM_{2.5}$ samples were collected in Beijing from March 2012 to February 2013 and their chemical composition was analysed. The main parameters that influenced sulfate formation (i.e., RH, O_3 concentration, TMIs, etc.) were determined. This valuable dataset enabled us to explore: (1) the specific role of each influencing factor in sulfate formation, and (2) how multiple sulfate formation routes compete in different seasons and under various pollution scenarios.

2 Measurements and methodology

2.1 Measurements

2.1.1 Measurement stations

The two measurement stations are shown in Fig. 1. The PKU station (116.30 °E, 39.99 °N) is about 20 m above ground level at the campus of Peking University, Beijing, China (Liang et al., 2017). Daily $PM_{2.5}$ samples were collected using a four-channel sampler (TH-16A; Wuhan Tianhong Instruments, China) at a flow rate of 16.7 L min^{-1} from 1 March 2012 to 28 February 2013. The gaseous pollutants SO_2, NO_x, and O_3 were measured with a pulsed fluorescence SO_2 analyser (Model 43i TLE; Thermo Fisher Scientific, Waltham, MA, USA), chemiluminescence NO–NO_2–NO_x analyser (Model 42i TL; Thermo Fisher Scientific), and an ultraviolet photometric O_3 analyser (Model 49i; Thermo Fisher Scientific), respectively. Temperature and RH were also monitored (MSO; Met One Instruments, Grants Pass, OR, USA). Solar radiation data were obtained from the Beijing Meteorological Observatory Station (116.47 °E, 39.81 °N). Daily averages were used for all analysis conducted in this work.

2.1.2 Filter sampling and analysis

Each $PM_{2.5}$ sample set consisted of one quartz filter (47 mm; Whatman QM/A, Maidstone, England) and three Teflon filters (47 mm; pore size = 2 μm; Whatman PTFE). The quartz filters were baked for 5.5 h at 550 ℃ before use. The Teflon filters were weighed in a weighing room before and after sampling using a delta range balance (0.01 mg/0.1 mg precision; AX105; Mettler Toledo, Switzerland). To minimise contamination, all Teflon filters were placed in a super clean room (temperature = 22 ± 1 ℃; RH = 40 ± 2 %) for 24 h before being weighed. After sampling, all filters were stored at −20 ℃ prior to analysis. Water soluble cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) were measured using ion chromatography (ICS-2500 and ICS-2000; DIONEX, USA). Trace elements (Na, Mg, Al, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, Mo, Cd, Ba, Tl, Pb, Th, and U) were analysed by inductively

coupled plasma–mass spectrometry (ICP–MS, X-Series; Thermo Fisher Scientific). Organic carbon (OC) and elemental carbon (EC) were measured using a thermal/optical carbon analyser (RT-4; Sunset Laboratory Inc., Tigard, OR, USA). The procedure for the measurement of water soluble Fe has been described in detail in a previous study (Xu et al., 2018).

2.2 Estimation of the mass concentrations of $PM_{2.5}$ components

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. The mass concentrations of OM, minerals, and TEOs were calculated from OC, Al, and trace element concentrations, respectively. The details of this method are provided in the supplementary information (SI). For minerals, validation of the method using only Al to represent all minerals is shown in Fig. S1. TEOs mostly originated from anthropogenic sources (Fig. S2).

2.3 Quality assurance and quality control

The $PM_{2.5}$ sampling instruments were cleaned and calibrated every 2–3 months. Before the daily filter replacement, filter plates were scrubbed with degreasing cotton that had been immersed in dichloromethane. For water soluble ions, OC/EC, and trace element measurements, standard solutions were analysed before each series of measurements. The R^2 values of the calibration curves were all > 0.999. For water soluble ion measurements, beakers, tweezers, and vials were cleaned with deionised water (18.2 MΩ; Milli-Q, USA) three times before use. Certified reference standards (National Institute of Metrology, China) were used for calibration. For OC/EC measurements, tweezers and scissors were scrubbed with degreasing cotton immersed in dichloromethane for every filter. Total organic carbon (TOC) was calculated based on calibration with external standard solutions. For trace element measurements, containers and tweezers were cleaned three times with nitric acid before use, and the analysis of a certified reference standard (NIST SRM-2783) was used to verify accuracy. The recovery of all measured trace elements fell within ± 20 % of their certified values. For gaseous pollutants and meteorological parameters, all instruments were maintained and calibrated weekly based on manufacturers' protocols.

3 Results and discussion

3.1 General description

The annual and seasonal mean (± one standard deviation (SD)) concentrations of $PM_{2.5}$ and its seven major known components are summarised in Table 1. The annual mean $PM_{2.5}$ concentration was 84.1 (± 63.1) μg m^{-3}, which is more than two times greater than the Chinese National Ambient Air Standard annual mean concentration of 35 μg m^{-3}. On 145 of the 318 (46 %) measurement days, daily mean $PM_{2.5}$ concentrations were above the Chinese National Ambient Air Standard 24 h mean concentration of 75 μg m^{-3}. Time series of $PM_{2.5}$ concentrations and its seven major known components are shown in Fig. 2. Seasonal variations in $PM_{2.5}$ loading are obvious, with spring and winter peaks and summer and autumn valleys. OM and EC concentrations displayed common seasonal variations, with a plateau from mid-October to mid-February and a valley in summer (Fig. 2), which resembles the variations in $PM_{2.5}$, K^+, Cl^-, and F^- (Figs. 2 and 3). The seasonal variations in minerals also indicate an important contribution of dust events to $PM_{2.5}$ loading during spring, which is a well-known phenomenon (Zhang et al., 2003; Zhuang et al., 2001). TEOs displayed no obvious seasonal variations (Fig. 2). SNA accounted for more than one-third of $PM_{2.5}$ annually and showed similar seasonal variations to that of $PM_{2.5}$ (Fig. 2), with the notable exception that sulfate became the highest contributor to $PM_{2.5}$ (~25 %) in summer (Fig. 4). The summer peak in sulfate could be accounted for by fast secondary formation, as will be discussed later. On an annual basis, the seven major known components accounted for over 80 % of $PM_{2.5}$ (Fig. 4). The diversity of the seasonal variations in $PM_{2.5}$ and its major components found in our study imply that there were seasonal variations in both the primary sources and secondary formation of $PM_{2.5}$.

3.2 Influence of various parameters on sulfate formation

To further explore the parameters that influenced sulfate formation, SORs were plotted against RH and the concentrations of O_3, NO_2, and Fe (total Fe, including both water soluble and water insoluble Fe), which is a major tracer of transition metals (Figs. 5 and 6).

As shown in Fig. 5a, an RH threshold of ~45 % was critical for efficient SO_2 oxidation (i.e., a high SOR). Such a threshold effect was thought to be reasonable given that AWC increases sharply when RH was above a threshold of 45 %, at which the aerosol undergoes a phase transition from a (semi-)solid particle to a droplet (Pan et al., 2009; Russell and Ming, 2002). Further correlation analysis between SOR and AWC further supports that the multiphase reactions are responsible for sulfate formation. (Fig. S3).

Our observation of a daily average RH threshold of ~45 % is in line with previous reports of 40–50 % (Liu et al., 2015; Quan et al., 2015; Xu et al., 2017; Yang et al., 2015; Zheng et al., 2015b), but is slightly lower than the *in situ* phase transition threshold RH of 50–60 % previously observed in Beijing (Liu et al., 2017b). Correlation analysis of SOR and RH (or AWC) has often been conducted in previous studies. For example, Wang et al. (2005) found a weak positive correlation of SORs with RH (R = 0.38), while Sun et al. (2006) found a strong positive correlation (R = 0.96). However, the analysis in the present work and those of a few previous studies revealed that the relationship between the SOR and RH is nonlinear (Sun et al., 2013; Sun et al., 2014; Zheng et al., 2015b). In fact, the RH threshold suggests that high RH (or AWC) is a prerequisite for fast sulfate formation via multiphase reactions, which are known to account for the majority of sulfate accumulation.

From the large scattering of data points around the fit line in Fig. 5a, it might be inferred that RH was not the only prerequisite for fast SO_2-to-sulfate conversion. As shown in Fig. 5b, a significant increase in the SOR was also observed at an O_3 concentration threshold of ~35 ppb. High O_3 concentrations (i.e., > 35 ppb) were accompanied by high SOR values of ~0.4 (right-hand side of Fig. 5b). Correlation analyses of SORs with O_3 have been conducted but inconsistent results were reported. Wang et al. (2005) found a weak positive correlation between SORs and O_3 (R = 0.47) for continuous observations in Beijing during 2001–2003. However, Liu et al (2015) found a weak negative correlation between SORs and O_3 (R = −0.53, p = 0.01) during a haze episode in September 2011. Zhang et al. (2018) found no correlation between SORs and O_3 during winter haze days in 2015. Quan et al. (2015) found that the SOR decreased with O_3 when O_3 concentrations were lower than 15 ppb, but increased with O_3 when O_3 concentrations were higher than 15 ppb, for observations made during autumn and winter 2012. In the present study, our observations revealed that the relationship between the SOR and O_3 concentration, like RH, was nonlinear and that a high O_3 concentration was another prerequisite for fast sulfate formation. Such a conclusion was a surprise first, since O_3 oxidation was not thought to be a major route for SO_2-to-sulfate conversion (He et al., 2018; Sievering et al., 2004). However, as a primary precursor to OH radicals and H_2O_2 (via HO_2), (Lelieveld et al., 2016; Lu et al., 2017), high O_3 concentrations (e.g., > 35 ppb) correspond to a high concentration of oxidants, which favors multiphase sulfate formation and thus a high SOR, whereas low O_3 concentrations suggest a lack of available oxidants for multiphase SO_2-to-sulfate conversion and thus a low SOR. In addition, the simultaneous occurrence of low SORs and low O_3 concentrations had a secondary cause. Low O_3 concentrations in the Beijing urban area were often due to the titration of O_3 by

NO (Li et al., 2016), which accumulated together with SO_2 (Fig. S4). The accumulation of SO_2, which "diluted" the SOR (Eq. 1), was thus naturally accompanied by the titration of O_3. The L-shaped dependence of the SOR on several other primary pollutants, such as EC, NO, and Se (Fig. S5), further confirmed this secondary cause. Therefore, the accumulation of primary pollutants might also help to explain the low SOR values of ~0.1 on the left-hand side of Fig. 5b, in addition to the lack of available oxidants for multiphase SO_2-to-sulfate conversion.

The large scattering of data points around the fit line in Fig. 5b suggests that O_3 concentration, like RH, was not the only prerequisite for fast SO_2-to-sulfate conversion. The dependence of the SOR on RH was separated into low (< 35 ppb) and high (> 35 ppb) O_3 groups (solid black circles and solid blue circles, respectively, in Fig. 5a). SOR values above the fit line are found mostly for the high O_3 group. After the dependence of the SOR on O_3 concentration was separated into low (< 45 %) and high (> 45 %) RH groups (solid black circles and solid blue circles, respectively, in Fig. 5b), a similar pattern was found for the high RH group. In other words, fast multiphase SO_2-to-sulfate conversion could only occur when both O_3 and RH exceeded their respective thresholds simultaneously.

The seasonal variation of such thresholds of RH and O_3 were further discussed. As shown in Fig. 6, RH threshold was roughly around 45 % during all four seasons in Beijing. While the threshold of O_3 varied among seasons (Fig.7). A turning point of 25–40 ppb was observed for fast SOR increase in spring, summer and autumn, while the turning point is not clear due to lack of high O_3 data in winter. The variation of O_3 threshold value might be due to the shifts of O_3-H_2O_2 relationship which might be modified by temperature etc. in different seasons. Despite of the variation of thresholds of RH and O_3 in different seasons or even in different sampling location (not discussed here), the thresholds of RH and O_3 for fast sulfate formation further found in our study has its implications on sulfate formation mechanism (see below).

The SORs was further plot against Fe and NO_2. No clear dependence of the SOR on concentrations of Fe or NO_2 was found (Figs. 8a and 8b). Possible reasons and implications of this result will be discussed in the following section.

3.3 Implications for sulfate formation mechanisms

Our observations of the factors that influence sulfate formation have implications for sulfate formation routes and its variations among seasons and pollution conditions.

In retrospect, thresholds in RH and O_3 concentrations were found to be critical to the SOR, suggesting that AWC and liquid phase oxidant were two prerequisites for fast multiphase SO_2-to-sulfate conversion. H_2O_2 and O_3 are the two liquid phase oxidants which are responsible for sulfate formation. The O_3 oxidation route was proposed not important in high aerosol acidity areas, such as Beijing (Guo et al., 2017; Sievering et al., 2004). A recent study on aerosol pH in Beijing showed that the $PM_{2.5}$ was acidic (RH > 30 %) (Ding et al., 2019), confirming a minor contribution from O_3 oxidation. H_2O_2 was then the only possible oxidant responsible for sulfate formation. Although direct measurements of aqueous H_2O_2 were not performed in this study, the H_2O_2 concentrations in Beijing reported by Fu (2014) were found to be positively correlated with temperature. By assuming the reported H_2O_2-Temperature relationship applicable to our measurements, a proxy H_2O_2 concentration was then estimated. As shown in Fig. S6, 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 measurement year. SOR was further plotted against H_2O_2 and positive correlation was found between them (Fig. S7). 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 oxidation route in sulfate formation (Ye et al., 2018). Based on the above discussions, we propose that H_2O_2 might be the major oxidant for sulfate formation in Beijing.

The plot of SORs against Fe, the dominant transition metal species, shows no clear dependence (Figs. 8a and S8). Similarly, the plot of SORs against NO_2 shows no clear dependence either (Fig. 8b). If Fe acted as a catalyst and thus its concentration might not be directly proportional to SORs. Therefore, such a pattern does not safely exclude TMIs + O_2 as a major route for sulfate formation. Several laboratory studies excluded NO_2 as a direct oxidant in SO_2-to-sulfate conversion. For example, Zhao et al. (2018) tested the oxidation of SO_2 by NO_2 in an N_2 atmosphere and concluded that NO_2 is not an important oxidant, since NO_2 was more likely to undergo disproportionation (Li et al., 2018). However, Yu et al. (2018) further explored this reaction, and found that the reaction rate was 2–3 orders of magnitude greater in an O_2 + N_2 atmosphere, indicating potentially important roles of NO_2 + O_2 oxidation in sulfate formation (He et al., 2014; Ma et al., 2018). As with Fe, if NO_2 acted as a catalyst, its concentration might not be directly proportional to that of sulfate. Therefore, such a pattern does not safely exclude NO_2 + O_2 as a major route for sulfate formation either. Although direct aerosol pH measurement is not available here, 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., 2017), which suggests that several routes of sulfate formation, including NO_2 + O_2,

TMIs + O_2, O_3 oxidation etc., are suppressed. Hence, we carefully propose here neither TMIs +O_2 nor NO_2+O_2 seem to be a major route for sulfate formation.

On one hand, a direct measurement of aerosol pH is also urgently needed in the future to examine our proposal here; on another hand, our proposal here has further implication on the understanding of sulfate formation. Previously, aerosol surface area and concentrations of Fe, Mn, and NO_2 were used in model evaluations of catalytic sulfate formation in the boundary layer (Wang et al., 2014a; Zheng et al., 2015a). However, our proposals here suggest that a careful reassessment of such calculations is required. In addition, model calculations have often suggested important contributions of in-cloud processes to sulfate accumulation near the ground (Barth et al., 2000), although few observational constraints are available for confirmation of these model results (Harris et al., 2014; Shen et al., 2012). The O_3 concentration and RH prerequisites found in the present work might indicate a major role of *in situ* sulfate formation in the boundary layer, via multiphase reactions with H_2O_2 as the main oxidant, rather than in-cloud processes and intrusion from the free troposphere.

As the two prerequisites showed strong seasonal and pollution level variations over the measurement year, the SOR exhibited corresponding variations. As shown in Fig. 9, SORs displayed clear seasonal variations, with the highest value (±1 SD) of 0.46 (±0.22) in summer, followed by spring (0.23 ± 0.14), autumn (0.18 ± 0.15), and winter (0.09 ± 0.05). The highest SOR (i.e., fastest SO_2-to-sulfate conversion rate) was found in summer, which is not surprising because the ambient conditions in summer were conducive SO_2-to-sulfate conversion (Wang et al., 2005). RH and O_3 concentrations in summer were not only the highest in the year, but on average were also both higher than their thresholds of 45 % and 35 ppb, respectively, which was unique among the four seasons. In summer, the median and mean (±1 SD) RH levels were 57.4 % and 57.6 (±13.6) %, respectively, and the median and mean O_3 concentrations were 46.9 ppb and 46.0 (± 18.3) ppb. It should be noted that the median and mean SO_2 concentrations were 2.6 and 4.0 (± 3.7) ppb, respectively, which were the lowest in the year. Despite the low concentrations of SO_2, there were considerable sulfate concentrations (Figs. 2 and 9), which can be accounted for by fast SO_2-to-sulfate conversion. Although the rapid accumulation of secondary sulfate during winter haze days in Beijing has been widely reported (Wang et al., 2014b; Zheng et al., 2015b), the lowest SOR was observed during winter in the present study (Fig. 9a), which is consistent with previous observations (Wang et al., 2005). On winter haze days, RH values of up to 73.6 % and $PM_{2.5}$ mass loadings of up to 375.3 μg m^{-3} were observed. Therefore, AWC was not the limiting factor in SO_2-

to-sulfate conversion (Figs. 9b and 9e). The SO_2-to-sulfate conversion rate in winter could have been limited by the reduced concentration of oxidants (Fig. 9c) as a result of both high emissions of the primary pollutant NO (Fig. S9) and low solar radiation levels (Fig. 9f). Sulfate concentrations in winter were comparable to those in summer, which might have been driven by high SO_2 concentrations in winter (Fig. 9d), despite slow SO_2-to-sulfate conversion. The lower boundary layer height in winter relative to other seasons would also have encouraged the accumulation of both $PM_{2.5}$ and its components, including sulfate (Gao et al., 2015; Zhang et al., 2015). The SORs in spring and autumn were comparable and moderate, possibly representing a transition in conditions between summer and winter.

For each season, four pollution scenarios were classified according to $PM_{2.5}$ level. The lowest 25 %, 25–50 %, 50–75 %, and highest 25 % of pollution levels were defined as "clean", "moderate pollution", "heavy pollution", and "severe pollution", respectively. The relative contributions of the seven major known components of $PM_{2.5}$ among the four pollution scenarios are shown in Fig. 10. In all four seasons, the relative contribution of SNA increased with $PM_{2.5}$ loading. This phenomenon has been reported in previous studies, but data availability was limited in autumn (Xu et al., 2017) and winter (Zheng et al., 2015b). The SOR increased consistently in all four seasons as pollution accumulated, where both the highest value and strongest variability were observed in summer (Fig. 11a). Although SO_2 should have reduced the SOR (Eq. 1), concurrent increases in primary SO_2 and SORs were observed (Figs. 11a and 11b), indicating a significant increase in the SO_2-to-sulfate conversion rate with $PM_{2.5}$ loading, which offset the "dilution" effect (Eq. 1). Such variations in sulfate formation with pollution levels can be accounted for by the corresponding variations in both O_3 concentrations and RH (Figs. 11c and 11d). In all four seasons, RH increased consistently as pollution accumulated (Fig. 11d). O_3 concentrations decreased consistently as pollution evolved in all of the seasons except for summer (Fig. 11c). The distinct variations in O_3 during summer, imply strong photochemistry and high concentrations of OH, which might result in a non-negligible contribution of gas phase reactions to the formation of sulfate. However, gas phase reactions alone could not account for the rate of sulfate formation either in Beijing or globally (Finlayson-Pitts and Pitts, 2000; He et al., 2018), 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 $molecule^{-1}$ s^{-1} (Brothers et al., 2010). However, the overall oxidation lifetime of SO_2 is on the order of hours (Berglen et al., 2004; He et al., 2018). Overall, the increase in SO_2-to-sulfate conversion with $PM_{2.5}$

loading can be attributed to the self-catalytic nature of the multiphase formation of sulfate, i.e., both RH and $PM_{2.5}$ increased continuously with the accumulation of $PM_{2.5}$, resulting in a rapid rise in AWC and providing greater reaction volume for further sulfate formation. Therefore, the increases in RH and $PM_{2.5}$ could have compensated for the low concentration of oxidants, resulting in fast sulfate formation as pollution evolved. Particularly in summer, not only did both RH and O_3 concentrations increase as pollution evolved, but both RH and O_3 concentrations were generally above their respective thresholds at all pollution levels (dashed lines in Figs. 11c and 11d). This explains our observations of both the highest values and strongest dependence on pollution level for SORs in summer.

4 Conclusions

In this study, the annual mean concentration of $PM_{2.5}$ in Beijing during 2012–2013 was 84.1 (±63.1) μg m^{-3}, with clear seasonal and pollution level variations in its chemical components, highlighting the contribution of SNA formation to the accumulation of $PM_{2.5}$ in all seasons. RH and O_3 concentrations were identified as two prerequisites for fast SO_2-to-sulfate conversion. RH above a threshold of ~45 % greatly accelerated the conversion rate. A similar effect was also found for O_3 at a concentration threshold of ~35 ppb. Such dependences have interesting implications. First, they indicate a major role of the H_2O_2 route in sulfate formation, which might further indicate a major role of *in situ* sulfate production in the boundary layer, rather than in-cloud processes and intrusion from the free troposphere. Second, the observed dependences were also able to account for the seasonal and pollution level variations in SO_2-to-sulfate conversion rates. Both the highest value and strongest variability of SOR were observed in summer, which might be attributed to the highest values of O_3 concentrations and RH in summer. SO_2-to-sulfate conversion accelerated as pollution accumulated, which was primarily attributed to a shift from gas phase oxidation to the multiphase oxidation route, which is self-catalytic in nature. The increase in RH was able to offset the low concentration of oxidants under heavily polluted conditions, and resulted in increasingly fast SO_2-to-sulfate conversion as pollution accumulated. While our simultaneous observations of the SOR and concentrations of Fe and NO_2 could not exclude TMIs + O_2 and NO_2-based reactions, a reassessment of the relationships between sulfate formation, aerosol surface area, and the concentrations of Fe and NO_2 is necessary. Future quantitative studies of the relative contributions of different sulfate formation routes should include additional measurements, namely NH_3 for the proxy calculation of pH values, and H_2O_2 to confirm its contribution under different condition.

Author contributions

TZ designed the study. YHF, CXY, and TZ prepared the manuscript with input from all co-authors. YHF and JXW collected and weighed the $PM_{2.5}$ filter samples and carried out the analysis of the components of $PM_{2.5}$. FFX carried out the measurement of water soluble Fe. YSW and MH provided the data for gaseous pollutants, temperature, and RH. WLL provided the solar radiation data.

Competing interests.

The authors declare that they have no conflict of interest.

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Figures and Tables

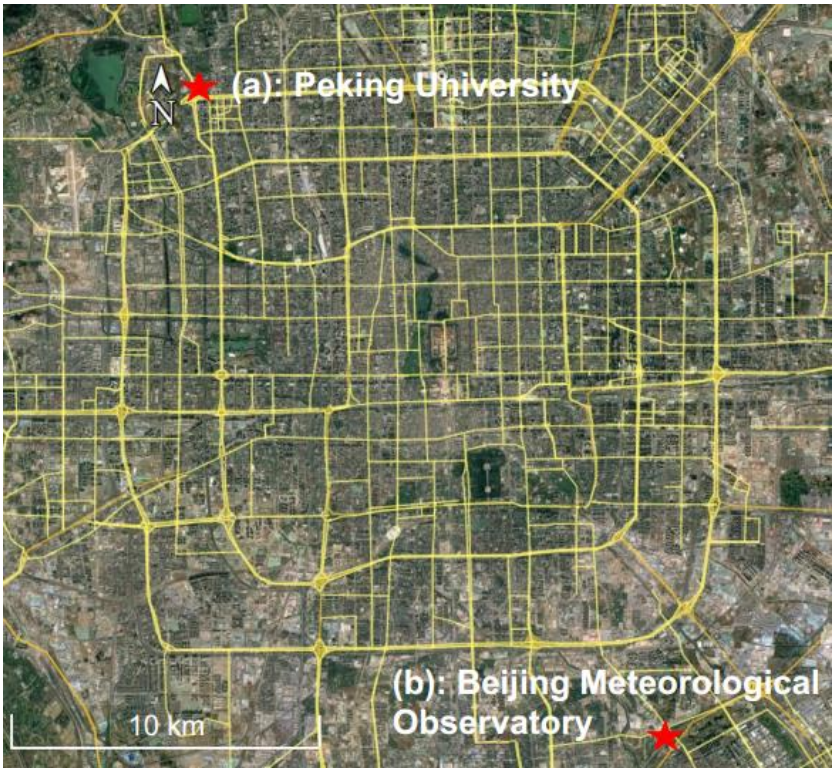


Figure 1. Sample sites in this study (red stars): (a) Peking University and (b) Beijing Meteorological Observatory.

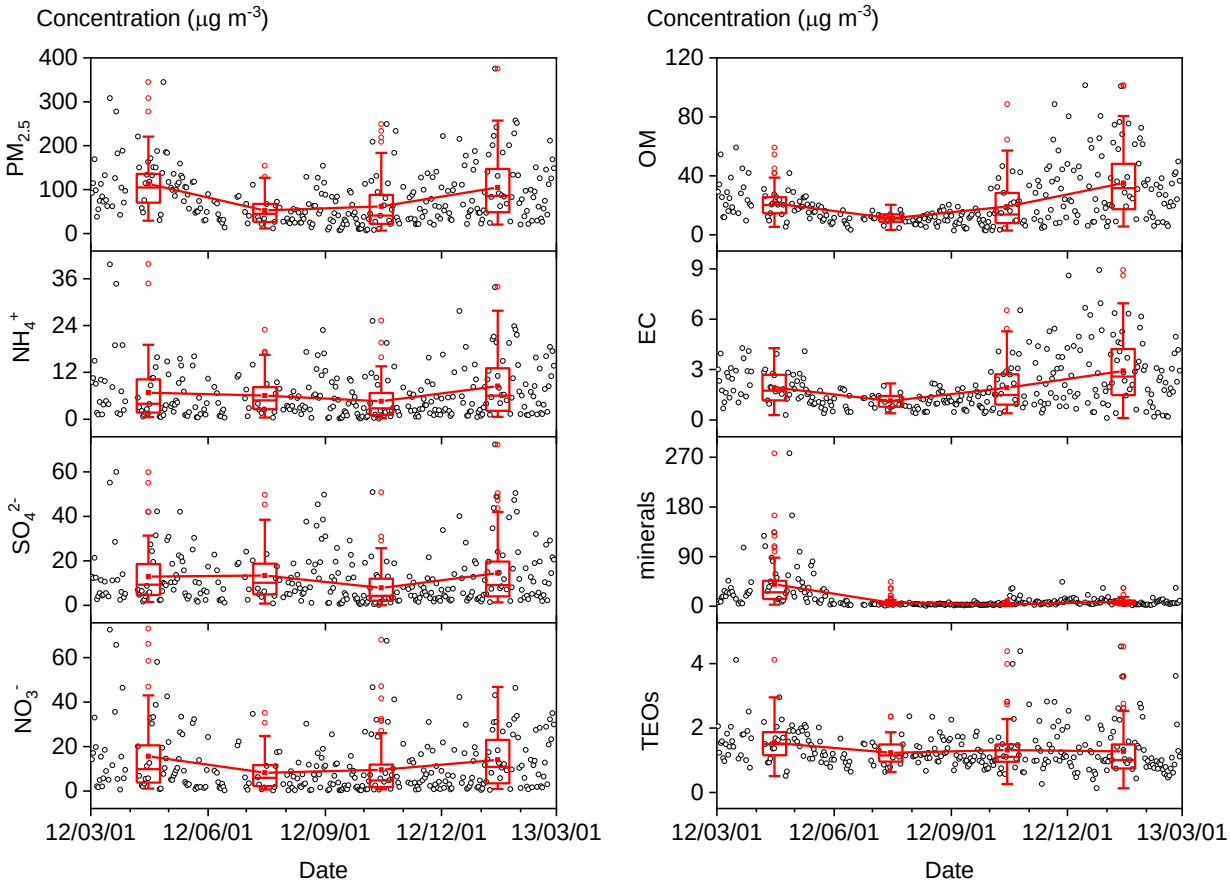
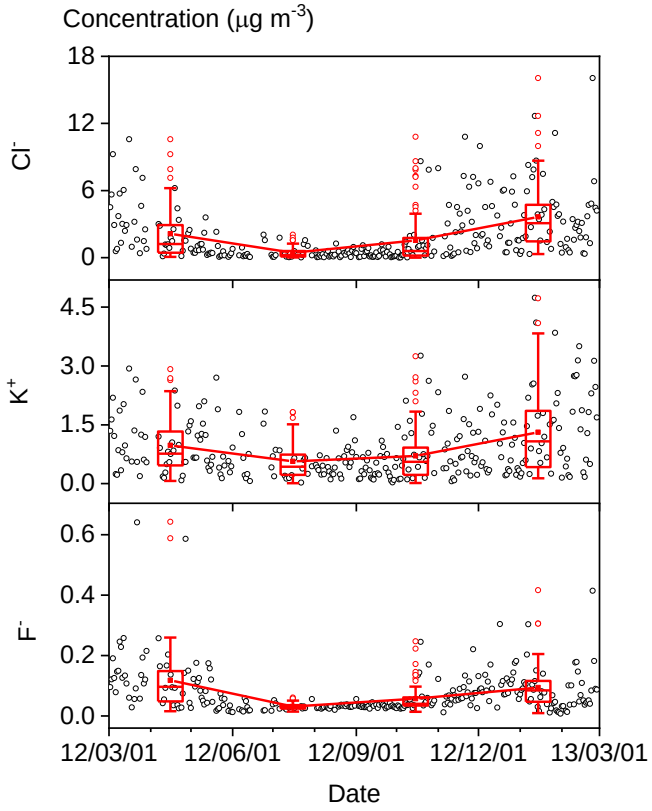
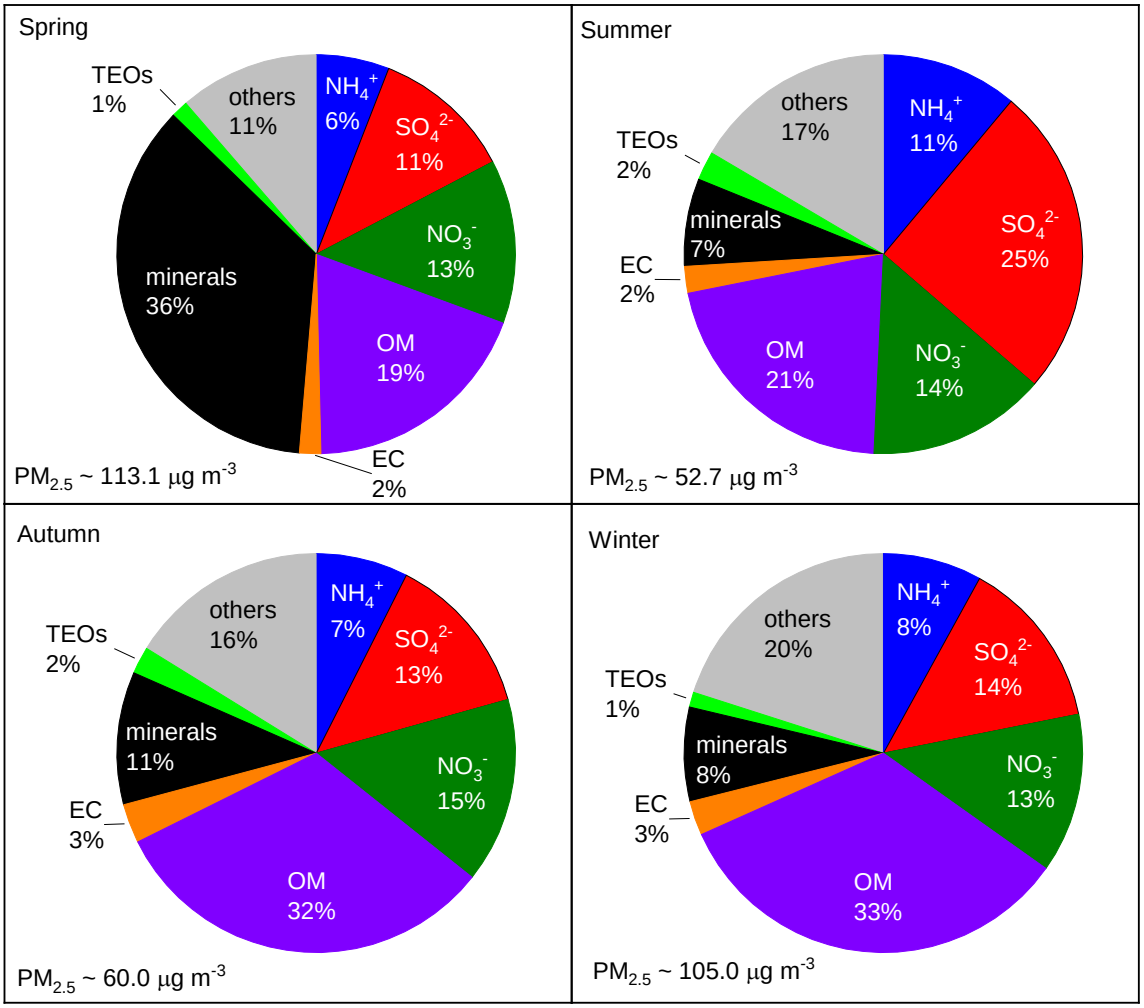


Figure 2. Time series of fine particulate matter ($PM_{2.5}$) concentrations and its seven major known components from March 2012 to February 28 2013 (open black circles). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles for each season. The whiskers, solid red squares, and open red circles represent 1.5 times the interquartile range (IQR), seasonal mean values, and outlier data points, respectively.



572

573 **Figure 3.** Time series of Cl^-, K^+, and F^- from 1 March 1 2012 to February 28 2013.



574

575 **Figure 4.** Seasonal variations in $PM_{2.5}$ and its eight major components from March 1 2012 to February 28 2013

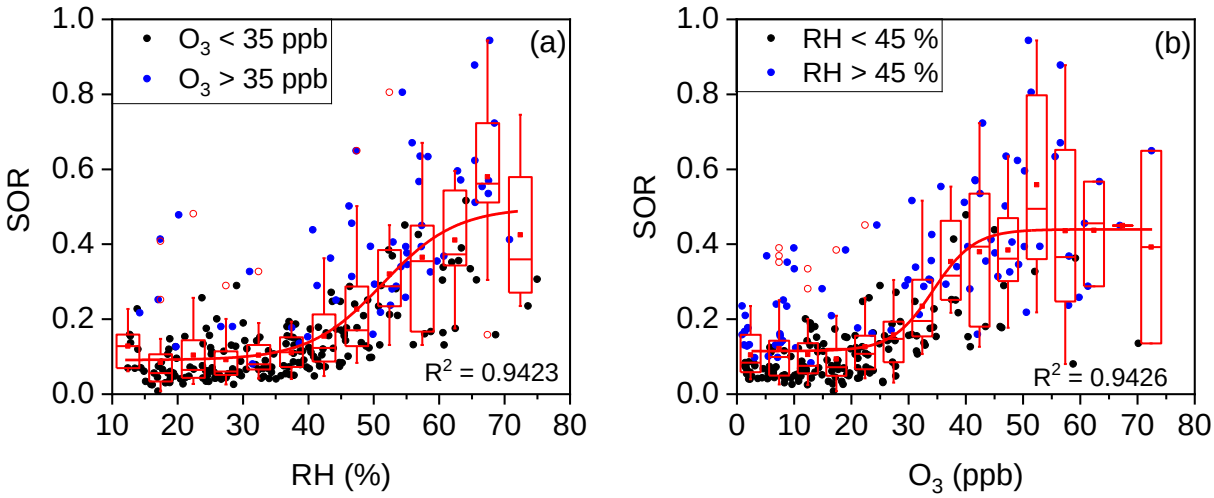
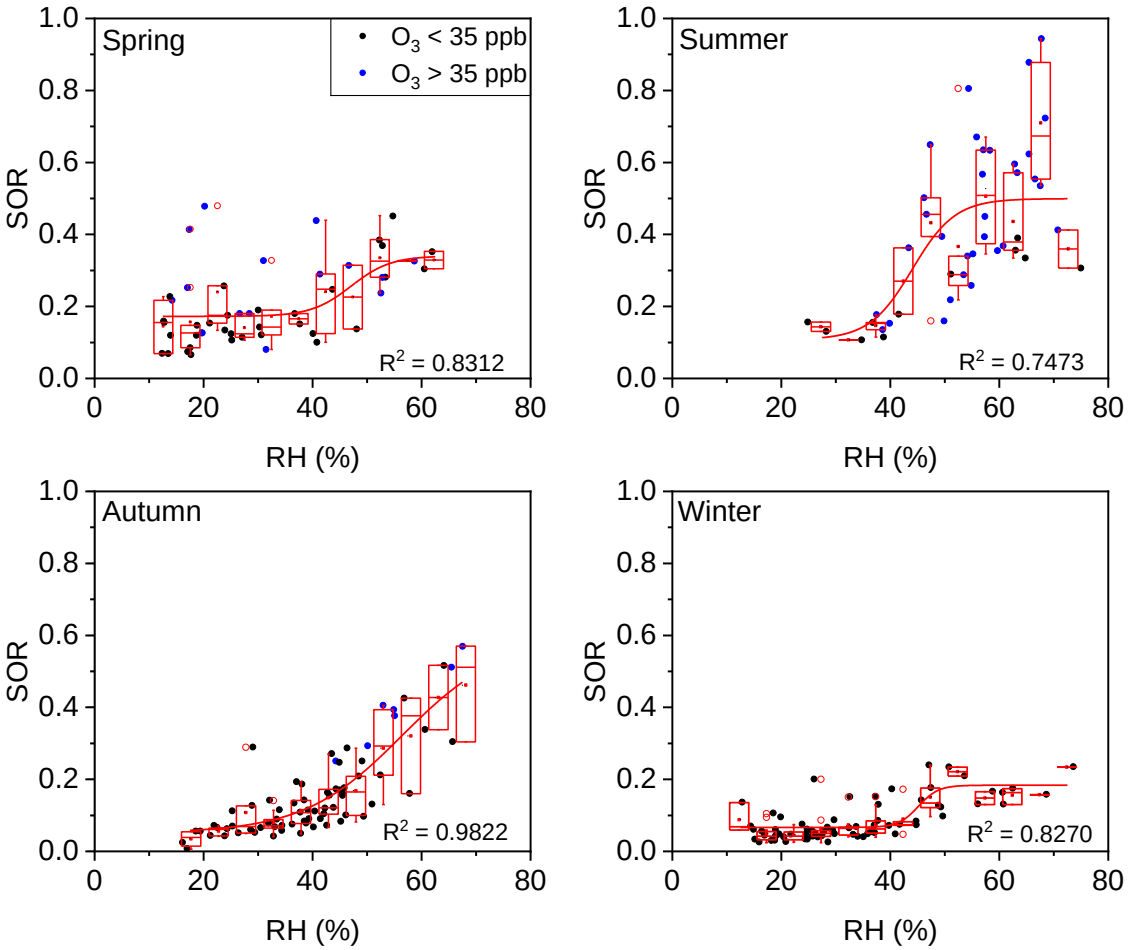


Figure 5. (a) Plot of the sulfur oxidation ratio (SOR) against relative humidity (RH) grouped by O_3 concentration. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. (b) Plot of the SOR against O_3 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin (ΔRH = 5 %; ΔO_3 = 5 ppb). 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 a sigmoid function. Data for days with rain or snow were excluded from these plots.



583

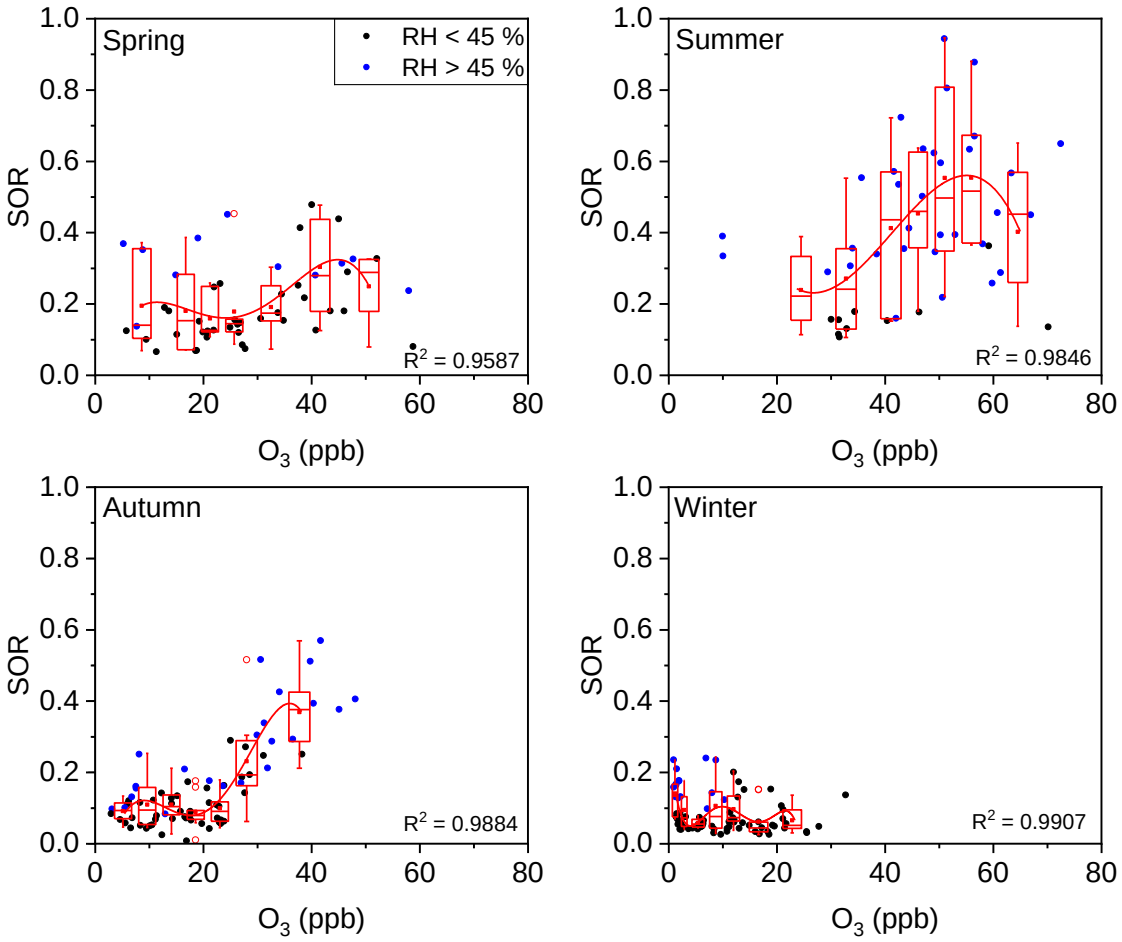
584 **Figure 6**. Plot of SOR against RH grouped by O_3 concentration in four seasons. The solid blue circles represent O_3 > 35 ppb

585 and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles

586 in each bin (ΔRH = 5 %). The whiskers, solid red squares, and open red circles represent 1.5 times the IQR, mean values, and

587 outlier data points, respectively. The red lines are best fits to mean values based on a sigmoid function. Data for days with rain

588 or snow were excluded from these plots.



589

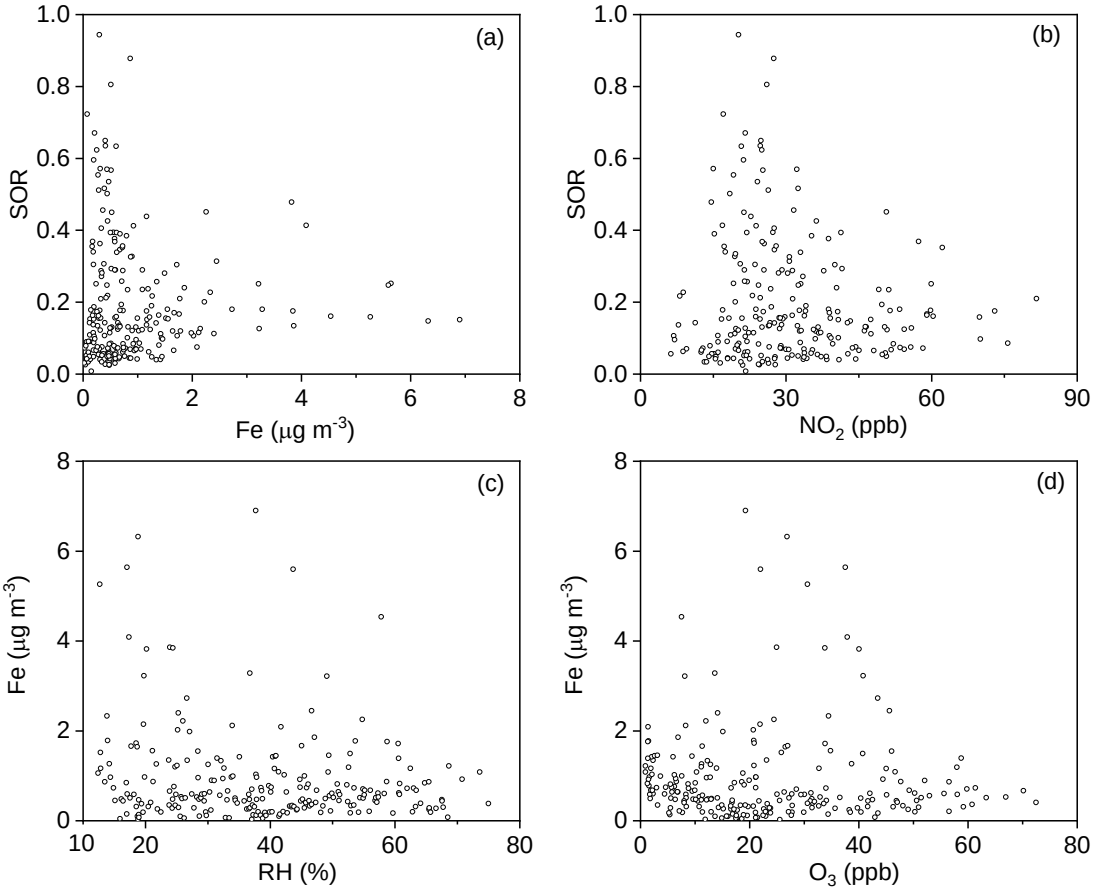
590 **Figure 7**. Plot of the SOR against O_3 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles

591 represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths

592 were set such that there were an approximately equal number of data points in each bin The whiskers, solid red squares, and open red

593 circles represent 1.5 times the IQR, mean values, and outlier data points, respectively. The red lines are best fits to mean values

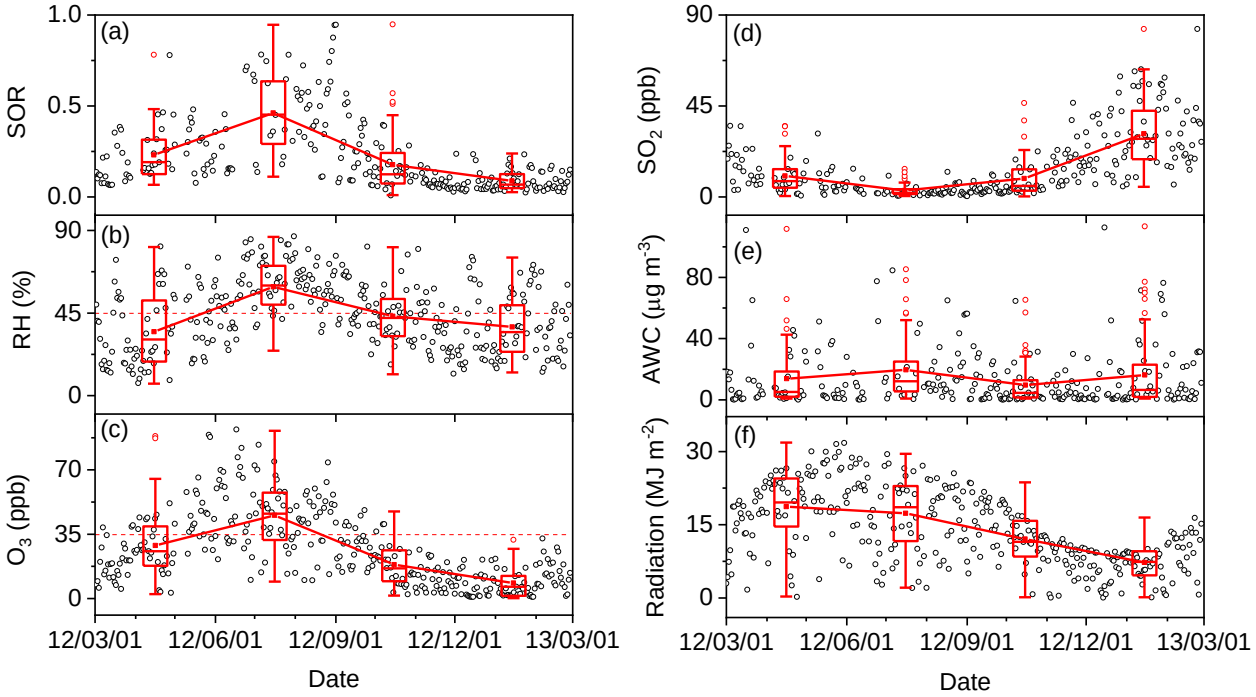
594 based on polynomial functions. Data for days with rain or snow were excluded from these plots.



595

596 **Figure 8**. Plots of SORs against (a) Fe and (b) NO_2. Plots of Fe against (c) RH and (d) O_3. Data for days with rain or snow

597 were excluded from these plots.



598

599 **Figure 9**. Time series of (a) SORs, (b) RH, (c) O_3, (d) SO_2, (e) aerosol water content (AWC), and (f) solar radiation from

600 March 1 2012 to February 28 2013 (open black circles). The boxes represent, from top to bottom, the 75th, 50th, and 25th

601 percentiles for each season. The whiskers, solid red squares, and open red circles represent 1.5 times the IQR, seasonal mean

602 values, and outlier data points, respectively. The horizontal dashed lines in panels (b) and (c) represent thresholds of RH = 45 %

603 and O_3 = 35 ppb, respectively.

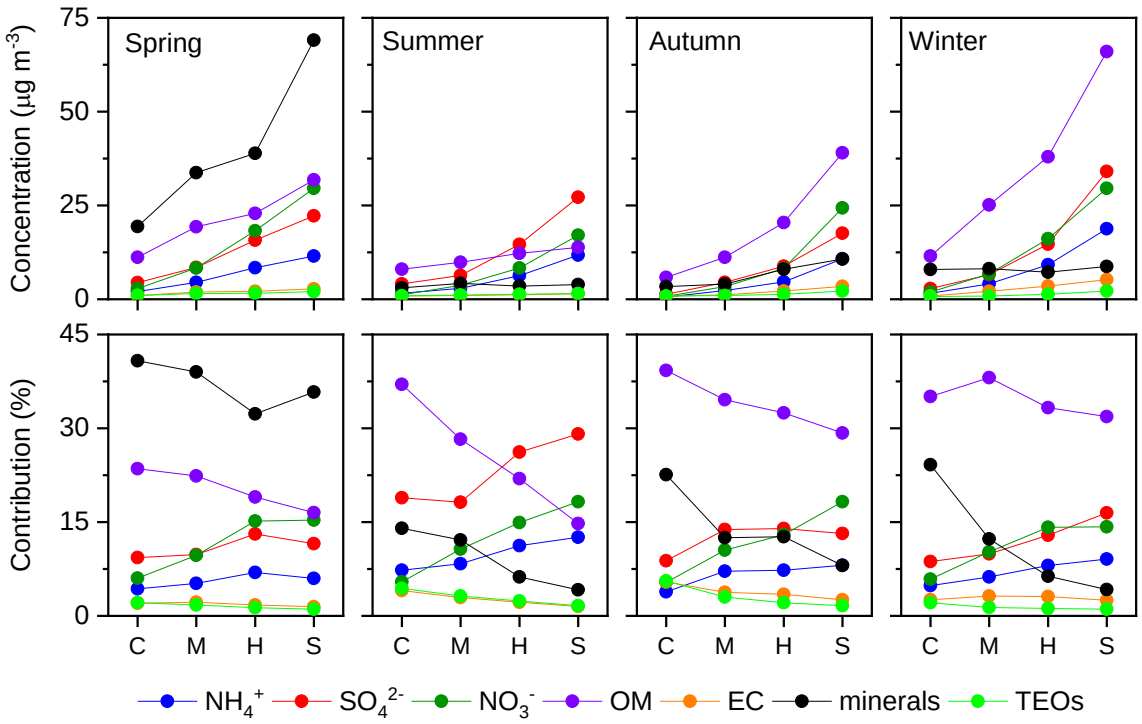
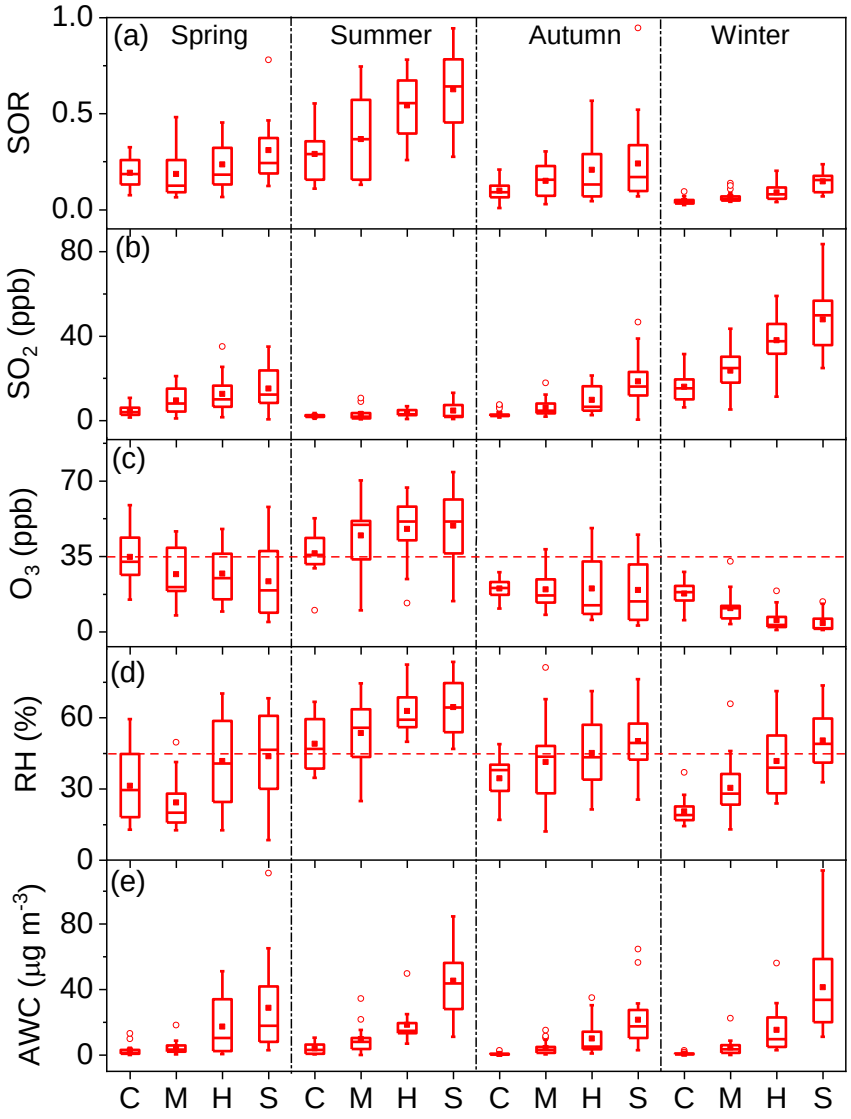


Figure 10. Variations in the mean concentrations (upper panels) and contributions (lower panels) of the seven major known components of $PM_{2.5}$ with pollution levels in each season. C, clean; M, moderate pollution; H, heavy pollution; S, severe pollution.



608

609 **Figure 11**. Variations in (a) SORs, (b) SO_2, (c) O_3, (d) RH, and (e) AWC with pollution levels in each season. C, clean; M,

610 moderate pollution; H, heavy pollution; S, severe pollution. The boxes represent, from top to bottom, the 75^{th}, 50^{th}, and 25^{th}

611 percentiles for each pollution level. The whiskers, solid red squares, and open red circles represent 1.5 times the IQR, mean

612 values, and outlier data points, respectively. The horizontal dashed lines in panels (c) and (d) represent thresholds of O_3 = 35

613 ppb and RH = 45 %, respectively.

614 **Table 1**. Annual and seasonal mean concentrations (μg m^{-3}, ± 1 standard deviation) of $PM_{2.5}$ and its seven major known

615 components.

Component	Annual	Spring	Summer	Autumn	Winter
$PM_{2.5}$	84.1 ± 63.1	113.1 ± 62.0	52.7 ± 32.6	60.0 ± 51.3	105.0 ± 71.7
NH_4^+	6.4 ± 6.4	6.7 ± 7.3	5.9 ± 5.0	4.5 ± 4.8	8.4 ± 7.4
SO_4^{2-}	12.0 ± 12.2	12.9 ± 12.4	13.3 ± 11.5	7.9 ± 8.7	14.5 ± 14.4
NO_3^-	11.5 ± 12.6	15.0 ± 16.0	7.6 ± 8.0	9.0 ± 11.8	13.6 ± 12.1
OM	22.7 ± 18.1	21.5 ± 10.5	11.1 ± 3.8	19.2 ± 16.1	35.2 ± 23.4
minerals	14.7 ± 27.0	40.7 ± 45.0	3.7 ± 1.6	6.5 ± 7.0	8.0 ± 5.6
TEOs	1.3 ± 0.7	1.5 ± 0.6	1.2 ± 0.4	1.3 ± 0.7	1.3 ± 0.8
EC	2.1 ± 1.5	1.9 ± 1.0	1.1 ± 0.5	1.9 ± 1.3	2.9 ± 2.0

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617

Supplementary information

S1. Methodology for estimation of the mass concentrations of $PM_{2.5}$ components

S1.1 Organic matter

The mass concentration of organic matter (OM) was calculated from organic carbon (OC) measurements by multiplying OC by a factor that represents the mass contributions of other elements, such as oxygen, hydrogen, and nitrogen. The OM/OC ratio varies from 1.4 to 2.2 and is expected to increase as aerosols age (El-Zanan et al., 2005). We chose a factor of 1.6 to calculate OM in Beijing following advice in the literature (Xing et al., 2013).

S1.2 Minerals

The total mass concentration of minerals, referred to as "minerals", can be estimated by the following equation (Chan et al., 1997):

$$[\text{minerals}] = 2.2[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}] \quad , \qquad \text{(Eq. 1)}$$

where [*x*] represents the mass concentration of species *x*. According to Zhang et al. (2003), on average Al accounted 7 % of total mineral dust mass concentrations in North, Northwest, and West China. Mineral concentrations can thus also be estimated by Eq. 2:

$$[\text{minerals}] = [\text{Al}]/0.07 \quad , \qquad \text{(Eq. 2)}$$

We calculated [minerals] with the two methods above and found no significant differences (Fig. S1). Equation 2 was therefore employed to calculate [minerals] in this study.

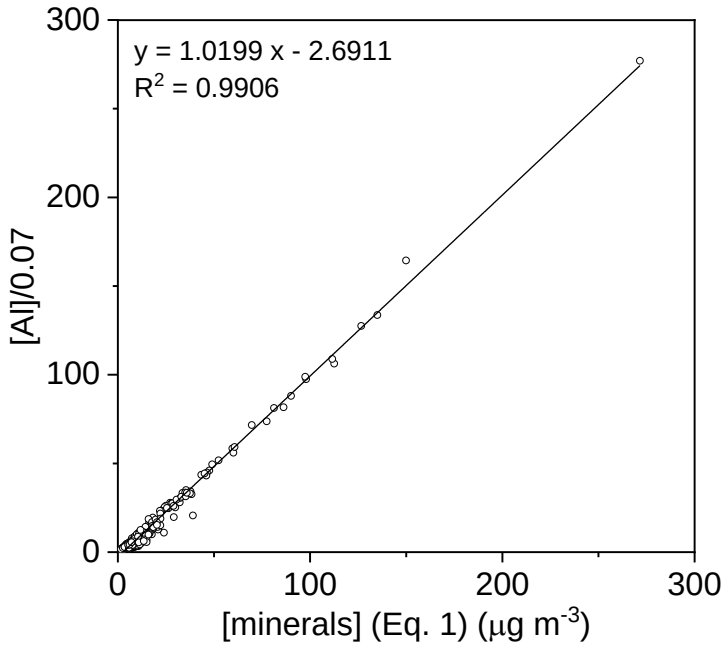


Figure S1. Comparison of the two methods for the calculation of [minerals].

S1.3 Trace element oxides

The enrichment factors (EFs) of trace element oxides (TEOs) can be used to determine whether natural or anthropogenic sources dominated our observations. The EF value of element *i* was defined as follows:

$$EF_i = \frac{[X_i/X_{ref}]_{sample}}{[X_i/X_{ref}]_{crust}} \quad \text{(Eq. 3)}$$

where $[X_i/X_{ref}]_{sample}$ is the mass concentration ratio of element *i* to the reference element in our samples and $[X_i/X_{ref}]_{crust}$ is the mass concentration ratio of element *i* to the reference element in average crust (Hans Wedepohl, 1995). Al was used as the reference element in this study. The EFs of each element are depicted in Fig. S2.

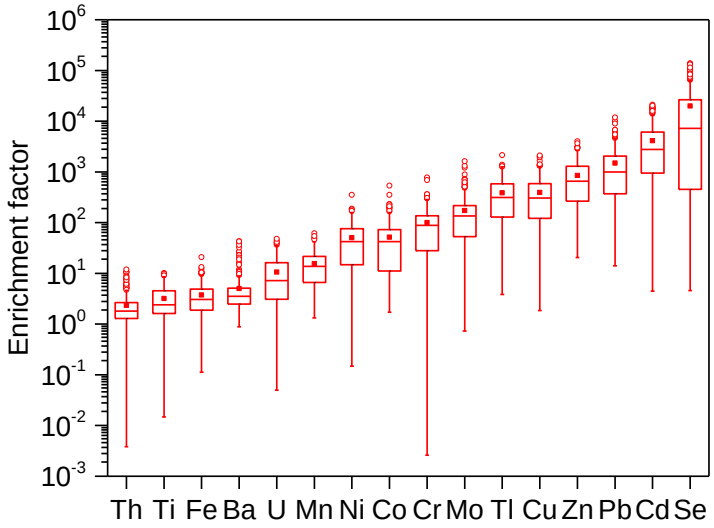


Figure S2. Elemental enrichment factors (EFs) of our samples. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles for each element. The whiskers, solid red squares, and open red circles represent 1.5 times the interquartile range (IQR), mean values, and outlier data points, respectively.

If the EF was < 5, the element was considered to originate mainly from natural sources; if 5 < EF< 20, the element originated from both natural and anthropogenic sources; if EF > 20, the element originated mainly from anthropogenic sources. According to Zhang et al. (2013), the mass concentrations of TEOs can be estimated by multiplied a correction factor to represent the contribution of oxygen. For elements originating from anthropogenic sources only, a factor of 1 was applied, whereas for elements of both natural and anthropogenic origin, a factor of 0.5 was applied to represent the anthropogenic part. As multiple forms of metal oxides were identified, which were hard to quantify, a multiplicative factor of 1.3 was used when considering the metal abundance. The mass concentration of TEOs was calculated as described in Zhang et al. (2013):

$$[\mathrm{TEOs}] = 1.3 \times [0.5 \times (\mathrm{Ba} + \mathrm{Mn} + \mathrm{U}) + (\mathrm{Ni} + \mathrm{Co} + \mathrm{Cr} + \mathrm{Mo} + \mathrm{Tl} + \mathrm{Cu} + \mathrm{Zn} + \mathrm{Pb} + \mathrm{Cd} + \mathrm{Se})] \quad \text{, (Eq. 4)}$$

S1.4 Aerosol water content

Aerosol water content (AWC) was calculated using the ISORROPIA-II thermodynamic model (http://isorropia.eas.gatech.edu). The Na^+–K^+–Ca^{2+}–Mg^{2+}–NH_4^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aerosol system was applied in reverse mode (Fountoukis and Nenes, 2007; Nenes et al., 1998).

S2 Results and discussion

S2.1 Sulfate formation mechanism

Sulfate can be formed through the oxidation of SO_2 by OH radicals in the gas phase (Stockwell and Calvert, 1983), through the oxidation of dissolved SO_2 by various oxidants (e.g., O_3, H_2O_2, NO_2, and O_2) in the aqueous phase (Seinfeld and Pandis, 2006), which may be transition metal ions (TMIs)-catalysed, or through heterogeneous reaction on the surface of sea-salt or dust aerosols (Gurciullo et al., 1999; Usher, 2002).

The rate of the SO_2 + OH reaction can be expressed as:

$$R_{SO_2+OH} = k_0[SO_2(g)][OH(g)] \quad , \qquad \text{(Eq. 5)}$$

where k_0 is the rate constant and $[x]$ represents the concentration of species x. The production rate of sulfate through OH radical oxidation can be expressed as:

$$P_{OH} = \frac{3600 \times 96 \times p \times R_{SO_2+OH}}{RT} \quad , \qquad \text{(Eq. 6)}$$

where 3600 is a time conversion factor (s h^{-1}), 96 is the molar mass of SO_4^{2-} (g mol^{-1}), p is atmospheric pressure (kPa), R is the gas constant (8.31 Pa m^3 mol^{-1} K^{-1}), and T is the temperature (K).

SO_2 reacts with H_2O_2, O_3, NO_2, and O_2 (TMIs-catalysed) in the aqueous phase. The rates of the four main aqueous reactions are expressed as (He et al., 2018; Seinfeld and Pandis, 2006):

$$R_{SO_2+O_3} = (k_1[SO_2 \cdot H_2O] + k_2[HSO_3^-] + k_3[SO_3^{2-}])[O_3(aq)] \quad , \qquad \text{(Eq. 7)}$$

$$R_{SO_2+H_2O_2} = \frac{k_4[H^+][HSO_3^-][H_2O_2(aq)]}{1 + K[H^+]} \quad , \qquad \text{(Eq. 8)}$$

$$R_{SO_2+NO_2} = k_5[S(IV)][NO_2(aq)] \quad , \qquad \text{(Eq. 9)}$$

$$R_{SO_2+O_2} = k_6[H^+]^{-0.74}\,[S(IV)][Mn(II)][Fe(III)] \qquad (pH < 4.2) \quad , \qquad \text{(Eq. 10)}$$

$$R_{SO_2+O_2} = k_7[H^+]^{0.67}\,[S(IV)][Mn(II)][Fe(III)] \qquad (pH > 4.2) \quad , \qquad \text{(Eq. 11)}$$

The production rate of sulfate through aqueous oxidation routes can be expressed as:

$$P_{aqu(ox_i)} = 3600 \times 96 \times R_{SO_2+ox_i} \times \frac{LWC}{\rho_{H_2O}} \quad , \qquad \text{(Eq. 12)}$$

where k_n (n = 1–7) is the rate constant of each oxidation route, K = 13 M^{-1} at 298 K, LWC is the liquid water content (mg m^{-3}), ρ_{H2O} is the density of water (1 kg L^{-1}), and ox_i (i = O_3, H_2O_2, NO_2, and O_2) represents different oxidants.

The heterogeneous reaction rate $R_{het(ox_i)}$ can be expressed as (Jacob, 2000; Wang et al., 2012; Zheng et

al., 2015):

$$R_{\mathrm{het}(\mathrm{ox}_i)} = k_{\mathrm{ox}_i}[\mathrm{SO_2(g)}] \ , \qquad \text{(Eq. 13)}$$

where

$$k_{\mathrm{ox}_i} = \left(\frac{d_\mathrm{p}}{2D_\mathrm{i}} + \frac{4}{v_i\,\gamma_i}\right)^{-1} S_\mathrm{p} \ , \qquad \text{(Eq. 14)}$$

d_p is the effective diameter of the particles (m), D_i is the gas phase molecular diffusion coefficient ($\mathrm{m^2\ s^{-1}}$), v_i is the mean molecular speed in the gas phase ($\mathrm{m\ s^{-1}}$), and S_p is the aerosol surface area ($\mathrm{m^2\ m^{-3}}$). The uptake coefficient γ_i depends on RH:

$$\gamma_i = \begin{cases} \gamma_{\mathrm{low}} & 0 < \mathrm{RH} \le 50\ \% \\ \gamma_{\mathrm{low}} + \dfrac{(\gamma_{\mathrm{high}} - \gamma_{\mathrm{low}})(\mathrm{RH} - 0.5)}{\mathrm{RH_{max}} - 0.5} & 50\ \% < \mathrm{RH} \le \mathrm{RH_{max}} \\ \gamma_{\mathrm{high}} & \mathrm{RH_{max}} < \mathrm{RH} \le 100\ \% \end{cases} \qquad \text{(Eq. 15)}$$

where γ_{low} and γ_{high} can be obtained from Wang et al. (2012) and $\mathrm{RH_{max}}$ is the RH at which γ reaches γ_{high}..

The rate of sulfate production via heterogeneous reactions $P_{\mathrm{het}(\mathrm{ox}_i)}$ can be expressed as:

$$P_{\mathrm{het}(\mathrm{ox}_i)} = \frac{3600 \times 96 \times p \times R_{\mathrm{het}(\mathrm{ox}_i)}}{RT} \ , \qquad \text{(Eq. 16)}$$

S2.2 Influencing parameters

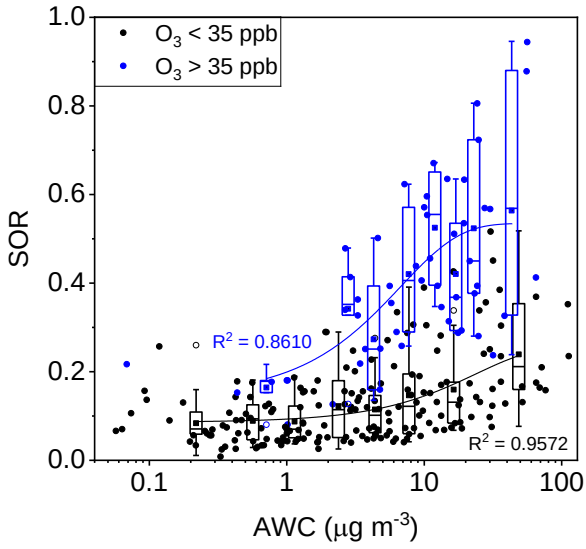


Figure S3. Plot of the SOR against aerosol water content (AWC) (note log scale), grouped by O_3 concentration. The solid blue circles represent O_3 > 35 ppb and the solid black circles represent O_3 < 35 ppb. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin, which 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 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.

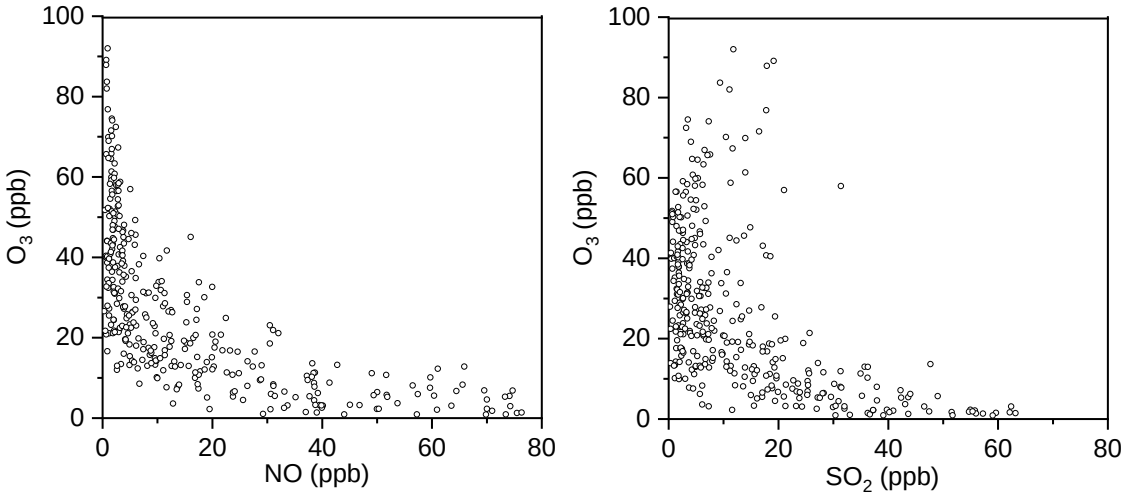
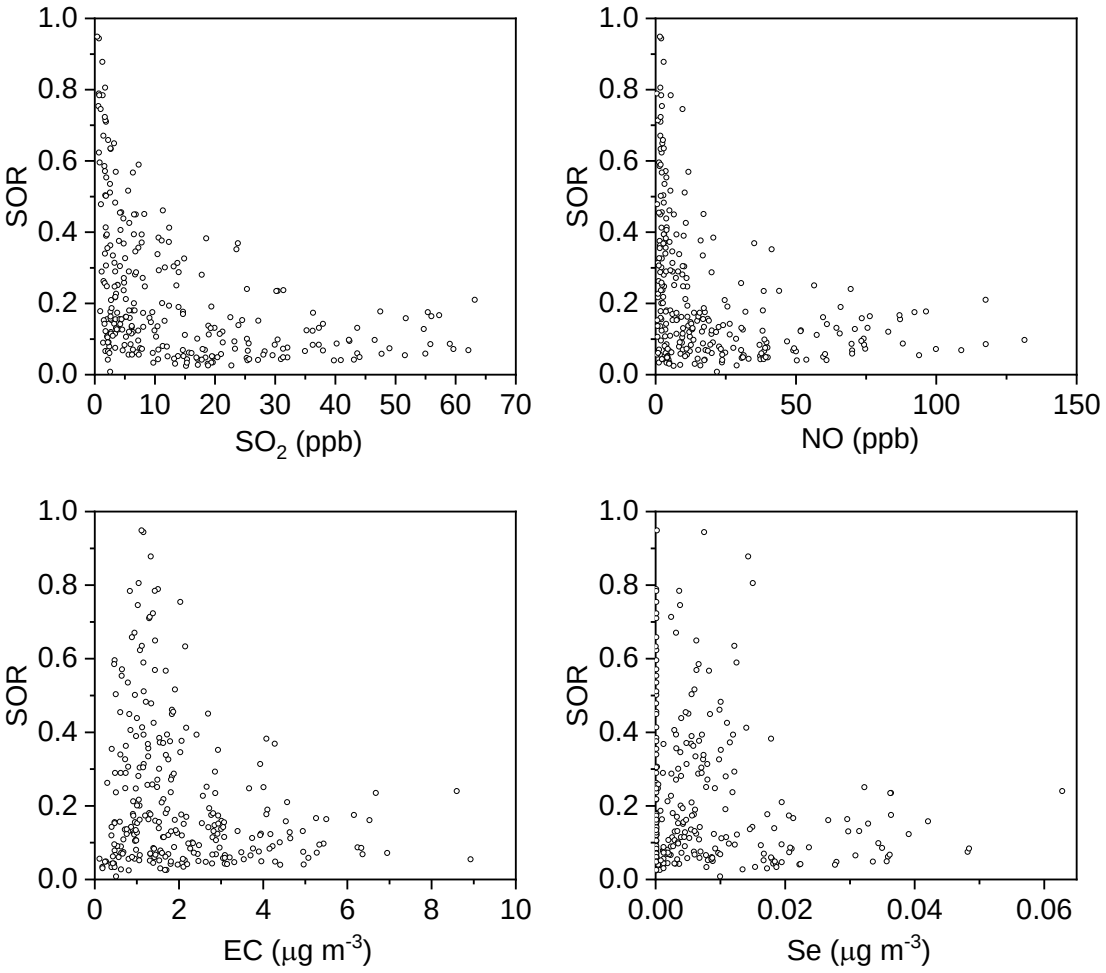


Figure S4. Plots of O_3 against the primary emission tracers NO and SO_2.



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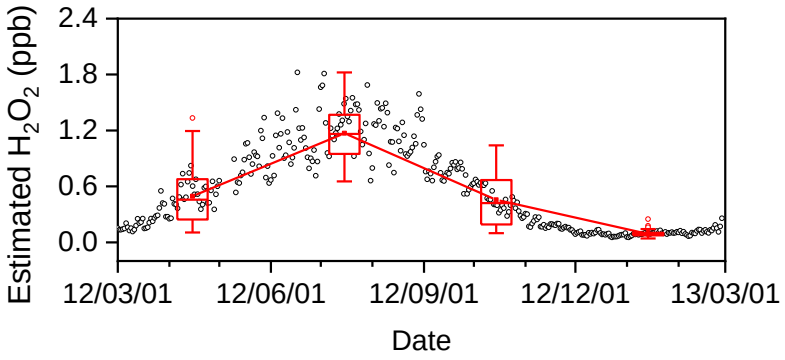
713 **Figure S5.** Plots of sulfur oxidation ratios (SORs) against the primary emission tracers SO_2, NO, EC, and Se.

714



715

716 **Figure S6**. Time series of estimated H_2O_2 from March 1 2012 to February 28 2013. H_2O_2 was estimated from temperature (T)

717 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,

718 50th, and 25th percentiles for each season. The whiskers, solid red squares, and open red circles represent 1.5 times the

719 interquartile range (IQR), seasonal mean values, and outlier data points, respectively.

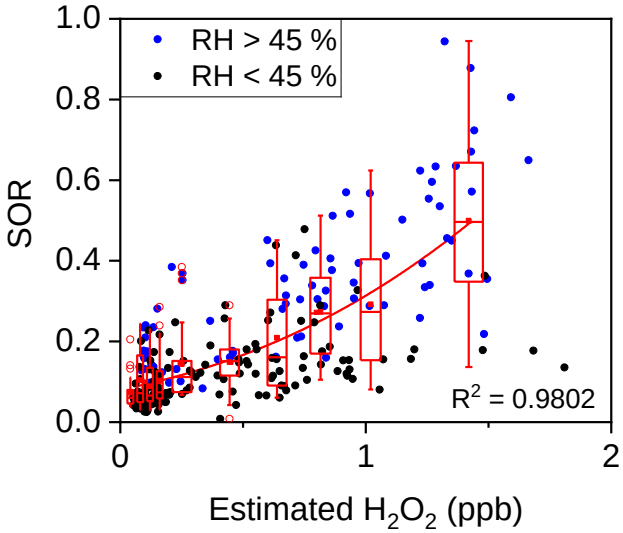


Figure S7. Plot of the SOR against estimated H_2O_2 grouped by RH. The solid blue circles represent RH > 45 % and the solid black circles represent RH < 45 %. The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles in each bin. The bin widths were set such that there were an approximately 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.

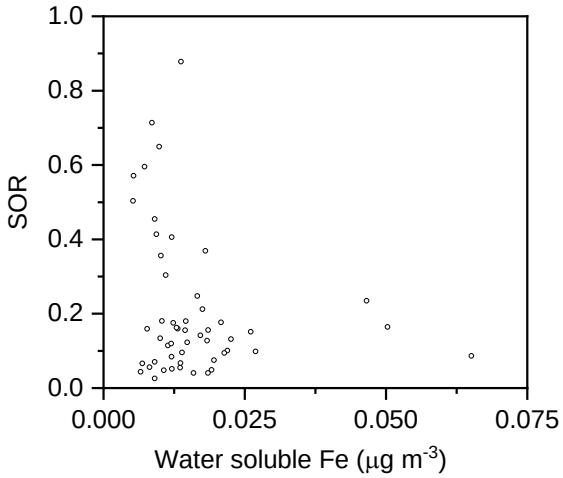


Figure S8. Plot of the SOR against water soluble Fe (54 samples selected every 6 days throughout the sampling period).

S2.3 Seasonal variations

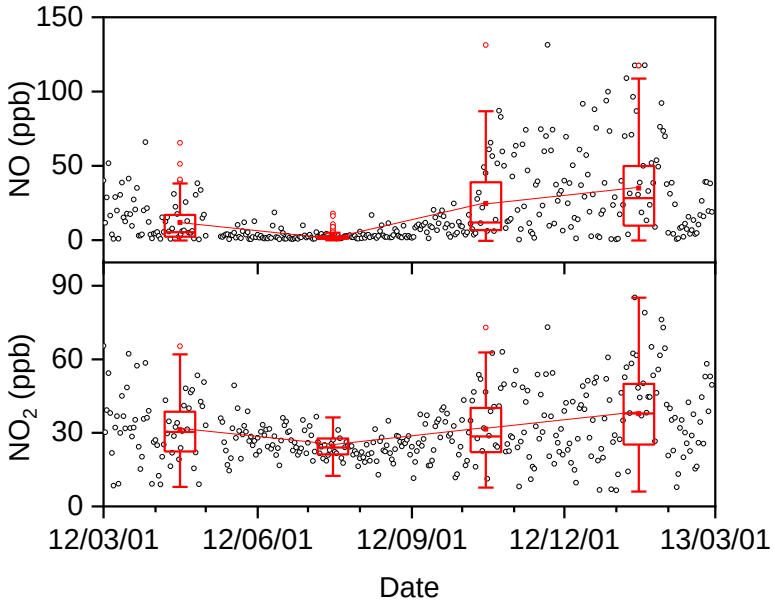


Figure S9. Time series of NO and NO_2 from March 1 2012 to February 28 2013 (open black circles). The boxes represent, from top to bottom, the 75th, 50th, and 25th percentiles for each season. The whiskers, solid red squares, and open red circles represent 1.5 times the IQR, seasonal mean values, and outlier data points, respectively.

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