A point-by-point response to the reviews

We are very thankful to two reviewers for your valuable comments and thoughtful suggestions. The followings are our responses to your comments. The comments of the reviewers are shown in black, our responses to the comments are presented in blue, and the new or modified texts are provided in blue in *italics*.

Response to Reviewer #1

Comment 1: This study investigates the pollution characteristics and formation mechanisms of sulfate and nitrate during the winter haze pollution periods in Beijing in 2016 based on the field observations, which is helpful for us to understand the winter haze formation in China and better control it. However, some discussions are confusing. This paper cannot be accepted before the authors have addressed the following comments.

Answer: Thank you for your pertinent evaluation of our work. The followings are our responses to your comments.

Comment 2: Line 257-258: The variation of NO_2 should be given in Figure 1, because the discussion in this study is based on NO_2, not NO_x. Are the concentrations of SO_2 a factor of 5 lower than the concentrations of NO_2? Based on Table 1, it's not true.

Answer: The time series of NO_x have been replaced with the variations of NO_2 in the revised Figure 1 (Figure R1). On the basis of Figure R1 and Table 1, the concentrations of SO_2 were about a factor of 5-6 lower than those of NO_x, but were approximately a factor of 3 lower than those of NO_2. This sentence has been changed in the revised manuscript as following:

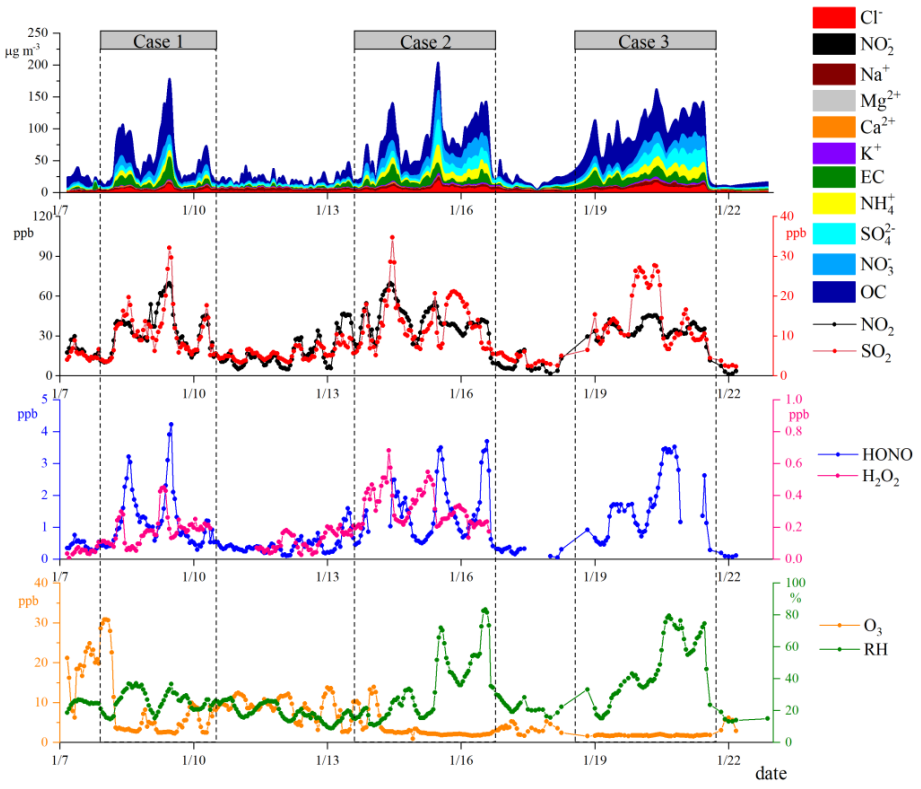


Figure R1. Time series of the species in $PM_{2.5}$ and typical gaseous pollutants (NO_2, SO_2, O_3, HONO and H_2O_2) as well as atmospheric RH during the sampling period.

"Although the concentrations of SO_2 were obviously lower than the concentrations of NO_2 in both Case 2 and Case 3 (Figure 1 and Table 1), ..."

Comment 3: Line 262: NOR is commonly defined as "NOR = NO_3^-/ (NO_3^-+NO_2)" in the previous studies. Why is "NOR = NO_3^-/ (NO_3^-+NO_x)" used in this study? We know that NO_x is usually much higher than NO_2, especially at night. Are the discussion and results different if you use "NOR = NO_3^-/ (NO_3^-+NO_2)" in this study? If you use "NOR = NO_3^-/ (NO_3^-+NO_2)", why do you use "NO_2 × O_3", "Dust × NO_2" and "HONO × DR × NO_2" in the following discussion, rather than "NO_x × O_3", "Dust × NO_x" and "HONO × DR × NO_x"?

Answer: We are very sorry for our incorrect writing of the NOR formula. In fact, "NOR = NO_3^-/ (NO_3^-+NO_2)" rather than "NOR = NO_3^-/ (NO_3^-+NO_x)" was used in this study. As NO concentration usually accounted for relatively high fraction to that of NO_x in winter of Beijing city, especially during the morning and evening rushing hours, NOR calculated based on NO_2 was obviously higher than that based on NO_x (Figure R2). Because atmospheric nitrate is formed through the oxidation of NO_2 via gas-phase, heterogeneous and aqueous-phase reactions, "NOR = NO_3^-/ (NO_3^-+NO_2)" might reflect nitrogen oxidation ratio more accurately than "NOR = NO_3^-/ (NO_3^-+NO_x)". The mistake has been corrected in the revised manuscript as following:

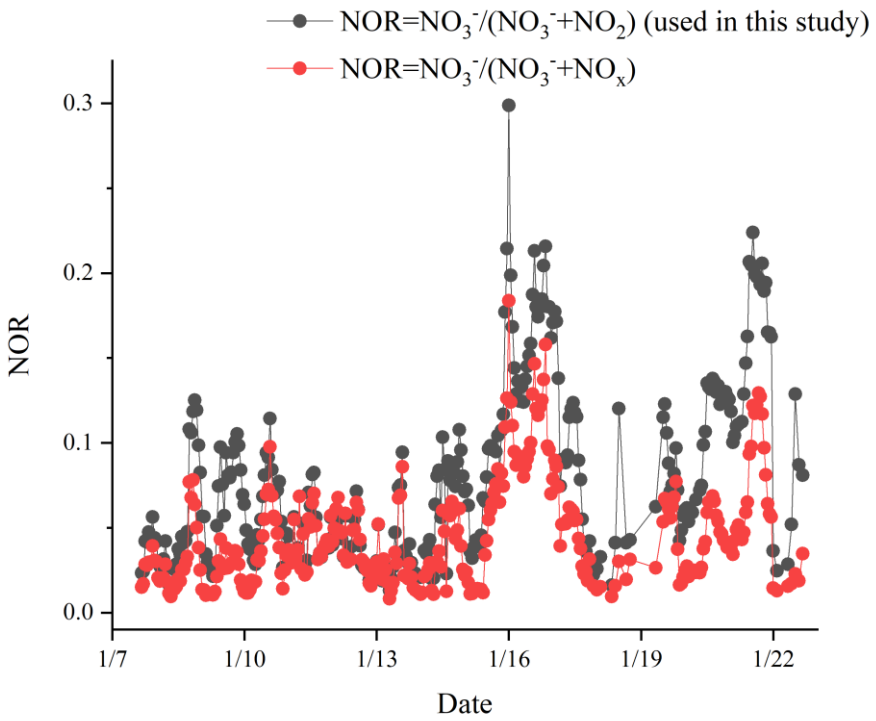


Figure R2. The comparison of the time series of NOR calculated based on NO_2 and NO_x during the sampling period.

"To further investigate the pollution characteristics of nitrate and sulfate during the serious pollution episodes, the relations between NOR (NOR = NO_3^- / (NO_3^-+NO_2)) as well as SOR (SOR = SO_4^{2-} / (SO_4^{2-}+SO_2)) and RH are shown in Figure 2."

Comment 4: Line 270-271: Why is the reduction of NOR due to the deliquescence of nitrate? Based on the reference you list, the deliquescence can change aerosol particle size distribution, but not decrease the nitrate concentration.

Answer: According to the Comment 4 from the Reviewer #2, the reduction of NOR might be ascribed to the suppressed heterogeneous reactions of NO_2 to nitrate formation under high RH condition (Tang et al., 2017). The heterogeneous reactions of NO_2 on particle surface have been found to be dependent on atmospheric RH due to the competition of water for surface reactive sites of particles (Ponczek et al., 2019), and thus relatively fast nitrate formation usually occurs when RH is below a certain value. This sentence has been rephrased in the revised manuscript as following:

"the variation trend of NOR slowly decreased whereas the variation trend of SOR significantly increased when atmospheric RH was above 60 %, which was very similar with the previous studies (Sun et al., 2013; Zheng et al., 2015b). Considering that the heterogeneous reactions of NO_2 on particle surface were dependent on atmospheric RH due to the competition of water for surface reactive sites of particles (Ponczek et al., 2019), the slow reduction of NOR might be due to the suppressed heterogeneous reaction of NO_2 to nitrate formation under high RH condition (Tang et al., 2017), while the elevation of SOR revealed the dominant contribution of the aqueous-phase reaction to sulfate formation."

Comment 5: Section 3.3.1: The discussion about the nitrate formation is not convincing and more analysis is needed.
(1) Line 295-299: Is the correlation analysis in Figure 3b proper to investigate the contribution of heterogeneous hydrolysis of N_2O_5? Why does a negative correlation exist between NOR and NO_2 × O_3 under the RH<60 % condition? It means that the heterogeneous hydrolysis of N_2O_5 is not important under the RH<60 % condition? If the authors use a similar figure with Figure 3b to analyze the correlation between NOR with Dust × NO_2 and HONO × DR × NO_2, what are the conclusion?

Answer: Considering that one molecule of N_2O_5 could be generated by two molecule of NO_2 reacting with one molecule of O_3, perhaps it's more proper to use the correlation between NOR and $[NO_2]^2$ × $[O_3]$ rather than $[NO_2]$ × $[O_3]$ for representing the contribution of the heterogeneous hydrolysis of N_2O_5 to atmospheric nitrate at night (the Comment 5 from the Reviewer #2). The correlations between NOR and $[NO_2]^2$ × $[O_3]$ at the nighttime (redefined as 18:00-7:00) under different RH conditions are shown in Figure R3. It's evident that the variations of $[NO_2]^2$ × $[O_3]$ were all positively correlated with NOR under the three different RH conditions, and their correlation under the RH ≥ 60% condition (R^2 = 0.552) was significantly stronger than those under the RH < 60% condition (R^2 ≤ 0.181). It has been acknowledged that the correlation between two species means the impact of changes in one species on another. The stronger the correlation is, the greater the impact is. Therefore, the positive correlations between NOR and $[NO_2]^2$ × $[O_3]$ indicated

that the heterogeneous hydrolysis of N_2O_5 could contribute to the formation of atmospheric nitrate at the nighttime under different RH conditions. The significantly stronger correlations between NOR and $[NO_2]^2 \times [O_3]$ under the RH ≥ 60% condition than under the RH < 60% condition revealed that the heterogeneous hydrolysis of N_2O_5 made a remarkable contribution to atmospheric nitrate at the nighttime under high RH condition. Additionally, the obviously lower slope of the correlation between NOR and $[NO_2]^2 \times [O_3]$ under the RH ≥ 60% condition (slope = 11691) than under the RH < 60% condition (slope ≥ 17399) also suggested that the formation of atmospheric nitrate at the nighttime under high RH condition was more sensitive to the pathway of N_2O_5. These sentences have been modified in the revised manuscript as stated above.

It should be noted that the correlations between NOR and $[NO_2]^2 \times [O_3]$ under the three different RH conditions were analyzed for verifying under which RH condition the heterogeneous hydrolysis of N_2O_5 made a remarkable contribution to atmospheric nitrate at the nighttime, while the daily variations of $[Dust] \times [NO_2]$ and $[HONO] \times [DR] \times [NO_2]$ under the 30% < RH < 60% condition were compared for exploring which reaction could play an important role in atmospheric nitrate at the daytime under moderate RH condition. Therefore, it may be lack of the purpose to analyze the correlations between NOR and $[Dust] \times [NO_2]$ as well as $[HONO] \times [DR] \times [NO_2]$ by using the similar method of Figure R3.

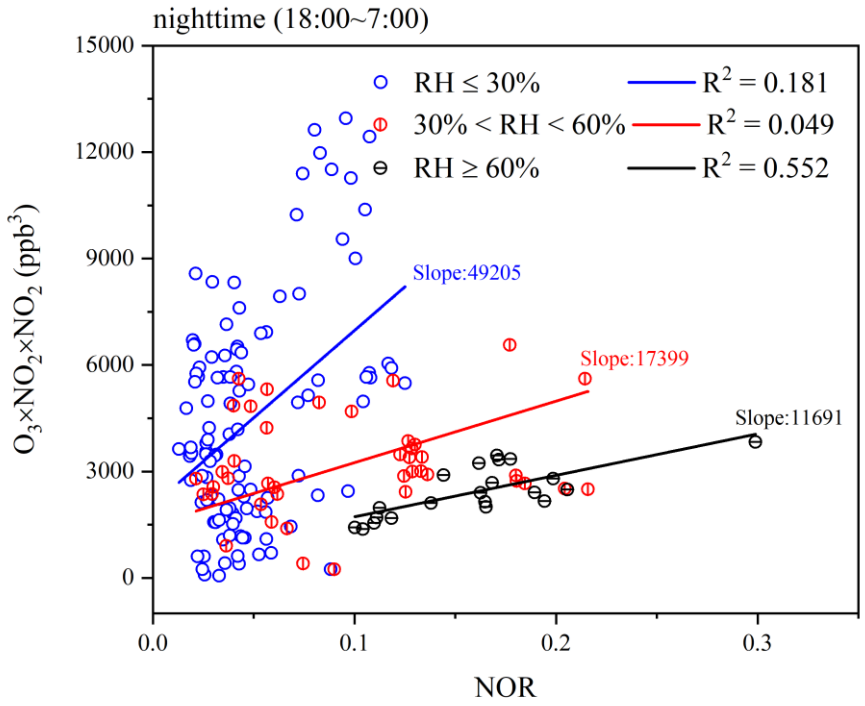


Figure R3. The correlations between NOR and $[NO_2]^2 \times [O_3]$ at the nighttime under different RH conditions.

(2) Figure 3a: Why does NOR decrease obviously during 0:00-4:00 under the RH>60 % condition?

Answer: As mentioned above, the heterogeneous hydrolysis of N_2O_5 was found to make a remarkable contribution to atmospheric nitrate at the nighttime under the RH ≥ 60% condition due

to the strong correlation between NOR and $[NO_2]^2 \times [O_3]$. Thus, the obvious reduction of the NOR values during 0:00-3:00 under the RH ≥ 60% condition was mainly ascribed to the decrease in the concentration levels of $[NO_2]^2 \times [O_3]$ (Figure R4).

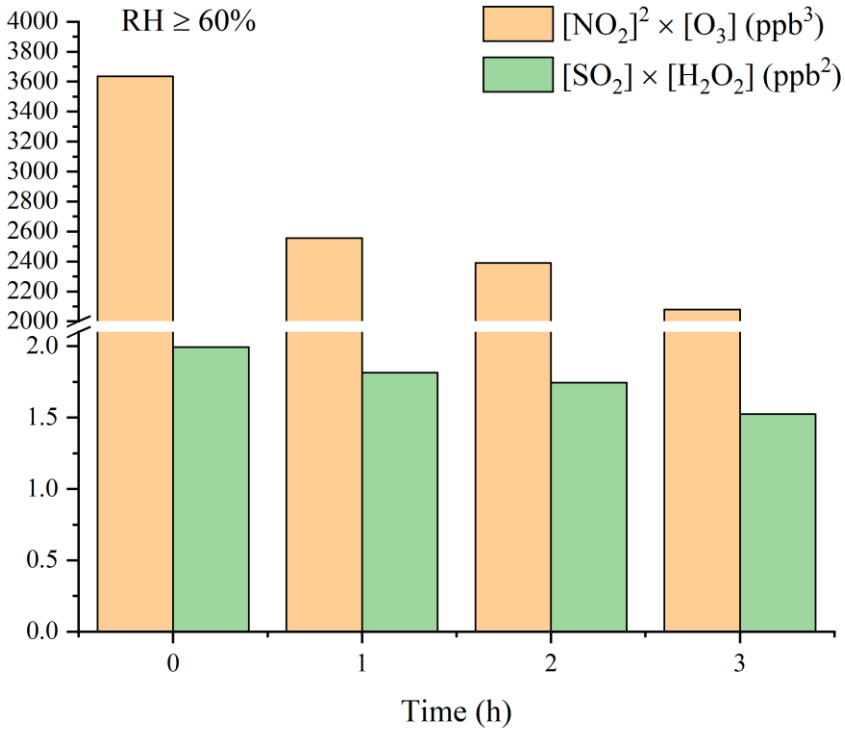


Figure R4. The variations of $[NO_2]^2 \times [O_3]$ and $[SO_2] \times [H_2O_2]$ during 0:00-3:00 under the RH ≥ 60% condition during the sampling period.

(3) Line 296-297: why is the nighttime defined as 19:00-6:00? Seeing from Figure 3d, DR is nearly zero during 18:00-7:00.

Answer: Thank you for your suggestion. The nighttime has been redefined as 18:00-7:00 and the associated figures have been changed in the revised manuscript.

(4) Line 300-302: A similar NOR increase during the daytime can be seen under the RH>60 % condition in Figure 3a. Why are the hourly variations of Dust × NO_2 and HONO × DR × NO_2 under the RH>60 % condition not included in Figure 3c-d. Seeing from the abstract (Line 27-30) and conclusion part (Line 365-368), the authors seem to conclude the gas-phase reaction of NO_2 with OH plays a key role just under moderate RH conditions. How about under the RH>60 % or RH<30 % condition?

Answer: The relatively high atmospheric RH (RH > 60%) usually occurred at the nighttime during the sampling period (Figure R4), and hence it was difficult by using [HONO] × [DR] × $[NO_2]$ to conclude whether the gas-phase reaction of NO_2 with OH played a key role under the RH > 60% condition. Furthermore, because the NOR values under the RH ≤ 30% condition were almost less

than 0.1 (Figure 2 in the revised manuscript) which reflected no occurrence of secondary formation of nitrate (Gao et al., 2011; Zhang et al., 2018), it might be not necessary to discuss the formation of nitrate under the RH ≤ 30% condition.

Comment 6: Section 3.3.2:

(1) Line 325-328: Why is the heterogeneous reaction of SO_2 on the surface of mineral aerosols not important before 14:00?

Answer: Atmospheric sulfate has been reported to come mainly from primary source emissions when the SOR is less than 0.1 (Gao et al., 2011; Zhang et al., 2018). Considering that the mean values of SOR before 14:00 both under the 30% < RH < 60% and RH ≤ 30% conditions were almost close to 0.1, secondary formation of SO_2 including the gas-phase reaction and heterogeneous reaction could be ignored before 14:00. To avoid possible confusing understanding for readers, this sentence has been rephrased in the revised manuscript as following:

"As shown in Figure 4, similar to the daily variations of NOR, the mean values of SOR were found to elevated remarkably under the 30%<RH<60% condition compared to the RH≤30% condition, especially during 14:00-22:00, which might be mainly ascribed to the enhanced gas-phase reaction and the heterogeneous reaction of SO_2 involving aerosol liquid water under the relatively high RH condition."

(2) Figure 4: Why does SOR decrease obviously during 0:00-4:00 under the RH>60 % condition?

Answer: Because the oxidation of SO_2 through the aqueous-phase reaction of H_2O_2 was found to contribute mainly to sulfate formation under the high RH condition, the depletion of the oxidant and the precursor ($[SO_2] \times [H_2O_2]$) during 0:00-3:00 was suspected to result in the obvious decrease of SOR under the RH ≥ 60% condition (Figure R4).

(3) Figure 4: Under 30 %<RH<60 %, why is the SOR during 13:00-23:00 much higher than that in other hours? We know that RH is commonly high at night, for example during 0:00-5:00.

Answer: Yes. atmospheric RH is indeed a key factor for influencing sulfate formation and commonly high at night. Except for atmospheric RH, the concentrations of the precursors such as SO_2 could also play a vital role in the formation of sulfate, and then affected SOR value. Therefore, the much higher mean values of SOR during 13:00-23:00 than those in other hours might be mainly attributed to the relatively high concentrations of SO_2 during 13:00-23:00 under 30 %<RH<60 % condition (Figure R5).

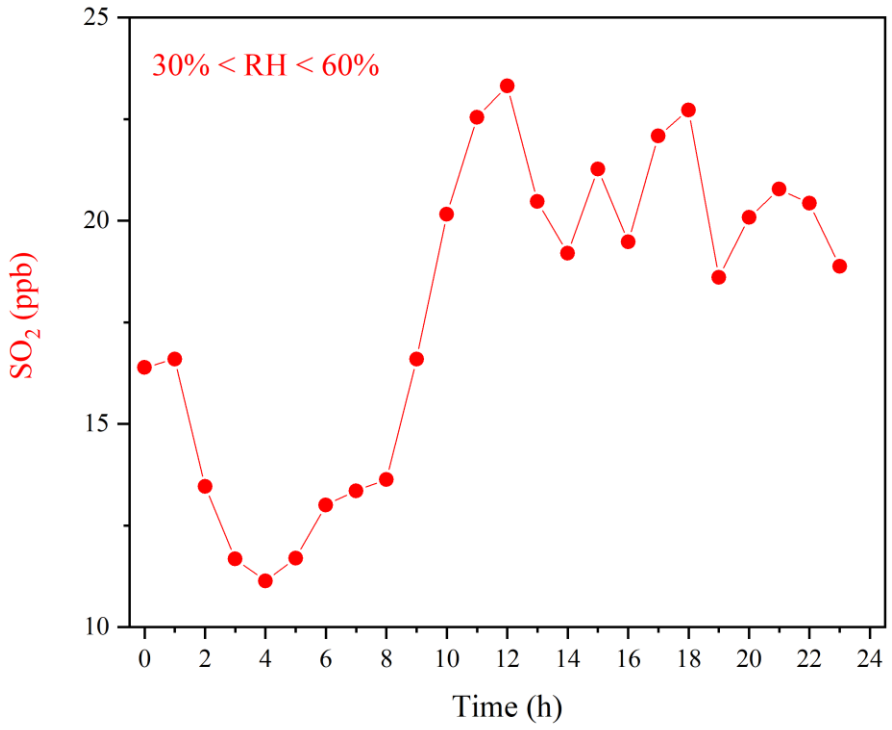


Figure R5. The daily variation of SO_2 under the 30% < RH <60% condition during the sampling period

Response to Reviewer #2

Comment 1: This study focused on the formation mechanisms of nitrate and sulfate in Beijing, especially the different mechanisms under various RH conditions. The heterogeneous hydrolysis of N_2O_5 was responsible for the nocturnal formation of nitrate at extremely high RH levels (RH>60 %), while homogeneous reaction between NO_2 and OH radical dominated the formation under moderate condition (30 %<RH<60 %). For SO_4^{2-}, aqueous reaction between SO_2 and H_2O_2 attributed to its formation under high RH condition. The target of this study is meaningful to understanding the formation mechanism of nitrate and sulfate in real atmosphere. There are several questions not very clear.

Answer: Thank you for your valuable evaluation of our work. The followings are our responses to your comments.

Comment 2: Please give a brief description of NOR and SOR in abstract.

Answer: the NOR and SOR formulas have been added in the revised abstract.

Comment 3: Did NOR and SOR represent the secondary formation of NO_3^- and SO_4^{2-}, respectively? Actually, when NO_x and SO_2 reached zero, the value of NOR and SOR were closed to the maximum. If NOR and SOR represent the secondary formation of NO_3^- and SO_4^{2-}, secondary formation of NO_3^-

and SO_4^{2-} showed up with low concentration of NO_x and SO_2. This result is confusing.

Answer: NOR (NOR = NO_3^-/ (NO_3^-+NO_2)) and SOR (SOR = SO_4^{2-}/ (SO_4^{2-}+SO_2)) didn't represent the secondary formation of NO_3^- and SO_4^{2-}, but could reflect their formation potentials to a certain degree due to the ratios counteracted the air diffusion effect on their concentrations, and thus NOR and SOR have been widely used to estimate the secondary formation of NO_3^- and SO_4^{2-}, respectively (Zheng et al., 2015). Yes, the NOR and SOR would be close to the maximal values if NO_2 and SO_2 reached zero. Actually, NO_2 and SO_2 are ubiquitous trace gases in the atmosphere, it is impossible that their concentrations reached zero. The values of NOR and SOR mainly depend on the conversion efficiencies of NO_2 and SO_2 to nitrate and sulfate through various atmospheric chemical reactions, rather than the concentrations of NO_2 and SO_2, because the concentrations of NO_2, SO_2, nitrate and sulfate usually have the similar variation trends which are mainly governed by meteorological conditions and boundary layer heights as well.

Comment 4: The authors mentioned that "The reduction of NOR might be due to the deliquescence of nitrate at atmospheric RH around 60 %" at line 270-271. However, the deliquescence of nitrate would not reduce the nitrate in particle but change its phase state. RH has been validated to affect the heterogeneous reaction of NO_x and HONO, which may result in the reduction of nitrate at high RH condition.

Answer: Thank you for your valuable comment. According to your suggestion, this sentence has been rephrased in the revised manuscript as following:

"the variation trend of NOR slowly decreased whereas the variation trend of SOR significantly increased when atmospheric RH was above 60 %, which was very similar with the previous studies (Sun et al., 2013; Zheng et al., 2015b). Considering that the heterogeneous reactions of NO_2 on particle surface were dependent on atmospheric RH due to the competition of water for surface reactive sites of particles (Ponczek et al., 2019), the slow reduction of NOR might be due to the suppressed heterogeneous reaction of NO_2 to nitrate formation under high RH condition (Tang et al., 2017), while the elevation of SOR revealed the dominant contribution of the aqueous-phase reaction to sulfate formation."

Comment 5: One N_2O_5 could be generated by two NO_2 reacting with one O_3. Hence, is it more suitable to use $[NO_2]^2 \times [O_3]$ rather than $[NO_2] \times [O_3]$ for representing the heterogeneous hydrolysis of N_2O_5 to atmospheric nitrate at night?

Answer: Thank you for your valuable suggestion. Relevant figure (Figure R3) and sentences have been modified accordingly in the revised manuscript as following:

"…Therefore, the correlation between $[NO_2]^2 \times [O_3]$ and NOR can represent roughly the contribution of the heterogeneous hydrolysis of N_2O_5 to atmospheric nitrate at night…"

Comment 6: Though HONO is a main source OH, the diurnal variation of HONO may be different from OH radical. Have the author ever analyzed the correlation between DR × NO_2 and NOR?

Because the diurnal variation of OH radical should be highly correctly with radiation.

Answer: Because the photolysis of atmospheric HONO has been considered as the dominant OH source in polluted areas (Wang et al., 2017), the nitrate formation rate through the gas-phase reaction of NO_2 with OH radicals could be reflected by the product of [HONO] × [DR] × [NO_2]. The evident difference for the diurnal variations between the products of [HONO] × [DR] × [NO_2] and [DR] × [NO_2] implied that the relatively high HONO concentrations in the morning under the 30% < RH 60% condition played a significant role in nitrate formation (Figure R6), which was in line with the variations of NOR (Figure 3 in the revised manuscript). Therefore, it may be more proper to use [HONO] × [DR] × [NO_2] rather than [DR] × [NO_2] for representing the gas-phase reaction of NO_2 with OH.

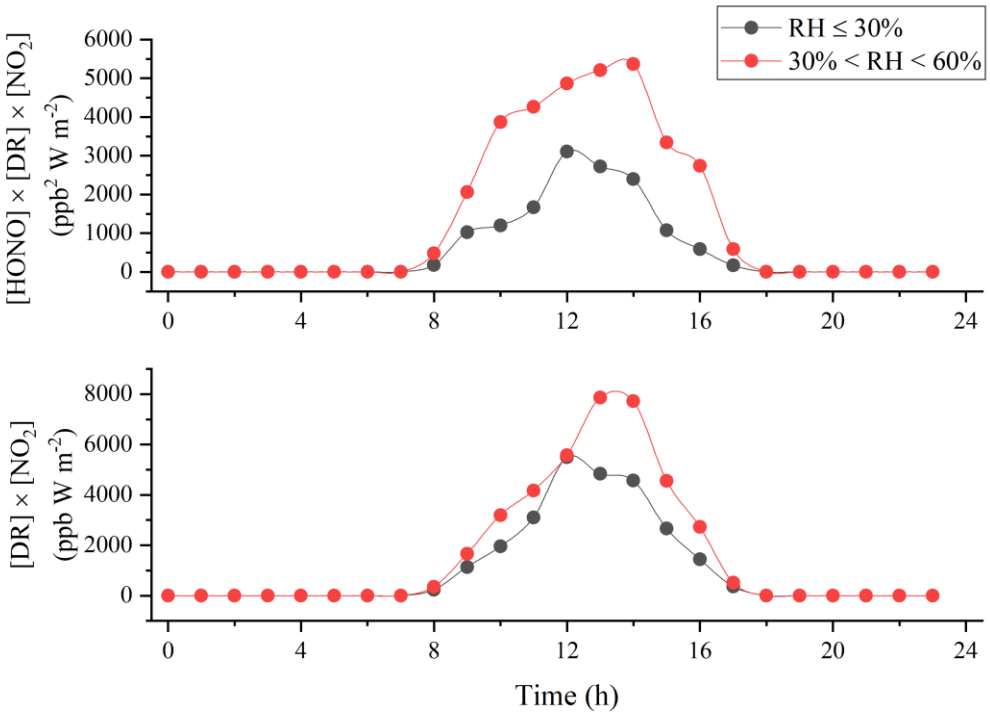


Figure R6. The comparison of the daily variations of [HONO] × [DR] × [NO_2] and [DR] × [NO_2] under the RH ≤ 30% condition and under the 30% < RH < 60% condition during the sampling period.

References

Gao, X., Yang, L., Cheng, S., Gao, R., Zhou, Y., Xue, L., Shou, Y., Wang, J., Wang, X., Nie, W., Xu, P., and Wang, W.: Semi-continuous measurement of water-soluble ions in PM2.5 in Jinan, China: Temporal variations and source apportionments, Atmospheric Environment, 45, 6048-6056, 10.1016/j.atmosenv.2011.07.041, 2011.

Ponczek, M., Hayeck, N., Emmelin, C., and George, C.: Heterogeneous photochemistry of dicarboxylic acids on mineral dust, Atmospheric Environment, 212, 262-271, 10.1016/j.atmosenv.2019.05.032, 2019.

Tang, M., Huang, X., Lu, K., Ge, M., Li, Y., Cheng, P., Zhu, T., Ding, A., Zhang, Y., Gligorovski, S., Song, W., Ding, X., Bi, X., and Wang, X.: Heterogeneous reactions of mineral dust aerosol:

implications for tropospheric oxidation capacity, Atmospheric Chemistry and Physics, 17, 11727-11777, 10.5194/acp-17-11727-2017, 2017.
Wang, J., Zhang, X., Guo, J., Wang, Z., and Zhang, M.: Observation of nitrous acid (HONO) in Beijing, China: Seasonal variation, nocturnal formation and daytime budget, The Science of the total environment, 587-588, 350-359, 10.1016/j.scitotenv.2017.02.159, 2017.
Zhang, R., Sun, X., Shi, A., Huang, Y., Yan, J., Nie, T., Yan, X., and Li, X.: Secondary inorganic aerosols formation during haze episodes at an urban site in Beijing, China, Atmospheric Environment, 177, 275-282, 10.1016/j.atmosenv.2017.12.031, 2018.
Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmospheric Chemistry and Physics, 15, 2969-2983, 10.5194/acp-15-2969-2015, 2015.

A list of all relevant changes made in the manuscript

Based on the valuable comments and suggestions of the two reviewers, the followings are a list of all relevant changes made in the revised manuscript.

1. A brief description of NOR and SOR formulas has been added in abstract, and the NOR formula (NOR = NO_3^-/ (NO_3^-+NO_2)" rather than "NOR = NO_3^-/ (NO_3^-+NO_x)) has been corrected in our revised manuscript.
2. Solid evidences about the contribution of the heterogeneous hydrolysis of N_2O_5 to the nocturnal formation of nitrate under the relatively high RH condition (the correlations and slopes between NOR and $[NO_2]^2 \times [O_3]$) have been added in our revised manuscript.
3. The reason (the suppressed heterogeneous of NO_2 rather than the deliquescence of nitrate) about the slow decrease of NOR under the RH ≥ 60% condition has been modified in our revised manuscript.
4. Figure 1 and Figure 3 have been amended for supporting the results and discussion in the manuscript.
5. the writing of the concentrations of species has been normalized by using square brackets in our revised manuscript.
6. Some logical and grammatical mistakes have been corrected in our revised manuscript.
7. Several references have been inserted to confirm our points in our revised manuscript.

Formation mechanisms of atmospheric nitrate and sulfate during the winter haze pollution periods in Beijing: gas-phase, heterogeneous and aqueous-phase chemistry

Pengfei Liu[1, 2, 3, 5], **Can Ye**[1, 3], **Chaoyang Xue**[1, 3], **Chenglong Zhang**[1, 2, 3], **Yujing Mu**[1, 2, 3, 4], **Xu Sun**[1, 6]

[1] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.
[2] Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China.
[3] University of Chinese Academy of Sciences, Beijing, 100049, China.
[4] National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing, 100049, China.
[5] Key Laboratory of Atmospheric Chemistry, China Meteorological Administration, Beijing, 100081, China.
[6] Beijing Urban Ecosystem Research Station, Beijing, 100085, China.
Correspondence: Yujing Mu (yjmu@rcees.ac.cn)

Abstract

A vast area in China is currently going through severe haze episodes with drastically elevated concentrations of $PM_{2.5}$ in winter. Nitrate and sulfate are main constituents of $PM_{2.5}$ but their formations via NO_2 and SO_2 oxidation are still not comprehensively understood, especially under different pollution or atmospheric relative humidity (RH) conditions. To elucidate formation pathways of nitrate and sulfate in different polluted cases, hourly samples of $PM_{2.5}$ were collected continuously in Beijing during the wintertime of 2016. Three serious pollution cases were identified reasonably during the sampling period and the secondary formations of nitrate and sulfate were found to make a dominant contribution to atmospheric $PM_{2.5}$ under the relatively high RH condition. The significant correlation between NOR (NOR = $NO_3^-/(NO_3^-+NO_2)$) and $[NO_2]^2 \times [O_3]$ during the nighttime under the RH≥60% condition indicated that the heterogeneous hydrolysis of N_2O_5 involving aerosol liquid water was responsible for the nocturnal formation of nitrate at the extremely high RH levels. The more coincident trend of NOR and [HONO] × [DR] (direct radiation) × $[NO_2]$

than [Dust] × [NO_2]~~Dust × NO_2~~ during the daytime under the 30%<RH<60% condition provided convincing evidence that the gas-phase reaction of NO_2 with OH played a pivotal role in the diurnal formation of nitrate at moderate RH levels. The extremely high mean values of SOR (SOR = SO_4^{2-} / (SO_4^{2-}+SO_2)) during the whole day under the RH≥60% condition could be ascribed to the evident contribution of SO_2 aqueous-phase oxidation to the formation of sulfate during the severe pollution episodes. Based on the parameters measured in this study and the known sulfate production rate calculation method, the oxidation pathway of H_2O_2 rather than NO_2 was found to contribute greatly to the aqueous-phase formation of sulfate.

1. Introduction

In recent years, severe haze has occurred frequently in Beijing as well as the North China Plain (NCP) during the wintertime, which has aroused great attention from the public due to its adverse impact on atmospheric visibility, air quality and human health (Chan and Yao, 2008;Zhang et al., 2012;Zhang et al., 2015).

To mitigate the severe haze pollution situations, a series of regulatory measures for primary pollution sources have been implemented by the Chinese government. For example, coal combustion for heating in winter has gradually been replaced with electricity and natural gas in the NCP, coal-fired power plants have been strictly required to install flue-gas denitration and desulfurization systems (Chen et al., 2014), the stricter control measures such as terminating production in industries and construction as well as the odd and even number rule for vehicles have been performed in megacities during the period of the red alert for haze and so on. These actions have made tremendous effects to decline pollution levels of primary pollutants including $PM_{2.5}$ (fine particulate matter with an aerodynamic diameter less than 2.5 μm) in recent years (Li et al., 2019).

However, the serious pollution events still occurred in many areas of Beijing-Tianjin-Hebei (BTH) region in December 2016 and January 2017 (Li et al., 2019). It has been acknowledged that the severe haze pollution is mainly ascribed to stagnant meteorological conditions with high atmospheric relative humidity (RH) and low mixed boundary layer height, strong emissions of primary gaseous pollutants and rapid formation of secondary inorganic aerosols (SIAs, the sum of sulfate, nitrate and ammonium), especially sulfate and nitrate (Cheng et al., 2016;Guo et al., 2014;Huang et al., 2014). Some studies suggested that the contribution of SIAs to $PM_{2.5}$ was higher than 50% during the most serious haze days (Quan et al., 2014;Xu et al., 2017;Zheng et al., 2015a).

Generally, atmospheric sulfate and nitrate are formed through the oxidations of the precursor gases (SO_2 and NO_2) by oxidants (e.g. OH radical, O_3) via gas-phase, heterogeneous and aqueous-phase reactions (Ravishankara, 1997;Wang et al., 2013;Yang et al., 2015). It should be noted that the recent study proposed the remarkable emissions of primary sulfate from residential coal combustion with the sulfur contents of coal in range of 0.81-1.88% in Xi'an (Dai et al., 2019), but the primary emissions of sulfate could be neglected due to the extremely low sulfur content of coal (0.26-0.34%) used prevailingly in the NCP (Du et al., 2016;Li et al., 2016). Atmospheric RH is a key factor that facilitates the SIAs formation and aggravates the haze pollution (Wu et al., 2019), and hence the secondary formations of sulfate and nitrate are simply considered to be mainly via gas-phase reaction at relatively low atmospheric RH levels (RH<30%) and heterogeneous reactions and aqueous-phase reactions at relatively high atmospheric RH levels (RH>60%) (Li et al., 2017). However, their formation mechanisms at different atmospheric RH levels still remain controversial and unclear (Cheng et al., 2016;Ge et al., 2017;Guo et al., 2017;Li et al., 2018;Liu et al., 2017a;Wang et al., 2016;Yang et al., 2017). For example, the recent studies proposed that atmospheric SO_2

oxidation by NO_2 dissolved in aqueous aerosol phases under the extremely high atmospheric RH conditions played a dominant role in sulfate formation under almost neutral aerosol solutions (a pH range of 5.4-7.0) during the serious pollution periods (Cheng et al., 2016;Wang et al., 2018a;Wang et al., 2016). However, Liu et al. (2017a) and Guo et al. (2017) found that the aerosol pH estimated by ISORROPIA-II model was moderately acidic (a pH range of 3.0-4.9) and thus the pathway of SO_2 aqueous-phase oxidation by dissolved NO_2 was unimportant during severe haze events in China. Additionally, although the pathway of N_2O_5 heterogeneous hydrolysis has been recognized as being responsible for the nocturnal formation of NO_3^- under relatively high atmospheric RH conditions (Tham et al., 2018;Wang et al., 2018b;Wang et al., 2018c), the effects of NO_2 gas-phase chemistry and NO_2 heterogeneous chemistry on the diurnal formation of NO_3^- under moderate atmospheric RH conditions (30%<RH<60%) have not yet been understood. Therefore, measurements of the species in $PM_{2.5}$ in different polluted cases during the wintertime are urgently needed to elucidate formation pathways of sulfate and nitrate.

In this study, hourly filter samples of $PM_{2.5}$ were collected continuously in Beijing during the wintertime of 2016, and the pollution characteristics and formation mechanisms of sulfate and nitrate in the $PM_{2.5}$ samples were investigated comprehensively under different atmospheric RH conditions in relation to gas-phase, heterogeneous and aqueous-phase chemistry.

2. Materials and Methods

2.1. Sampling and analysis

The sampling site was chosen on the rooftop (around 25 m above the ground) of a six-story building in Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (RCEES, CAS), which was located in the northwest of Beijing and had been described in detail by

403 our previous studies (Liu et al., 2016a;Liu et al., 2017b). The location of the sampling site
404 (40°00′29.85″ N, 116°20′29.71″ E) is presented in Figure S1. Hourly $PM_{2.5}$ samples were collected
405 on prebaked quartz fiber filters (90mm, Munktell) from January 7th to 23th of 2016 by median-
406 volume samplers (Laoying-2030) with a flow rate of 100 L min^{-1}. Water-soluble ions (WSI),
407 including Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, NO_2^-, NO_3^- and SO_4^{2-}, as well as carbon components
408 including organic carbon (OC) and element carbon (EC) in the filter samples were analyzed by ion
409 chromatography (Wayeal IC6200) and thermal optical carbon analyzer (DRI-2001A), respectively
410 (Liu et al., 2017b). Analysis relevant for quality assurance & quality control (QA/QC) was presented
411 in detail in section M1 of the Supplementary Information (SIs). Atmospheric H_2O_2 and HONO were
412 monitored by AL2021-H_2O_2 monitor (AERO laser, Germany) and a set of double-wall glass
413 stripping coil sampler coupled with ion chromatography (SC-IC), respectively (Ye et al., 2018;Xue
414 et al., 2019a;Xue et al., 2019b). More details about the measurements of H_2O_2 and HONO were
415 ascribed in section M2 of the SIs. Meteorological data, including wind speed, wind direction,
416 ambient temperature and RH, as well as air quality index (AQI) derived by $PM_{2.5}$, SO_2, NO_x, CO
417 and O_3 were obtained from Beijing urban ecosystem research station in RCEES, CAS
418 (http://www.bjurban.rcees.cas.cn/).

419 **2.2. Aerosol liquid water contents and pH prediction by ISORROPIA-II model**

420 The ISORROPIA-II model was employed to calculate the equilibrium composition for Na^+-
421 K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Cl^--NO_3^--SO_4^{2-}-H_2O aerosol system, which is widely used in regional and
422 global atmospheric models and has been successfully applied in numerous studies for predicting the
423 physical state and composition of atmospheric inorganic aerosols (Fountoukis and Nenes, 2007;Guo
424 et al., 2015;Shi et al., 2017). It can be used in two modes: forward mode and reverse mode. Forward

mode calculates the equilibrium partitioning given the total concentrations of gas and aerosol species, whereas reverse mode involves predicting the thermodynamic compositions based only on the concentrations of aerosol components. Forward mode was adopted in this study because reverse mode calculations have been verified to be not suitable to characterize aerosol acidity (Guo et al., 2015;Hennigan et al., 2015;Murphy et al., 2017;Pathak et al., 2004;Weber et al., 2016). The ISORROPIA-II model is available in "metastable" or "solid + liquid" state solutions. Considering the relatively high RH during the sampling period, the metastable state solution was selected in this study due to its better performance than the latter (Bougiatioti et al., 2016;Guo et al., 2015;Liu et al., 2017a;Weber et al., 2016). Additionally, although the gaseous HNO_3, H_2SO_4, HCl and NH_3 were not measured in this study, gas-phase input with the exception of NH_3 has an insignificant impact on the aerosol liquid water contents (ALWC) and pH calculation due to the lower concentrations of HNO_3, H_2SO_4 and HCl than NH_3 in the atmosphere (Ding et al., 2019;Guo et al., 2017). Based on the long-term measurement in the winter of Beijing, an empirical equation between NO_x and NH_3 concentrations was derived from the previous study (Meng et al., 2011), that is, NH_3 (ppb) = 0.34 × NO_x (ppb) + 0.63, which was employed for estimating the NH_3 concentration in this study. The predicted daily average concentrations of NH_3 varied from 3.3 μg m^{-3} to 36.9 μg m^{-3}, with a mean value of 16.6 μg m^{-3} and a median value of 14.6 μg m^{-3}, which were in line with those (7.6-38.1 μg m^{-3}, 18.2 μg m^{-3} and 16.2 μg m^{-3} for the daily average concentrations, the mean value and the median value of NH_3, respectively) during the winter of 2013 in Beijing in the previous study (Zhao et al., 2016).

Then, the aerosol pH could be calculated by the following equation:

$$pH = -log_{10}\frac{1000\times H^+}{W}$$

where H^+ (μg m^{-3}) and W (μg m^{-3}) are the equilibrium particle hydrogen ion concentration and aerosol water contents, respectively, both of which could be output from ISORROPIA-II.

2.3. Production of sulfate in aqueous-phase reactions

The previous studies showed that there were six pathways of the aqueous-phase oxidation of SO_2 to the production of sulfate, i.e. H_2O_2 oxidation, O_3 oxidation, NO_2 oxidation, transition metal ions (TMI) + O_2 oxidation, methyl hydrogen peroxide (MHP) oxidation and peroxyacetic acid (PAA) oxidation (Cheng et al., 2016;Zheng et al., 2015a). Because some TMIs, such as Ti(III), V(III), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II), displayed much less catalytic activities (Cheng et al., 2016), only Fe(III) and Mn(II) were considered in this study. In addition, due to the extremely low concentrations of MHP and PAA in the atmosphere, their contributions to the production of sulfate could be ignored (Zheng et al., 2015a). To investigate the formation mechanism of sulfate during the serious pollution episodes, the contributions of O_3, H_2O_2, NO_2 and Fe(III) + Mn(II) to the production of sulfate in aqueous-phase reactions were calculated by the formulas as follows (Cheng et al., 2016;Ibusuki and Takeuchi, 1987;Seinfeld and Pandis, 2006):

$$-(\frac{d[S(IV)]}{dt})_{O_3} = (k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_{3(aq)}] \quad \text{(R1)}$$

$$-(\frac{d[S(IV)]}{dt})_{H_2O_2} = \frac{k_3[H^+][HSO_3^-][H_2O_{2(aq)}]}{1+K[H^+]} \quad \text{(R2)}$$

$$-(\frac{d[S(IV)]}{dt})_{Fe(III)+Mn(II)} = k_4[H^+]^a[Mn(II)][Fe(III)][S(IV)] \quad \text{(R3)}$$

$$-(\frac{d[S(IV)]}{dt})_{NO_2} = k_5[NO_{2(aq)}][S(IV)] \quad \text{(R4)}$$

where $k_0 = 2.4\times10^4$ M^{-1} s^{-1}, $k_1 = 3.7\times10^5$ M^{-1} s^{-1}, $k_2 = 1.5\times10^9$ M^{-1} s^{-1}, $k_3 = 7.45\times10^7$ M^{-1} s^{-1}, K = 13 M^{-1}, $k_4 = 3.72\times10^7$ M^{-1} s^{-1}, a = -0.74 (pH≤4.2) or $k_4 = 2.51\times10^{13}$ M^{-1} s^{-1}, a = 0.67 (pH>4.2), and $k_5 = (1.24\text{-}1.67)\times10^7$ M^{-1} s^{-1} (5.3≤pH≤8.7, the linear interpolated values were used for pH between 5.3 and 8.7) at 298 K (Clifton et al., 1988); $[O_{3(aq)}]$, $[H_2O_{2(aq)}]$ and $[NO_{2(aq)}]$ could be calculated by

the Henry's constants which are 1.1×10^{-2} M atm^{-1}, 1.0×10^{5} M atm^{-1} and 1.0×10^{-2} M atm^{-1} at 298 K for O_3, H_2O_2 and NO_2 respectively (Seinfeld and Pandis, 2006). As for [Fe(III)] and [Mn(II)], their concentrations entirely depended on the values of pH due to the precipitation equilibriums of $Fe(OH)_3$ and $Mn(OH)_2$ (Graedel and Weschler, 1981). Considering the aqueous-phase ionization equilibrium of SO_2, the Henry's constants of HSO_3^-, SO_3^{2-} and S(IV) could be expressed by the equations as follows (Seinfeld and Pandis, 2006):

$$H^*_{HSO_3^-} = H_{SO_2}\frac{K_{S1}}{[H^+]} \quad \text{(R5)}$$

$$H^*_{SO_3^{2-}} = H_{SO_2}\frac{K_{S1}K_{S2}}{[H^+]^2} \quad \text{(R6)}$$

$$H^*_{S(IV)} = H_{SO_2}(1+\frac{K_{S1}}{[H^+]}+\frac{K_{S1}K_{S2}}{[H^+]^2}) \quad \text{(R7)}$$

where H_{SO2} = 1.23 M atm^{-1}, K_{S1} = 1.3×10^{-2} M and K_{S2} = 6.6×10^{-8} M at 298 K. In addition, all of rate constants (k), Henry's constants (H) and ionization constants (K) are evidently influenced on the ambient temperature and are calibrated by the formulas as follows (Seinfeld and Pandis, 2006):

$$k(T) = k(T_0)e^{[-\frac{E}{R}(\frac{1}{T}-\frac{1}{T_0})]} \quad \text{(R8)}$$

$$H(T) = H(T_0)e^{[-\frac{\Delta H}{R}(\frac{1}{T}-\frac{1}{T_0})]} \quad \text{(R9)}$$

$$K(T) = K(T_0)e^{[-\frac{E}{R}(\frac{1}{T}-\frac{1}{T_0})]} \quad \text{(R10)}$$

where T is the ambient temperature, T_0=298 K, both E/R and ΔH/R varied in the different equations and their values could be found in Cheng et al., (2016).

Furthermore, mass transport was also considered for multiphase reactions in different medium and across the interface in section M3 of the SIs.

3. Results and Discussion

3.1. Variation characteristics of the species in $PM_{2.5}$ and typical gaseous pollutants

The concentrations of the species in $PM_{2.5}$ and typical gaseous pollutants including ~~NO_x~~NO_2,

491 SO_2, O_3, HONO and H_2O_2 as well as atmospheric RH are shown in Figure 1. The meteorological
492 parameters (wind speed, wind direction, ambient temperature and direct radiation (DR)) as well as
493 the concentrations of $PM_{2.5}$ are displayed in Figure S2. During the sampling period, the
494 concentrations of the species in $PM_{2.5}$ and typical gaseous pollutants varied similarly on a timescale
495 of hours with a distinct periodic cycle of 3-4 days, suggesting that meteorological conditions played
496 a vital role in accumulation and dispersion of atmospheric pollutants (Xu et al., 2011;Zheng et al.,
497 2015b). For example, the relatively high levels of $PM_{2.5}$ (>100 μg m^{-3}) usually occurred under the
498 relatively stable meteorological conditions with the low south wind speed (<2 m s^{-1}) and the high
499 RH (>60%) which favored the accumulation of pollutants. Besides meteorological conditions, the
500 extremely high concentrations of the species in $PM_{2.5}$ might be mainly ascribed to strong emissions
501 of primary pollutants and rapid formation of secondary aerosols during the wintertime in Beijing.
502 The average concentrations of the species in $PM_{2.5}$ and typical gaseous pollutants during clean
503 or slightly polluted (C&SP) episodes ($PM_{2.5}$<75 μg m^{-3}), during polluted or heavy polluted (P&HP)
504 episodes ($PM_{2.5}$≥75 μg m^{-3}) and during the whole sampling period are illustrated in Table 1. It is
505 evident that the average concentrations of NO_3^-, SO_4^{2-}, NH_4^+, OC and EC during P&HP episodes
506 were about a factor of 5.0, 4.1, 6.1, 3.6 and 3.2 greater than those during C&SP episodes,
507 respectively, indicating that the formations of SIAs were more efficient compared to other species
508 in $PM_{2.5}$ during the serious pollution episodes. Given that the average concentrations of gaseous
509 precursors (NO_2 and SO_2) during P&HP episodes were approximately a factor of 2.0-2.2 greater
510 than those during C&SP episodes, the obviously higher elevation of NO_3^- and SO_4^{2-} implied that the
511 oxidations of NO_2 and SO_2 by the major atmospheric oxidizing agents (OH radicals, O_3 and H_2O_2
512 etc.) might be greatly accelerated due to the relatively high concentrations of oxidants and

atmospheric RH during the serious pollution episodes (Figure 1). The average concentration of H_2O_2 was found to be a factor of 1.7 greater during P&HP episodes than during C&SP episodes, indicating that atmospheric H_2O_2 might contribute to the formation of SIAs especially sulfate during the serious pollution episodes with high atmospheric RH, which will be discussed in Sect. 3.3.2. However, the obvious decrease in O_3 average concentration was observed during P&HP episodes compared to C&SP episodes, which was mainly attributed to the relatively weak solar radiation and the titration of NO during the serious pollution episodes (Ye et al., 2018). In addition, the evidently higher average concentration of HONO during P&HP episodes than during C&SP episodes might be also due to the relatively weak solar radiation as well as the heterogeneous reaction of NO_2 on particle surfaces during the serious pollution episodes (Tong et al., 2016;Wang et al., 2017).

3.2. Three serious pollution cases during the sampling period

Based on the transition from the clean to polluted periods, three haze cases were identified during the sampling period (Figure 1 and Figure S2): from 13:00 on January 8th to 1:00 on January 11th (Case 1), from 14:00 on January 14th to 7:00 on January 17th (Case 2), and from 8:00 on January 19th to 2:00 on January 22nd (Case 3). The serious pollution duration in the three cases could last 1-3 days due to the differences of their formation mechanisms.

In Case 1, the variation trends of the concentrations of the species in $PM_{2.5}$, ~~NO_x~~NO_2, SO_2, HONO and H_2O_2 were almost identical and exhibited three pollution peaks at night (Figure 1), which might be ascribed to the possibility that the decrease of nocturnal mixed boundary layer accelerated the pollutant accumulation (Bei et al., 2017;Zhong et al., 2019). Considering the relatively low RH (15-40%) and wind speeds (<2 m s^{-1}) in Case 1 (Figure S2), primary emissions around the sampling site were suspected to be a dominant source for the increase in the $PM_{2.5}$

concentrations. Further evidence is that the correlation between the concentrations of $PM_{2.5}$ and CO is better in Case 1 (R^2=0.55) than in Case 2 and Case 3 (R^2=0.20~0.52) (Figure S3). Identical to Case 1, three obvious pollution peaks were also observed in Case 2 (Figure 1). The variation trends of the concentrations of the species in $PM_{2.5}$ and typical gaseous pollutants at the first peak in Case 2 were found to be similar with those in Case 1, which were mainly attributed to their similar formation mechanism. However, the evident decreases in NO_x and SO_2 were observed when the concentrations of the species in $PM_{2.5}$ were increasing and the atmospheric oxidation pollutant (e.g. H_2O_2) concentration peaks were prior to others at the last two peaks in Case 2, suggesting that secondary formation from gaseous precursors might be dominant for $PM_{2.5}$ pollution. The relatively high RH (50-80%) and the low south wind speeds (<2 m s^{-1}) in Case 2 (Figure S2) provided further evidence for the above speculation. In contrast to Case 1 and Case 2, the relatively high south wind speeds (>3 m s^{-1}) (Figure S2) with the concentrations of the species in $PM_{2.5}$ and typical gaseous pollutants increasing slowly (Figure 1) at the beginning of Case 3 indicated that regional transportation might be responsible for the atmospheric species. Subsequently, the concentrations of the species in $PM_{2.5}$ remained relatively high when the atmospheric RH lasted more than 60%, implying that secondary formation from gaseous precursors dominated $PM_{2.5}$ pollution during the late period of Case 3.

The average mass proportions of the species in $PM_{2.5}$ in the three cases are illustrated in Figure S4, the proportions of the primary species such as EC (10-13%), Cl^- (6-7%) and Na^+ (4%) in the three cases were almost identical, indicating that primary particle emissions were relatively stable during the sampling period. However, the proportions of SIA in Case 2 (42%) and Case 3 (38%) were conspicuously greater than that in Case 1 (28%), further confirming that secondary formation

of inorganic ions (e.g. nitrate, sulfate) made a significant contribution to atmospheric $PM_{2.5}$ in Case 2 and Case 3.

3.3. Formation mechanism of nitrate and sulfate during serious pollution episodes

As for nitrate and sulfate in the three cases, the highest mass proportion (18%) of nitrate was observed in Case 2, whereas the highest mass proportion (15%) of sulfate was found in Case 3 (Figure S4). Although the concentrations of SO_2 were ~~about a factor of 5~~ obviously lower than the concentrations of NO_2 in both Case 2 and Case 3 (Figure 1 and Table 1), the extremely high proportion of sulfate in Case 3 might be ascribed to the long-lasting plateau of RH (Figure S2) because the aqueous-phase reaction could accelerate the conversion of SO_2 to SO_4^{2-}. To further investigate the pollution characteristics of nitrate and sulfate during the serious pollution episodes, the relations between NOR (NOR = NO_3^- / (NO_3^-+NO_x)) as well as SOR (SOR = SO_4^{2-} / (SO_4^{2-} +SO_2)) and RH are shown in Figure 2. There were obvious differences in the variations of NOR and SOR under different atmospheric RH conditions. The variation trends of NOR and SOR almost stayed the same when atmospheric RH was below 30%, and then simultaneously increased with atmospheric RH in the range of 30-60%. The enhanced gas-phase reaction and the heterogeneous reaction involving aerosol liquid water might make a remarkable contribution to the elevation of NOR and SOR, respectively, which were further discussed in the following section. Subsequently, the variation trend of NOR slowly decreased whereas the variation trend of SOR significantly increased when atmospheric RH was above 60%, which was very similar with the previous studies (Sun et al., 2013;Zheng et al., 2015b). Considering that the heterogeneous reactions of NO_2 on particle surface were dependent on atmospheric RH due to the competition of water for surface reactive sites of particles (Ponczek et al., 2019), t~~T~~he slow reduction of NOR might be due to the

suppressed heterogeneous reaction of NO_2 to nitrate formation ~~deliquescence of nitrate at atmospheric~~ under high RH condition ~~around 60 %~~ (Tang et al., 2017)~~(Kuang et al., 2016;Liu et al., 2016b;Xue et al., 2014)~~, while the elevation of SOR revealed the dominant contribution of the aqueous-phase reaction to ~~the~~ sulfate formation ~~of sulfate~~.

3.3.1. Formation mechanism of nitrate

Atmospheric nitrate is considered to be mainly from NO_2 oxidation by OH radical in the gas phase, heterogeneous uptake of NO_2 on the surface of particles and heterogeneous hydrolysis of N_2O_5 on wet aerosols or chloride-containing aerosols (He et al., 2014;He et al., 2018;Nie et al., 2014;Ravishankara, 1997;Wang et al., 2018b). Since atmospheric N_2O_5 is usually produced by the reaction of NO_3 radical with NO_2 as well as both NO_3 radical and N_2O_5 are easily photolytic during the daytime, the heterogeneous hydrolysis of N_2O_5 is a nighttime pathway for the formation of atmospheric nitrate (He et al., 2018;Wang et al., 2018b). As shown in Figure 3a, the mean values of NOR during the nighttime remarkably elevated with atmospheric RH increasing, the disproportionation of NO_2 and the heterogeneous hydrolysis of N_2O_5 involving aerosol liquid water were suspected to dominate the nocturnal formation of nitrate under high RH conditions during the sampling period (Ma et al., 2017;Wang et al., 2018b;Li et al., 2018). However, the productions of HONO and nitrate should be equal through the disproportionation of NO_2 (Ma et al., 2017), which could not explain the wide gaps between the average concentrations of HONO (about 6.5 μg m^{-3}) and nitrate (about 20.1 μg m^{-3}) observed at the nighttime under high RH conditions during the sampling period. Thus, the disproportionation of NO_2 made insignificant contribution to the nocturnal formation of nitrate under high RH conditions. Considering that the formation of atmospheric NO_3 radical is mainly via the oxidation of NO_2 by O_3, the heterogeneous hydrolysis of

N_2O_5 occurs only at high O_3 and NO_2 levels during the nighttime (He et al., 2018;Wang et al., 2018b). Therefore, the correlation between $[NO_2]^2 \times [O_3]$ and NOR can represent roughly the contribution of the heterogeneous hydrolysis of N_2O_5 to atmospheric nitrate at night. As shown in Figure 3b, the variations of $[NO_2]^2 \times [O_3]$ at the nighttime (18:00-7:00) were all positively correlated with NOR under the three different RH conditions, and their correlation under the RH ≥ 60% condition (R^2 = 0.552) was significantly stronger than those under the RH < 60% condition ($R^2 \leq 0.181$). It has been acknowledged that the correlation between two species means the impact of changes in one species on another. The stronger the correlation is, the greater the impact is. Therefore, the positive correlations between NOR and $[NO_2]^2 \times [O_3]$ indicated that the heterogeneous hydrolysis of N_2O_5 could contribute to the formation of atmospheric nitrate at the nighttime under different RH conditions. The significantly stronger correlations between NOR and $[NO_2]^2 \times [O_3]$ under the RH ≥ 60% condition than under the RH < 60% condition revealed that the heterogeneous hydrolysis of N_2O_5 made a remarkable contribution to atmospheric nitrate at the nighttime under high RH condition. Additionally, the obviously lower slope of the correlation between NOR and $[NO_2]^2 \times [O_3]$ under the RH ≥ 60% condition (slope = 11691) than under the RH < 60% condition (slope ≥ 17399) (Figure 3b) also suggested that the formation of atmospheric nitrate at the nighttime under high RH condition was more sensitive to the pathway of N_2O_5.~~the more significant correlation between $NO_2 \times O_3$ and NOR under the RH≥60% condition (R^2=0.534) than under the RH<60% condition (R^2<0.005) at the nighttime (19:00-6:00) during the sampling period further confirmed that the heterogeneous hydrolysis of N_2O_5 on wet aerosols made a great contribution to atmospheric nocturnal nitrate under high RH conditions.~~

However, the obvious increase in the mean values of NOR during the daytime (especially for

623 10:00-17:00) under the 30%<RH<60% condition (Figure 3a) indicated that additional sources rather
624 than the heterogeneous hydrolysis of N_2O_5 were responsible for the formation of nitrate. To explore
625 the possible formation mechanisms of nitrate in this case, the daily variations of [Dust] (the sum of
626 Ca^{2+} and Mg^{2+}) × [NO_2] and [HONO] (the main source of OH) × [DR] × [NO_2], which can represent
627 roughly the heterogeneous reaction of NO_2 on the surface of mineral aerosols and the gas-phase
628 reaction of NO_2 with OH, are shown in Figure 3c and Figure 3d, respectively. The mean values of
629 [HONO] × [DR] × [NO_2]~~HONO × DR × NO_2~~ during the daytime were found to be remarkably
630 greater under the 30%<RH<60% condition than under the RH≤30% condition, whereas the mean
631 values of [Dust] × [NO_2]~~Dust × NO_2~~ almost stayed the same under the two different RH conditions.
632 Considering the coincident trend of NOR and [HONO] × [DR] × [NO_2]~~HONO × DR × NO_2~~ during
633 the daytime (10:00-17:00) under the 30%<RH<60% condition, the gas-phase reaction of NO_2 with
634 OH played a key role in the diurnal formation of nitrate at moderate RH levels with the haze
635 pollution accumulating. It should be noted that the mean values of [HONO] × [DR] × [NO_2]~~HONO~~
636 ~~× DR × NO_2~~ decreased dramatically from 14:00 to 17:00 (Figure 3d), which was not responsible for
637 the high mean values of NOR at that time (Figure 3a). However, the slight increase in the mean
638 values of [Dust] × [NO_2]~~Dust × NO_2~~ after 14:00 was observed under the 30%<RH<60% condition
639 (Figure 3c) and hence the heterogeneous reaction of NO_2 on the surface of mineral aerosols was
640 suspected to contribute to the diurnal formation of nitrate at that time under moderate RH condition.

641 **3.3.2. Formation mechanism of sulfate**

642 Atmospheric sulfate is principally from SO_2 oxidation pathway, including gas-phase reactions
643 with OH radical or stabilized Criegee intermediates, heterogeneous-phase reactions on the surface
644 of particles and aqueous-phase reactions with dissolved O_3, NO_2, H_2O_2 and organic peroxides, as

well as autoxidation catalyzed by TMI (Cheng et al., 2016;Li et al., 2018;Ravishankara, 1997;Shao et al., 2019;Wang et al., 2016;Xue et al., 2016;Zhang et al., 2018). As shown in Figure 4, similar to the daily variations of NOR, ~~the remarkable elevation of~~ the mean values of SOR were found to elevated remarkably ~~after 14:00~~ under the 30%<RH<60% condition compared to the RH≤30% condition, especially during 14:00-22:00, which might be ~~also~~ mainly ascribed to the enhanced gas-phase reaction and the heterogeneous reaction of SO_2 involving aerosol liquid water~~on the surface of mineral aerosols~~ under the relatively high RH condition. The extremely high mean values of SOR during the whole day under the RH≥60% condition implied that aqueous oxidation of SO_2 dominated the formation of sulfate during the severe pollution episodes, which was in line with previous studies (Zhang et al., 2018;Cheng et al., 2016). A key factor that influenced the aqueous oxidation pathways for sulfate formation has been considered to be the aerosol pH (Guo et al., 2017;Liu et al., 2017a), varying from 4.5 to 8.5 at different atmospheric RH and sulfate levels during the sampling period (Figure 5a) on the basis of the ISORROPIA-II model. Considering that the aqueous-phase chemistry of sulfate formation usually occurs in severe haze events with relatively high atmospheric RH, the aerosol pH (4.5-5.3) under the RH≥60% condition, which was lower than those (5.4-7.0) in the studies of Wang et al., (2016) and Cheng et al., (2016) but was slightly higher than those (3.0-4.9) in the studies of Liu et al., (2017a) and Guo et al., (2017), was adopted for evaluating sulfate production in this study. In addition, in terms of oxidants, the obvious increase in the average concentration of NO_2 (Figure 5b) and the evident decrease in the average concentration of O_3 (Figure 5d) were observed with the deterioration of $PM_{2.5}$ pollution. Furthermore, the average concentration of H_2O_2 was also found to be extremely high (0.25 ppb) under the HP condition (Figure 5c) and was above 1 order of magnitude higher than that (0.01 ppb) assumed by Cheng et

al., (2016), which probably resulted in the underestimation of the contribution of H_2O_2 to sulfate formation in the study of Cheng et al., (2016).

To further explore the contribution of H_2O_2 to sulfate production rate under the HP condition, the parameters measured in this study (Table 2) and the same approach that was adopted by Cheng et al., (2016) were used to calculate sulfate production. As shown in Figure 6, the relationships between different aqueous oxidation pathways and aerosol pH in this study were found to be very similar with those of Cheng et al., (2016). However, the contribution of H_2O_2 to sulfate production rate was about a factor of 17 faster in this study (about 1.16 μg m^{-3} h^{-1}) than in the study (about 6.95×10^{-2} μg m^{-3} h^{-1}) of Cheng et al., (2016), implying that the contribution of H_2O_2 to sulfate formation was largely neglected. Furthermore, considering the aerosol pH calculated under the HP condition during the sampling period, the oxidation pathway of NO_2 might play an insignificant role in sulfate production rate (8.96×10^{-2}-0.56 μg m^{-3} h^{-1}) and its importance proposed by the previous studies (1.74-10.85 μg m^{-3} h^{-1}) was not necessarily expected.

4. Conclusion

Based on the comprehensive analysis of the pollution levels, the variation characteristics and the formation mechanisms of the key species in $PM_{2.5}$ and the typical gaseous pollutants during the winter haze pollution periods in Beijing, three serious haze pollution cases were obtained during the sampling period and the SIAs formations especially nitrate and sulfate were found to make an evident contribution to atmospheric $PM_{2.5}$ under the relatively high RH condition. The significant correlation between $[NO_2]^2 \times [O_3]$ and NOR at night under the RH≥60% condition indicated that the heterogeneous hydrolysis of N_2O_5 on wet aerosols was responsible for the nocturnal formation of nitrate under extremely high RH conditions. The more coincident trend of NOR and [HONO] ×

[DR] × [NO_2]~~HONO × DR × NO_2~~ than [Dust] × [NO_2]~~Dust × NO_2~~ during the daytime under the 30%<RH<60% condition suggested that the gas-phase reaction of NO_2 with OH played a key role in the diurnal formation of nitrate under moderate RH conditions. The extremely high mean values of SOR during the whole day under the RH≥60% condition could be explained by the dominant contribution of aqueous-phase reaction of SO_2 to atmospheric sulfate formation during the severe pollution episodes. According to the parameters measured in this study and the same approach that was adopted by Cheng et al., (2016), the oxidation pathway of H_2O_2 rather than NO_2 was found to contribute greatly to atmospheric sulfate formation.

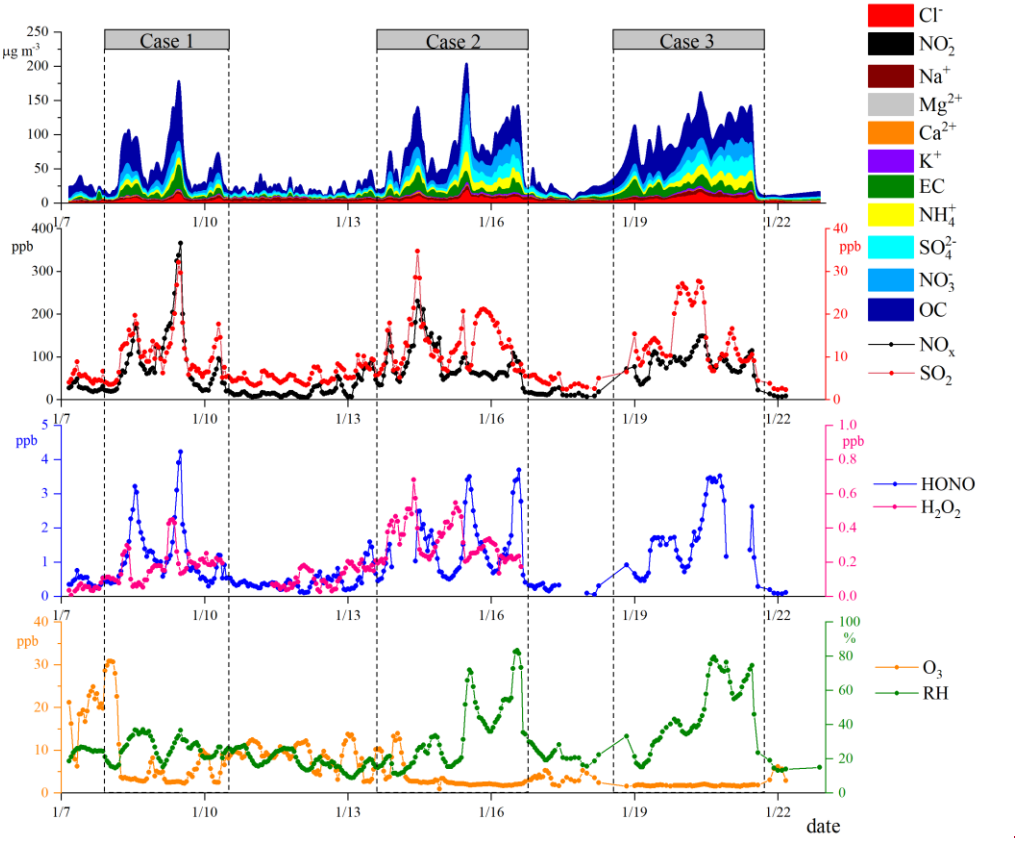
Our results revealed that the heavy pollution events in winter usually occurred with high concentration levels of pollutants and oxidants as well as high liquid water contents of moderately acidic aerosols in the NCP. Thus, emission controls of NO_x, SO_2 and VOCs especially under the extremely high RH conditions are expected to reduce largely the pollution levels of nitrate and sulfate in northern China and even in other pollution regions of China.

Data availability. Data are available from the corresponding author upon request (yjmu@rcees.ac.cn)

Author contributions. YJM designed the experiments. PFL carried out the experiments and prepared the manuscript. CY and CYX carried out the experiments. CLZ was involved in part of the work. XS provided the meteorological data and trace gases in Beijing.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgement. This work was supported by the National research program for Key issues in air pollution control (No. DQGG0103, DQGG0209, DQGG0206), the National Natural Science Foundation of China (No. 91544211, 4127805, 41575121, 21707151), the National Key Research and Development Program of China (No. 2016YFC0202200, 2017YFC0209703, 2017YFF0108301) and Key Laboratory of Atmospheric Chemistry, China Meteorological Administration (No. 2018B03).



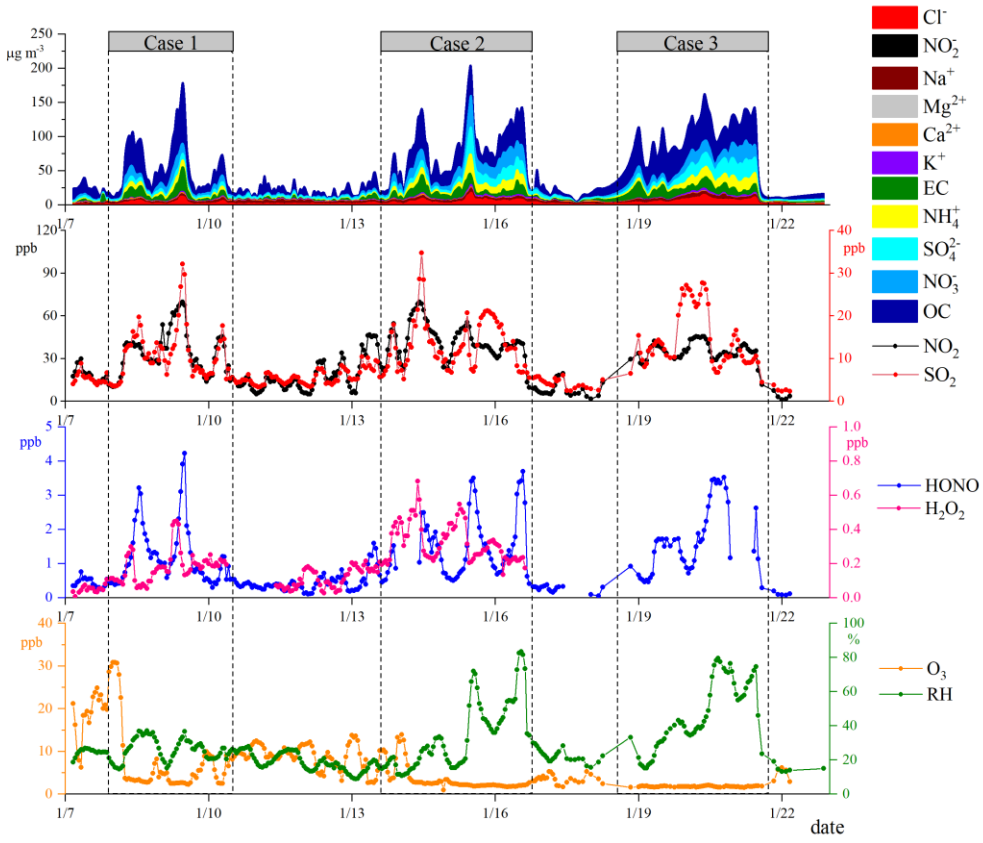


Figure 1. Time series of the species in $PM_{2.5}$ and typical gaseous pollutants (~~NO_x~~NO_2, SO_2, O_3, HONO and H_2O_2) as well as atmospheric RH during the sampling period.

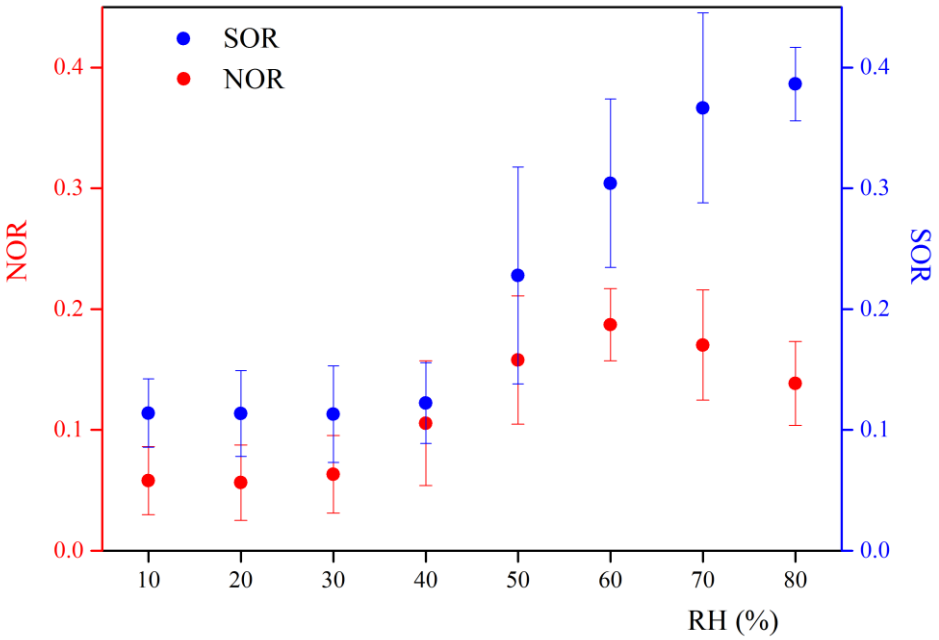
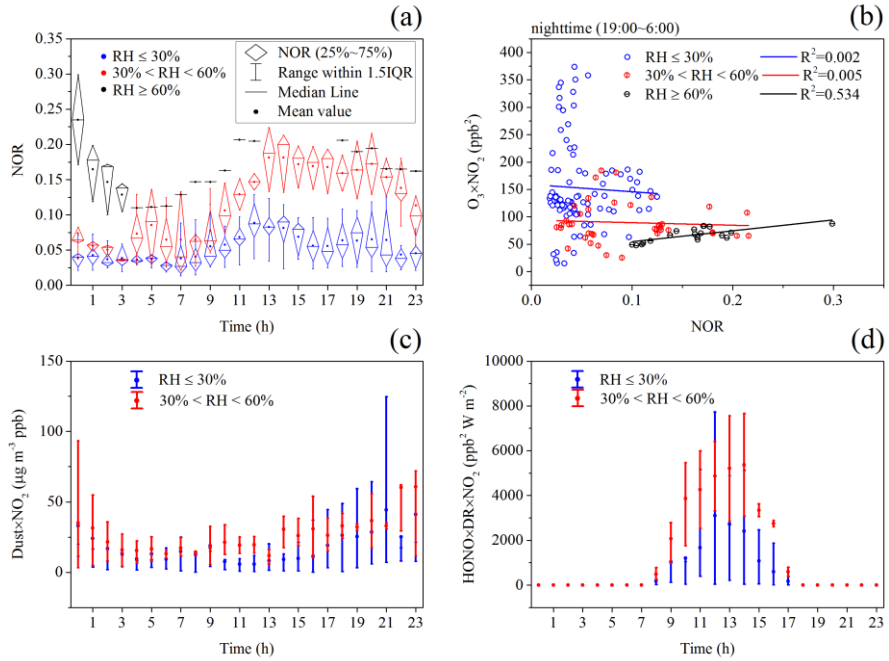


Figure 2. The relations between NOR as well as SOR and RH during the sampling period.



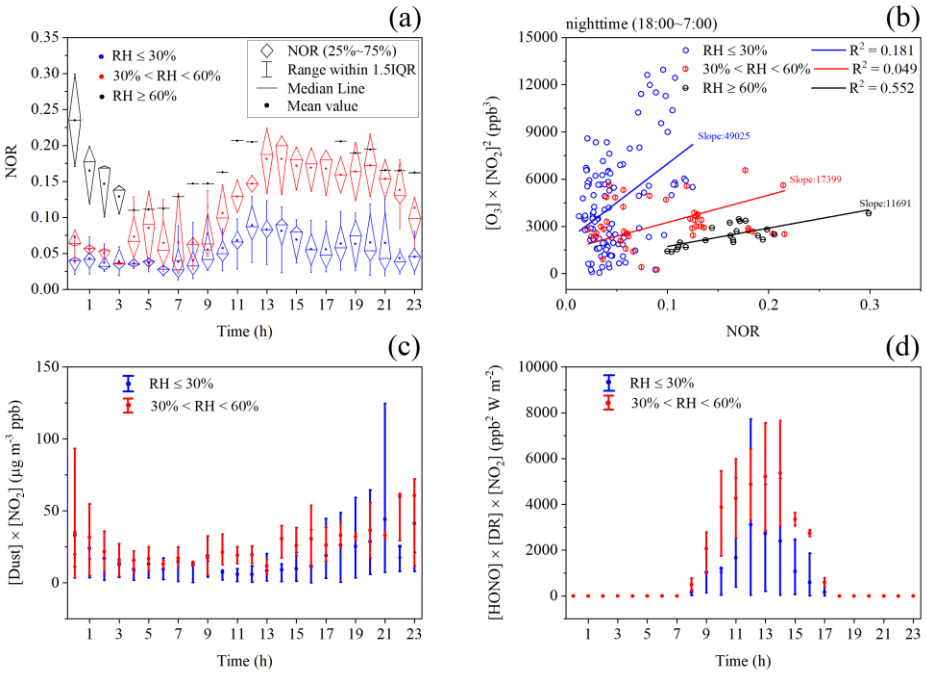


Figure 3. Daily variation of NOR (a), the correlation between NOR and $[NO_2]^2 \times [O_3]$~~$O_3 \times NO_2$~~ at the nighttime (18:00-7:00) (b), daily variations of [Dust] × [NO_2] and [HONO] × [DR] × [NO_2] (c, d) under different atmospheric RH conditions during the sampling period.

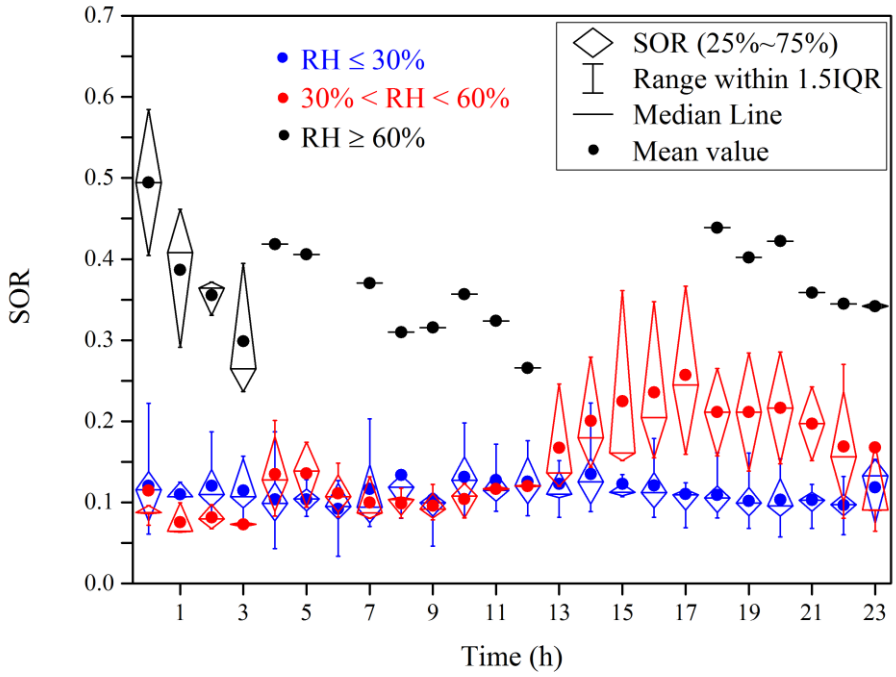


Figure 4. Daily variation of SOR under different atmospheric RH conditions during the sampling period.

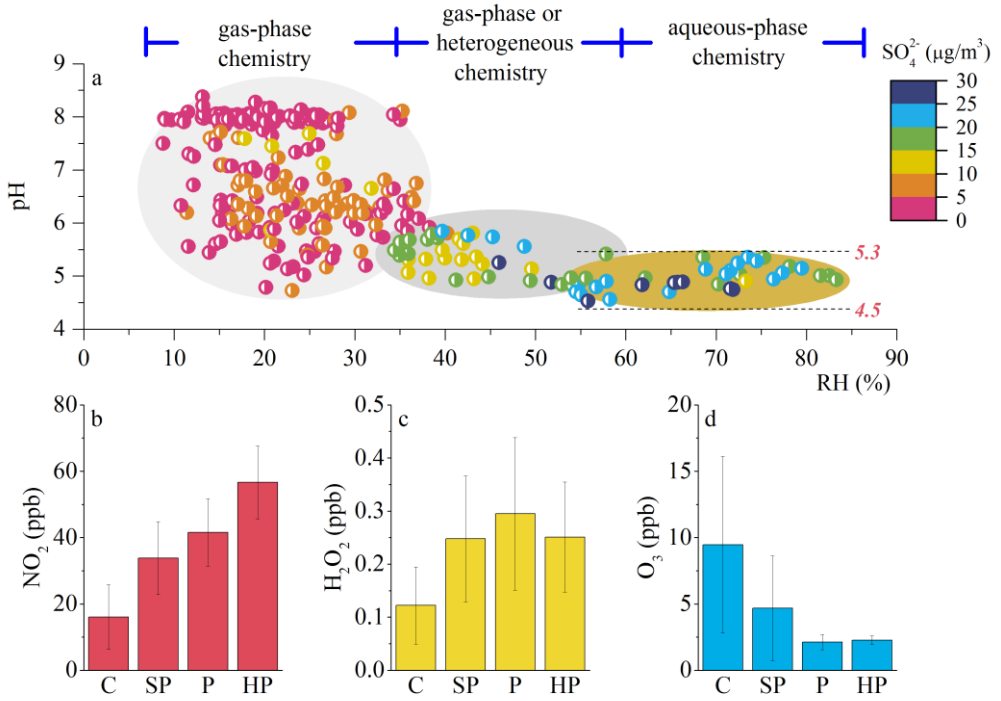


Figure 5. The correlations among aerosol pH, atmospheric RH and atmospheric SO_4^{2-} (a), the average concentrations of NO_2, H_2O_2 and O_3 (b, c, d) under different pollution conditions (clean (C), $PM_{2.5}$<35 μg m^{-3}; slightly polluted (SP), 35 μg m^{-3}<$PM_{2.5}$<75 μg m^{-3}; polluted (P), 75 μg m^{-}

^{3}<$PM_{2.5}$<150 μg m^{-3}; heavy polluted (HP), $PM_{2.5}$>150 μg m^{-3}) during the sampling period.

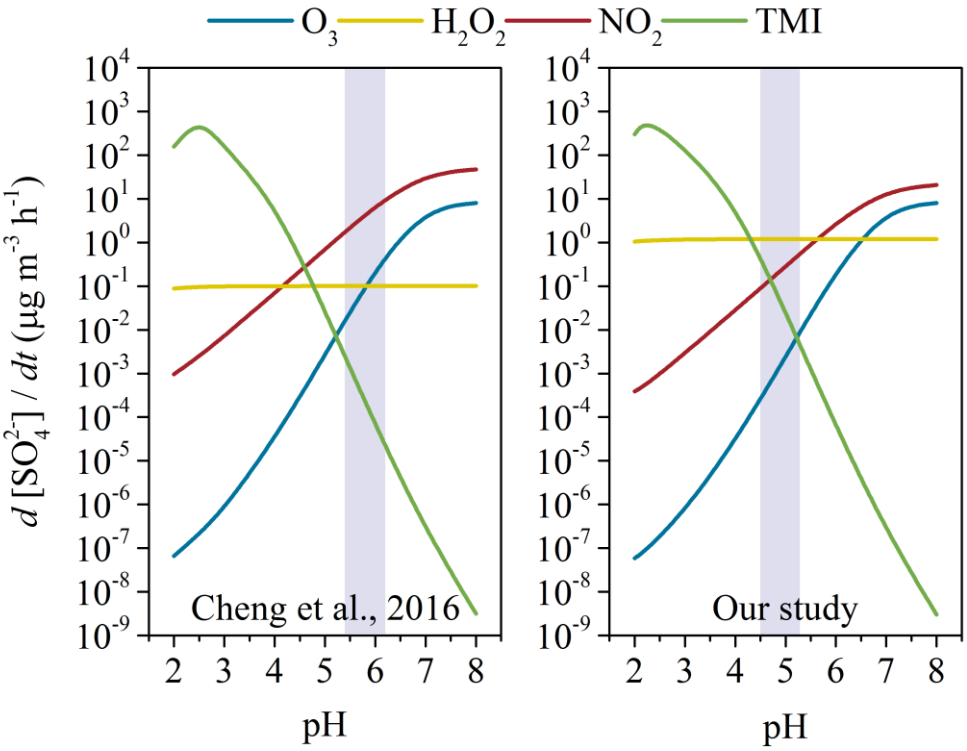


Figure 6. The comparison of aqueous-phase sulfate production by SO_2 oxidation under different aerosol pH conditions between in the study of Cheng et al., (2016) and in this study.

Table 1. The average concentrations of the species in $PM_{2.5}$ (μg m^{-3}) and typical gaseous pollutants (ppb) during C&SP episodes ($PM_{2.5}$<75 μg m^{-3}), during P&HP episodes ($PM_{2.5}$≥75 μg m^{-3}) and during the whole sampling period.

species	during C&SP episodes (n=210)	during P&HP episodes (n=108)	total (n=318)
$PM_{2.5}$	30.00 ± 17.79	113.35 ± 28.10	58.31 ± 45.15
Na^+	2.88 ± 1.11	3.68 ± 1.19	3.15 ± 1.21
Mg^{2+}	0.05 ± 0.03	0.08 ± 0.06	0.06 ± 0.04
Ca^{2+}	0.52 ± 0.33	0.67 ± 0.48	0.58 ± 0.40
K^+	0.81 ± 0.42	1.84 ± 0.73	1.16 ± 0.73
NH_4^+	1.90 ± 1.90	11.52 ± 4.93	5.17 ± 5.62
SO_4^{2-}	3.64 ± 1.87	14.96 ± 7.80	7.47 ± 7.18
NO_3^-	3.44 ± 3.57	17.15 ± 7.36	8.10 ± 8.32
Cl^-	1.89 ± 1.20	7.35 ± 2.97	3.73 ± 3.26
NO_2^-	0.06 ± 0.08	0.06 ± 0.05	0.06 ± 0.07
OC	12.10 ± 9.25	43.34 ± 13.88	22.73 ± 18.48
EC	3.98 ± 3.42	12.69 ± 6.43	7.58 ± 6.51
NO_x	39.38 ± 35.25	107.71 ± 58.44	62.59 ± 54.98
NO_2	21.46 ± 13.04	42.81 ± 10.96	28.71 ± 15.98
SO_2	6.99 ± 3.64	15.70 ± 6.55	9.95 ± 6.35

O_3	8.01 ± 6.35	2.13 ± 0.56	6.01 ± 5.87
HONO	0.60 ± 0.43	1.90 ± 0.97	1.01 ± 0.87
H_2O_2	0.17 ± 0.11	0.29 ± 0.14	0.20 ± 0.13

Table 2. The comparisons for parameters of sulfate production rate calculations between in the study of Cheng et al., (2016) and in this work during the most polluted haze periods

Parameters	This study	Cheng et al., (2016)
NO_2	57 ppb	66 ppb
H_2O_2	0.25 ppb	0.01 ppb
O_3	2 ppb	1 ppb
SO_2	35 ppb	40 ppb
Fe(III)[a]	18 ng m^{-3}	18 ng m^{-3}
Mn(II)[a]	42 ng m^{-3}	42 ng m^{-3}
ALWC	146 μg m^{-3}	300 μg m^{-3}
Aerosol droplet radius (R)[a]	0.15 μm	0.15 μm
Temperature	270 K	271 K
pH	4.5-5.3	5.4-6.2

[a]: both the concentrations of Fe(III) and Mn(II) and aerosol droplet radius were not measured in this study and were derived from Cheng et al., (2016).

References

Bei, N., Wu, J., Elser, M., Feng, T., Cao, J., El-Haddad, I., Li, X., Huang, R., Li, Z., Long, X., Xing, L., Zhao, S., Tie, X., Prévôt, A. S. H., and Li, G.: Impacts of meteorological uncertainties on the haze formation in Beijing–Tianjin–Hebei (BTH) during wintertime: a case study, Atmospheric Chemistry and Physics, 17, 14579-14591, 10.5194/acp-17-14579-2017, 2017.

Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., and Mihalopoulos, N.: Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability, Atmospheric Chemistry and Physics, 16, 4579-4591, 10.5194/acp-16-4579-2016, 2016.

Chan, C. K., and Yao, X.: Air pollution in mega cities in China, Atmospheric Environment, 42, 1-42, 10.1016/j.atmosenv.2007.09.003, 2008.

Chen, L. H., Sun, Y. Y., Wu, X. C., Zhang, Y. X., Zheng, C. H., Gao, X., and Cen, K.: Unit-based emission inventory and uncertainty assessment of coal-fired power plants, Atmospheric Environment, 99, 527-535, 10.1016/j.atmosenv.2014.10.023, 2014.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Science Advances, 2, 1-11, 10.1126/sciadv.1601530, 2016.

Clifton, C. L., Altstein, N., and Huie, R. E.: Rate-constant for the reaction of NO_2 with sulfur(IV) over the pH range 5.3-13, Environ. Sci. Technol., 22, 586-589, 10.1021/es00170a018, 1988.

Dai, Q., Bi, X., Song, W., Li, T., Liu, B., Ding, J., Xu, J., Song, C., Yang, N., Schulze, B. C., Zhang, Y., Feng, Y., and Hopke, P. K.: Residential coal combustion as a source of primary sulfate in Xi'an, China, Atmospheric Environment, 196, 66-76, 10.1016/j.atmosenv.2018.10.002, 2019.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing,

Atmospheric Chemistry and Physics, 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.
Du, Q., Zhang, C., Mu, Y., Cheng, Y., Zhang, Y., Liu, C., Song, M., Tian, D., Liu, P., Liu, J., Xue, C., and Ye, C.: An important missing source of atmospheric carbonyl sulfide: Domestic coal combustion, Geophysical Research Letters, 43, 8720-8727, 10.1002/2016gl070075, 2016.
Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols, Atmospheric Chemistry and Physics, 7, 4639-4659, 2007.
Ge, X., He, Y., Sun, Y., Xu, J., Wang, J., Shen, Y., and Chen, M.: Characteristics and Formation Mechanisms of Fine Particulate Nitrate in Typical Urban Areas in China, Atmosphere, 8, 62, 10.3390/atmos8030062, 2017.
Graedel, T. E., and Weschler, C. J.: Chemistry within aqueous atmospheric aerosols and raindrops, Reviews of Geophysics, 19, 505-539, 10.1029/RG019i004p00505, 1981.
Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmospheric Chemistry and Physics, 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.
Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific reports, 7, 12109, 10.1038/s41598-017-11704-0, 2017.
Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., Du, Z., Wu, Z., Shao, M., Zeng, L., Molina, M. J., and Zhang, R.: Elucidating severe urban haze formation in China, Proceedings of the National Academy of Sciences of the United States of America, 111, 17373-17378, 10.1073/pnas.1419604111, 2014.
He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NO_x promote the conversion of SO_2 to sulfate in heavy pollution days, Scientific reports, 4, 1-5, 10.1038/srep04172, 2014.
He, P., Xie, Z., Chi, X., Yu, X., Fan, S., Kang, H., Liu, C., and Zhan, H.: Atmospheric $\Delta 17O(NO_3^-)$ reveals nocturnal chemistry dominates nitrate production in Beijing haze, Atmospheric Chemistry and Physics, 18, 14465-14476, 10.5194/acp-18-14465-2018, 2018.
Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmospheric Chemistry and Physics, 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.
Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 10.1038/nature13774, 2014.
Ibusuki, T., and Takeuchi, K.: Sulfur-dioxide oxidation by oxygen catalyzed by mixtures of manganese(II) and iron(III) in aqueous-solutions at environmental reaction conditions, Atmospheric Environment, 21, 1555-1560, 10.1016/0004-6981(87)90317-9, 1987.
~~Kuang, Y., Zhao, C. S., Ma, N., Liu, H. J., Bian, Y. X., Tao, J. C., and Hu, M.: Deliquescent phenomena of ambient aerosols on the North China Plain, Geophysical Research Letters, 43, 8744-8750, 10.1002/2016gl070273, 2016.~~
Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X., and Molina, L. T.: A possible pathway for rapid growth of sulfate during haze days in China, Atmospheric Chemistry

and Physics, 17, 3301-3316, 10.5194/acp-17-3301-2017, 2017.
Li, J., Liao, H., Hu, J., and Li, N.: Severe particulate pollution days in China during 2013-2018 and the associated typical weather patterns in Beijing-Tianjin-Hebei and the Yangtze River Delta regions, Environ Pollut, 248, 74-81, 10.1016/j.envpol.2019.01.124, 2019.
Li, L., Hoffmann, M. R., and Colussi, A. J.: Role of nitrogen dioxide in the production of sulfate during Chinese haze-aerosol episodes, Environ Sci Technol, 52, 2686-2693, 10.1021/acs.est.7b05222, 2018.
Li, Q., Li, X., Jiang, J., Duan, L., Ge, S., Zhang, Q., Deng, J., Wang, S., and Hao, J.: Semi-coke briquettes: towards reducing emissions of primary $PM_{2.5}$, particulate carbon, and carbon monoxide from household coal combustion in China, Scientific reports, 6, 1-10, 10.1038/srep19306, 2016.
Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophysical Research Letters, 44, 1-9, 10.1002/2017GL073210, 2017a.
Liu, P., Zhang, C., Mu, Y., Liu, C., Xue, C., Ye, C., Liu, J., Zhang, Y., and Zhang, H.: The possible contribution of the periodic emissions from farmers' activities in the North China Plain to atmospheric water-soluble ions in Beijing, Atmospheric Chemistry and Physics, 16, 10097-10109, 10.5194/acp-16-10097-2016, 2016a.
Liu, P., Zhang, C., Xue, C., Mu, Y., Liu, J., Zhang, Y., Tian, D., Ye, C., Zhang, H., and Guan, J.: The contribution of residential coal combustion to atmospheric $PM_{2.5}$ in northern China during winter, Atmospheric Chemistry and Physics, 17, 11503-11520, 10.5194/acp-17-11503-2017, 2017b.
~~Liu, Q., Jing, B., Peng, C., Tong, S., Wang, W., and Ge, M.: Hygroscopicity of internally mixed multi-component aerosol particles of atmospheric relevance, Atmospheric Environment, 125, 69-77, 10.1016/j.atmosenv.2015.11.003, 2016b.~~
Ma, Q., Wang, T., Liu, C., He, H., Wang, Z., Wang, W., and Liang, Y.: SO_2 Initiates the efficient conversion of NO_2 to HONO on MgO Surface, Environ Sci Technol, 51, 3767-3775, 10.1021/acs.est.6b05724, 2017.
Meng, Z. Y., Lin, W. L., Jiang, X. M., Yan, P., Wang, Y., Zhang, Y. M., Jia, X. F., and Yu, X. L.: Characteristics of atmospheric ammonia over Beijing, China, Atmospheric Chemistry and Physics, 11, 6139-6151, 10.5194/acp-11-6139-2011, 2011.
Murphy, J. G., Gregoire, P. K., Tevlin, A. G., Wentworth, G. R., Ellis, R. A., Markovic, M. Z., and VandenBoer, T. C.: Observational constraints on particle acidity using measurements and modelling of particles and gases, Faraday Discussions, 200, 379-395, 10.1039/c7fd00086c, 2017.
Nie, W., Ding, A., Wang, T., Kerminen, V. M., George, C., Xue, L., Wang, W., Zhang, Q., Petaja, T., Qi, X., Gao, X., Wang, X., Yang, X., Fu, C., and Kulmala, M.: Polluted dust promotes new particle formation and growth, Scientific reports, 4, 1-6, 10.1038/srep06634, 2014.
Pathak, R. K., Louie, P. K. K., and Chan, C. K.: Characteristics of aerosol acidity in Hong kong, Atmospheric Environment, 38, 2965-2974, 10.1016/j.atmosenv.2004.02.044, 2004.
Ponczek, M., Hayeck, N., Emmelin, C., and George, C.: Heterogeneous photochemistry of dicarboxylic acids on mineral dust, Atmospheric Environment, 212, 262-271, 10.1016/j.atmosenv.2019.05.032, 2019.
Quan, J., Tie, X., Zhang, Q., Liu, Q., Li, X., Gao, Y., and Zhao, D.: Characteristics of heavy aerosol pollution during the 2012–2013 winter in Beijing, China, Atmospheric Environment, 88, 83-89, 10.1016/j.atmosenv.2014.01.058, 2014.
Ravishankara, A.: Heterogeneous and multiphase chemistry in the troposphere, Science, 276, 1058-1065, 1997.
Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics, from Air Pollution to Climate

Change, Wiley, 429-443 pp., 2006.
Shao, J., Chen, Q., Wang, Y., Lu, X., He, P., Sun, Y., Shah, V., Martin, R. V., Philip, S., Song, S., Zhao, Y., Xie, Z., Zhang, L., and Alexander, B.: Heterogeneous sulfate aerosol formation mechanisms during wintertime Chinese haze events: air quality model assessment using observations of sulfate oxygen isotopes in Beijing, Atmospheric Chemistry and Physics, 19, 6107-6123, 10.5194/acp-19-6107-2019, 2019.
Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A., and Russell, A. G.: pH of aerosols in a polluted atmosphere: source contributions to highly acidic aerosol, Environ Sci Technol, 51, 4289-4296, 10.1021/acs.est.6b05736, 2017.
Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., and Ge, X.: The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China, Atmospheric Environment, 77, 927-934, 10.1016/j.atmosenv.2013.06.019, 2013.
Tang, M., Huang, X., Lu, K., Ge, M., Li, Y., Cheng, P., Zhu, T., Ding, A., Zhang, Y., Gligorovski, S., Song, W., Ding, X., Bi, X., and Wang, X.: Heterogeneous reactions of mineral dust aerosol: implications for tropospheric oxidation capacity, Atmospheric Chemistry and Physics, 17, 11727-11777, 10.5194/acp-17-11727-2017, 2017.
Tham, Y. J., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., Ma, N., Yan, C., Kecorius, S., Wiedensohler, A., Zhang, Y., and Wang, T.: Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: roles of aerosol water content and chemical composition, Atmospheric Chemistry and Physics, 18, 13155-13171, 10.5194/acp-18-13155-2018, 2018.
Tong, S. R., Hou, S. Q., Zhang, Y., Chu, B. W., Liu, Y. C., He, H., Zhao, P. S., and Ge, M. F.: Exploring the nitrous acid (HONO) formation mechanism in winter Beijing: direct emissions and heterogeneous production in urban and suburban areas, Faraday Discussions, 189, 213-230, 10.1039/c5fd00163c, 2016.
Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proceedings of the National Academy of Sciences of the United States of America, 113, 13630-13635, 2016.
Wang, G., Zhang, F., Peng, J., Duan, L., Ji, Y., Marrero-Ortiz, W., Wang, J., Li, J., Wu, C., Cao, C., Wang, Y., Zheng, J., Secrest, J., Li, Y., Wang, Y., Li, H., Li, N., and Zhang, R.: Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts, Atmospheric Chemistry and Physics, 18, 10123-10132, 10.5194/acp-18-10123-2018, 2018a.
Wang, H., Lu, K., Chen, X., Zhu, Q., Wu, Z., Wu, Y., and Sun, K.: Fast particulate nitrate formation via N_2O_5 uptake aloft in winter in Beijing, Atmospheric Chemistry and Physics, 18, 10483-10495, 10.5194/acp-18-10483-2018, 2018b.
Wang, H., Lu, K., Guo, S., Wu, Z., Shang, D., Tan, Z., Wang, Y., Le Breton, M., Lou, S., Tang, M., Wu, Y., Zhu, W., Zheng, J., Zeng, L., Hallquist, M., Hu, M., and Zhang, Y.: Efficient N_2O_5 uptake and NO_3 oxidation in the outflow of urban Beijing, Atmospheric Chemistry and Physics, 18, 9705-9721, 10.5194/acp-18-9705-2018, 2018c.
Wang, J., Zhang, X., Guo, J., Wang, Z., and Zhang, M.: Observation of nitrous acid (HONO) in Beijing, China: Seasonal variation, nocturnal formation and daytime budget, The Science of the total environment,

587-588, 350-359, 10.1016/j.scitotenv.2017.02.159, 2017.
Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., Zhang, J., Sun, Y., Hu, B., and Xin, J.: Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China, Science China Earth Sciences, 57, 14-25, 10.1007/s11430-013-4773-4, 2013.
Weber, R. J., Guo, H., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geoscience, 9, 282-285, 10.1038/ngeo2665, 2016.
Wu, J., Bei, N., Hu, B., Liu, S., Zhou, M., Wang, Q., Li, X., Liu, L., Feng, T., Liu, Z., Wang, Y., Cao, J., Tie, X., Wang, J., Molina, L. T., and Li, G.: Is water vapor a key player of the wintertime haze in North China Plain?, Atmospheric Chemistry and Physics, 19, 8721-8739, 10.5194/acp-19-8721-2019, 2019.
Xu, L., Duan, F., He, K., Ma, Y., Zhu, L., Zheng, Y., Huang, T., Kimoto, T., Ma, T., Li, H., Ye, S., Yang, S., Sun, Z., and Xu, B.: Characteristics of the secondary water-soluble ions in a typical autumn haze in Beijing, Environ Pollut, 227, 296-305, 10.1016/j.envpol.2017.04.076, 2017.
Xu, W. Y., Zhao, C. S., Ran, L., Deng, Z. Z., Liu, P. F., Ma, N., Lin, W. L., Xu, X. B., Yan, P., He, X., Yu, J., Liang, W. D., and Chen, L. L.: Characteristics of pollutants and their correlation to meteorological conditions at a suburban site in the North China Plain, Atmospheric Chemistry and Physics, 11, 4353-4369, 10.5194/acp-11-4353-2011, 2011.
Xue, C., Ye, C., Ma, Z., Liu, P., Zhang, Y., Zhang, C., Tang, K., Zhang, W., Zhao, X., Wang, Y., Song, M., Liu, J., Duan, J., Qin, M., Tong, S., Ge, M., and Mu, Y.: Development of stripping coil-ion chromatograph method and intercomparison with CEAS and LOPAP to measure atmospheric HONO, The Science of the total environment, 646, 187-195, 10.1016/j.scitotenv.2018.07.244, 2019a.
Xue, C., Ye, C., Zhang, Y., Ma, Z., Liu, P., Zhang, C., Zhao, X., Liu, J., and Mu, Y.: Development and application of a twin open-top chambers method to measure soil HONO emission in the North China Plain, Sci. Total Environ., 659, 621-631, 10.1016/j.scitotenv.2018.12.245, 2019b.
~~Xue, J., Griffith, S. M., Yu, X., Lau, A. K. H., and Yu, J. Z.: Effect of nitrate and sulfate relative abundance in $PM_{2.5}$ on liquid water content explored through half-hourly observations of inorganic soluble aerosols at a polluted receptor site, Atmospheric Environment, 99, 24-31, 10.1016/j.atmosenv.2014.09.049, 2014.~~
Xue, J., Yuan, Z., Griffith, S. M., Yu, X., Lau, A. K., and Yu, J. Z.: Sulfate Formation Enhanced by a Cocktail of High NO_x, SO_2, Particulate Matter, and Droplet pH during Haze-Fog Events in Megacities in China: An Observation-Based Modeling Investigation, Environ Sci Technol, 50, 7325-7334, 10.1021/acs.est.6b00768, 2016.
Yang, T., Sun, Y., Zhang, W., Wang, Z., Liu, X., Fu, P., and Wang, X.: Evolutionary processes and sources of high-nitrate haze episodes over Beijing, Spring, J Environ Sci (China), 54, 142-151, 10.1016/j.jes.2016.04.024, 2017.
Yang, Y. R., Liu, X. G., Qu, Y., An, J. L., Jiang, R., Zhang, Y. H., Sun, Y. L., Wu, Z. J., Zhang, F., Xu, W. Q., and Ma, Q. X.: Characteristics and formation mechanism of continuous hazes in China: a case study during the autumn of 2014 in the North China Plain, Atmospheric Chemistry and Physics, 15, 8165-8178, 10.5194/acp-15-8165-2015, 2015.
Ye, C., Liu, P., Ma, Z., Xue, C., Zhang, C., Zhang, Y., Liu, J., Liu, C., Sun, X., and Mu, Y.: High H_2O_2 Concentrations Observed during Haze Periods during the Winter in Beijing: Importance of H_2O_2 Oxidation in Sulfate Formation, Environmental Science & Technology Letters, 5, 757-763, 10.1021/acs.estlett.8b00579, 2018.
Zhang, H., Chen, S., Zhong, J., Zhang, S., Zhang, Y., Zhang, X., Li, Z., and Zeng, X. C.: Formation of aqueous-phase sulfate during the haze period in China: Kinetics and atmospheric implications, Atmospheric Environment, 177, 93-99, 10.1016/j.atmosenv.2018.01.017, 2018.

Zhang, Q., He, K. B., and Huo, H.: Cleaning China's air, Nature, 484, 161-162, 2012.
Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of urban fine particulate matter, Chem Rev, 115, 3803-3855, 10.1021/acs.chemrev.5b00067, 2015.
Zhao, M., Wang, S., Tan, J., Hua, Y., Wu, D., and Hao, J.: Variation of Urban Atmospheric Ammonia Pollution and its Relation with PM2.5 Chemical Property in Winter of Beijing, China, Aerosol and Air Quality Research, 16, 1390-1402, 10.4209/aaqr.2015.12.0699, 2016.
Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China, Atmospheric Chemistry and Physics, 15, 2031-2049, 10.5194/acp-15-2031-2015, 2015a.
Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmospheric Chemistry and Physics, 15, 2969-2983, 10.5194/acp-15-2969-2015, 2015b.
Zhong, J., Zhang, X., Wang, Y., Wang, J., Shen, X., Zhang, H., Wang, T., Xie, Z., Liu, C., Zhang, H., Zhao, T., Sun, J., Fan, S., Gao, Z., Li, Y., and Wang, L.: The two-way feedback mechanism between unfavorable meteorological conditions and cumulative aerosol pollution in various haze regions of China, Atmospheric Chemistry and Physics, 19, 3287-3306, 10.5194/acp-19-3287-2019, 2019.