Dear Editor,

Thank you for your kind work on handling our manuscript. We apologize for the poor English text in the last version of our manuscript, and revised the text with the help of professional editing service. What is more important is the two referee's comments, we have carefully read through the comments and either reply it or make modifications accordingly. Our responses to the two referees' comments are itemized below. Please refer to the modifications in the revised manuscript. We also wonder if we could change the tittle of the paper to "Nitrate-dominated PM2.5 and elevation of particle pH observed in urban Beijing during the winter of 2017", since the original tittle might cause misunderstandings.

Anything about our manuscript, please feel free to contact us by ynxie@geo.ecnu.edu.cn (Dr.Yuning Xie) or ghwang@geo.ecnu.edu.cn (Prof. Gehui Wang)

Best regards!

Yuning Xie

12/25, 2019

Response to Anonymous Referee #1

General comments:

Comments: General this paper investigates the pH of nitrate-dominated $PM_{2.5}$. in Beijing in the winter of 2017. The acidity of particles is important in the discussion whether or not a S(IV) might be oxidized through NO_2. The English language of all the manuscript must be thoroughly checked and revised where needed. As the language correction alone is massive, I think the revision of the manuscript corresponds to 'major revision'. Other than this, the manuscript is a solid work with interesting and valuable information and good analysis which should not be missed when Beijing wintertime sulphate formation is discussed.

Response: We thank the referee for his/her kind reply. We have thoroughly checked and revised language. We hope that the current format of the manuscript is good enough in the aspect of language.

Detailed comments

Comments: Title: Maybe better 'nitrate-dominated' instead of 'nitrate dominant'?

Response: Suggestion taken. Please see the title on page 1.

Comments: Abstract, line 18: Better use 'Compared to historical records...' - see above comment, the English language of all of the manuscript has to be thoroughly checked, prefereble by a professional editor or a native speaker.

Response: Suggestion taken. We have asked a professional editor to help us revise the language problem. We modified it with "Compare with …", please see page 1, line 18-19.

Comments Introduction: Needs to be fully language-edited. I cannot do this in my review. Note especially singular/plural use is wrong very often

Response: Suggestion taken, as mentioned above, we have asked a professional editor to help us revise the language problem. We have corrected most of the singular/plural misusing in the text For example, page 2, line 42.

Comments: line 55ff: Maybe the role of non-classical H_2O_2 formation possibly contributing to S(VI) formation should be mentioned here.

Response: Yes, suggestion taken. Non-classical H_2O_2 formation pathways are important in various conditions, especially in the haze episodes of China. We have added some related

introduction into the text. Please see page 3, line 50-61.

Comments: line 183ff: How much of the observed pattern is due to weather conditions? Is there a possibility to 'de-weather' these observations?

Response: The referee gave us a very good future direction. The pollution -weather feedback might be more complicated than the chemistry itself only. However, we believe this topic is beyond the scope of this paper. We would have further investigation on the 'de-weather' pattern's link to physiochemical properties of particles in next studies.

Comments: Figures 5 & 6: All together, this is the most interesting finding of the MS. As the nitrate/sulphate ratio increases, pH is expected to increase.

Response: Thanks for the comment, and we have modified the discussion on the cause of it, please refer to page 12-13, line 270-288。

Comments: line 242: Give the correlation coefficient of the straight line plotted in Figure 6 line 308: Please do not start a paragraph like this.

Response: We apologize for the inconvenience by the poor language, and revised the language accordingly. The correlation coefficient was added on the figure.

Comments: Figure 2: Maybe use identical y-axis scaling for (a), (b) and (c) ?

Response: It should be a good idea to use identical axis in data comparison. However, if we use identical y-axis, then the trend might not be significant since the magnitude is quite different among the three situations.

Respongse to anonymous Referee #2

General comments:

Comments: This article evaluates the ongoing changes in the pH and nitrate content of $PM_{2.5}$ in Beijing as strict controls on sulfur sources are reducing particle sulfate. This is a timely and important topic and the article is within the scope of ACP, however the particle requires extensive revisions to help clarify the authors points and to make it a useful contribution to the literature.

Response: Suggestion taken. We have extensively revised the manuscript including language modification. We will present the details in the next point-to-point replies to your comments.

Comments: The authors use a detailed set of pollution measurements made in Beijing from Dec 2017 – Feb 2018 and compare their typical values measured for various pollutants (e.g. NO_2, SO_2) to those measured in previous years in Beijing. The most important dataset for the calculation of the aerosol pH is the water-soluble gas and $PM_{2.5}$ constituents by IGAC, however the timeseries for these measurements are not shown in the manuscript or in the SI. Given that the campaign period was ten weeks (15/12/2017 – 25/02/2018), there should be ~1700 hourly data points for each compound. However there only appears to be, at most, a few hundred data points in Figures 3, 6, 7, 8, 9. This implies that perhaps the data coverage of the IGAC measurements was not very extensive during the campaign period, or that the data quality were often not sufficient. It would be useful for the authors to provide more explanation about the amount of valid data used in their pH calculations and to what extent it can be viewed

as representative of the entire winter season. In fact, in Figures 4 and 5, it seems that the hi-volume sampler data is used for nitrate and sulfate, rather than the hourly data – is this true and why?

Response: We thank the reviewer for his/her concerning about the data points in our manuscript figures. Not all of the data points were shown in this paper. From section 3.3 it could be easily seen that the SNA composition of $PM_{2.5}$ significantly changed during the pollution periods. Therefore, the main purpose of this article lies in the examination on the impact of nitrate fraction elevation on the pH of particles. During the winter of 2017, the pollution happened less than before and the weather was quite dry. Only data during pollutions were used to plot the referee mentioned figures. More to that, the data were chosen with a criterion of whether ALWC was sufficient. Therefore, it might seem much less data were shown in the paper but it was intended. The data measured with IGAC are hourly data. Several places in the text were modified, mainly the captions of figures. Please see page 30, line 640-642; page 31, line 645 -646; page 32, line 649-650.

Comments: One confusing aspect of the manuscript is that the authors consistently refer to aerosol with a pH of 5.4 as 'near neutral', despite the proton activity being ~ 40 times higher than a solution with a truly neutral pH (i.e. 7). From this, I believe they mean that a pH value of 5.4 is close to what one calculates for a solution exposed to 400 ppm of CO_2 in the ambient atmosphere. I suggest changing this language because 'neutral' has a very specific meaning, different from what is being used here. If the authors want to emphasize that the pH is close to what might be expected in the absence of high particle pollution, they could explain that a value of 5.5 is expected in 'unpolluted' conditions. However, even at very low $PM_{2.5}$ mass loadings, the contributions of solutes other than carbonic acid/bicarbonate will dominate the ion balance and set the pH and I do not think there is anything special about a pH of 5.4.

Response: Thanks for the suggestion. We revised the description to "less acidic" and "more neutralized". A pH of 5.4 is an especially important value in previous literature (Cheng et al. 2016; Wang et al.2016; Seinfeld et al.2006), which discussed the topic on whether NO_2

promotes sulfate formation in China. Please see the related discussions in the paper.

Comments: Section 3.4 addresses the main question of the publication – how changes in particle composition are linked to changes in particle pH. Because nitrate is a semi-volatile component of the particle, its gas-particle partitioning is sensitive to the particle pH (and to its LWC and temperature). Thus, it does not necessarily make sense to frame the question as 'the effect of nitrate fraction elevation on particle acidity'. I would view it from the opposite perspective – for a given amount of total ammonia, less $PM_{2.5}$ sulfate allows the particle pH to be higher, allowing for nitrate to be present in the particle phase. In other words, the pH is not responding to the nitrate to sulfate ratio, as is suggested by the choice of axes in Figure 6. Rather, the pH is responding to the reductions in sulfate and thus leading to a change in the partitioning of nitrate. This is the converse of the explanation provided on Lines 290-291.

Response: We disagree with the reviewer on the above comments. It has been found that the decrease of sulfate would not inevitably lead to an increase in particle pH and nitrate. For example, combing the field measurements and thermodynamic model simulations, Webber et al have investigated the variation trends of chemical composition and pH of $PM_{2.5}$ in the southeastern US during the past 15 years (Weber et al,.2016). They found that pH of $PM_{2.5}$ in US has kept constant in the range of 0-2 and litter change in particle ammonium nitrate, although sulfate in the fine particles has significantly decreased from about 7 $\mu g/m^3$ in 1999 to 2 $\mu g/m^3$ in 2014. However, it is not the case in China. In the past five years many studies have found that along with the sharp decreased in sulfate concentrations due to SO_2 emission controls, relative abundance of nitrate of $PM_{2.5}$ in many cities of China has significantly increased (Ji et al., 2018; Wu et al., 2018), as those found in this study. Such a different variation trend of nitrate suggests that aerosol chemistry (e.g., acidity) in China especially in haze periods is different from that in US and other developed countries, which is the motivation of this work why we would like to investigate the impact of changes in chemical compositions of $PM_{2.5}$ on particle acidity in Beijing. It's of our special interest to point the difference of how particle's acidity reacts to its chemical composition's change. This study highlights the difference of particle acidity calculated by the same method between China and

the U.S.

Comments: In particular, the statement on Lines 253-254 is very confusing: 'Less predicted H^+ ion in aerosol liquid water is found to be the major cause of the higher pH…' A lower concentration (or activity) of H^+ is the definition of higher pH (pH = -log[H^+]), not just a major cause! Similarly, there is no reason to examine the [HSO_4^-]/[SO_4^{2-}] ratio to consider the 'aerosol's ability of excess H^+ formation' (Line 270). This ratio derived from the model output is going to be self-consistent with the pH calculated by the model given that the [HSO_4^-]/[SO_4^{2-}] ratio depends on the pKa of bisulfate and the pH of the aerosol liquid water. There isn't any additional insight provided by this ratio is you already know the pH, which is well above the pKa in almost all cases.

Response: We have reconsidered the comment by referee #2 and take it carefully. Our first intention is to use the ratio as a proxy of H^+ production and to find the physiochemical nature by comparing the proxy to nitrate/sulfate ratio. However, after studying the referee#2's comment, we found that the ratio calculated from the result of ISORROPIA II model is almost equivalent to the pH, and thus Fig.8 is equivalent to Fig.6. Therefore, this figure and related discussion were deleted from the text. Besides this, we present more discussion on the effect of nitrate fraction elevation on NH_3 partition ratio and its potential effect in the following part. The analysis shows that the partition of NH_3 is more sensitive to nitrate content, and it is caused by the enhanced nitric acid partitioning due to higher particle pH. The deleted context were in section 3.4, before the paragraph in page 12, line 270. The added discussion were mainly in the last part of section 3.4, please refer to page12-13, line 270-288.

Comments: Generally, I found the frequent references to the mechanisms of sulfur oxidation scattered through the text to be distracting. It would be preferable to state in one section of the introduction how and why the pH might impact the sulfur oxidation mechanism and rate and then return to it in the discussion. Other mentions of it in the results section, e.g. Lines 244-247 are distracting because the observational data themselves do not evaluate this

mechanism.

Response: Suggestion taken. We added some introduction about SO_2 oxidation into the introduction section and shortened the NO_2 oxidation mechanism discussion in the results. See page 3, line 50-61; page 11, line 246-248;

Comments: Section 4 – The authors assess the changes in hygroscopicity in more nitrate-rich particles by comparing the ALWC when the RH is increased by 10%. The authors should clarify whether these calculations were performed using the particle components only as inputs, or the particle and gas (e.g. NH_3 and HNO_3) components as well. This is because increasing the RH would also increase the gas-to-particle partitioning of the gases, so the increase in ALWC results not just from the increased water activity in the particle, but also from dissolving more solutes into the aqueous phase for semi-volatile constituents like nitrate and ammonium.

Response: Suggestion taken. In our calculation, input NH_3 was set as NH_3 plus NH_4^+. But the input of HNO_3 was only nitrate measured, since there were no HNO_3(g) measurements. As a result, there will only be as much NH_4NO_3 as measured and the increase of ALWC is not from more solutes.

Specific comments:

Comments: Page 3, L77 – The Song et al., 2018 reference identified a coding error in ISORROPIA that led to unreliable results for calculations done for closed, stable systems. Several of the references discussed by the authors in this section used this approach for their calculations of pH and therefore it would useful for the authors to identify which of the papers may have reported pH values that are in need of revision.

Response: Right now, we couldn't get the fixed code to run the model in a more proper way. We would have further investigation on the model coding error in future work.

Comments: Page 7, Lines 215-220, Why is the ratio of ammonium/sulfate of 1.5 set as the

threshold or limit for nitrate formation? It should be possible to carry out a more sophisticated analysis of the threshold for nitrate formation than what was performed in Pathak et al.2009 and 2011.

Response: The RatioA-to-S is set to 1.5 by the definition of "excess ammonium", meaning that there was enough ammonia to form ammonium nitrate. Many field observations on the Chinese atmospheric aerosols including the work reported by Pathak et al,. (2004) found that nitrate aerosols can be significantly detected only when molar ratio of ammonium to sulfate is larger than 1.5. Actually, there was a quite comprehensive analysis based on experiments, please refer to Pathak et al, 2004. Thus, we think it is not necessary to repeat the analysis on this threshold, which was already done by Pathak et al. We have cited this work and readers can refer to this paper for the details.

Comments: Page 7, Lines 230 -232 The Shah et al. and Weber et al. studies do not necessarily contradict each other as they each examine trends and sensitivities in pH in different seasons and regions of the U.S.

Response: We found it inappropriate and rephrased the sentence. See page11, line235-237

Comments: Page 8, Line 279 and Figure 9 - The authors use inconsistent language and definitions for the ratio of particle NH_4^+ to total ammonium (conversion ratio in Figure 9 and 'ammonia partition fraction' on Line 279.

Response: We've checked through the article and made revisions to make the language consistent on fig.9 (now as fig.8) and on page 13, line279-288.

Comments: Reference list - Wang 2016a and Wang 2016b are the same reference

Response: Thanks for the referee, we've modified this part. Other repeated reference like Cheng et al. 2016, Guo et al. 2017. See Page 19, line 417-419; Page 20, line 454 – 455; Page 25, line 560-565.

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Pathak, R. K., Yao, X., and Chan, C. K.: Sampling Artifacts of Acidity and Ionic Species in PM2.5, Environ. Sci. Technol., 38, 254-259, 10.1021/es0342244, 2004.

Webber et al. High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. Nature Geoscience, 2016, Vol.9, 282-286, DOI: 10.1038/NGEO2665

Wu, C., et al. Chemical characteristics of haze particles in Xi'an during Chinese Spring Festival: Impact of fireworks burning. Journal of Environmental Sciences, Vol. 71, 179-187, 2018.

~~Observation of nitrate dominant~~Nitrate-dominated $PM_{2.5}$ and elevation of particle pH ~~elevation~~observed in urban Beijing during the winter of 2017~~–~~

Yuning Xie [1], Gehui Wang [1,2,*], Xinpei Wang [1], Jianmin Chen[2,3], Yubao Chen [1], Guiqian Tang [4], Lili Wang [4], Shuangshuang Ge [1], Guoyan Xue [1], Yuesi Wang[4], Jian Gao[5]

[1]Key Laboratory of Geographic Information Science of the Ministry of Education, School of Geographic Sciences, East China Normal University, Shanghai 200241, China

[2]Institute of Eco-Chongming, 3663 N. Zhongshan Rd., Shanghai 200062, China

[3]Department of Environmental Science and Technology, Fudan University, Shanghai, China

[4]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100080, China

[5]Chinese Research Academy of Environmental Sciences, Beijing 100000, China;

Correspondence to: Prof. Gehui Wang (ghwang@geo.ecnu.edu.cn)

Abstract~~. Particle acidity is crucial~~: Chinese government has exerted strict emission controls to ~~understand secondary formation processes in~~ mitigate air pollution ~~events~~ since ~~acidity has substantial impacts~~2013, which resulted in significant decreases in the concentrations of air pollutants such as SO_2, NOx and $PM_{2.5}$. To investigate the impact of such changes on the ~~physiochemical properties of $PM_{2.5}$. Quantification of particle acidity with simulated pH yielded various values range from 0-7 and conflicting conclusions on sulfate formation~~

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~~mechanisms~~chemistry of atmospheric aerosols in China ~~recently. In this article~~, we ~~found that particle pH could increase to near neutral (5.4) as a result of effective sulfur emission control. Benefit from strict~~ conducted a comprehensive characterization on $PM_{2.5}$ in Beijing during the winter of 2017. Strict pollution control actions~~,~~ also reduced the average $PM_{2.5}$ concentration ~~reduced~~ to a low level ~~(~~of 39.7 μg~~/m³)~~ m^{-3} in urban Beijing during the winter of 2017. ~~Compare to history~~Compared with the historical record (2014–2017), SO_2 ~~gradually~~ decreased to a low level ~~(~~of 3.2~~ppbv~~2 ppbv in ~~2017~~the winter~~) while~~ of 2017 but NO_2 ~~kept increasing~~ level was still high (21.4~~ppbv~~4 ppbv in ~~2017~~the winter~~). As a response, nitrate's~~ of 2017). Accordingly, contribution of nitrate (23.0 μg~~/m³~~ m^{-3}) to $PM_{2.5}$ ~~become dominant~~far exceeded over sulfate (13.1 μg~~/m³~~ m^{-3}) during ~~$PM_{2.5}$~~the pollution episodes~~. The~~, resulting in a significant increase of nitrate to sulfate molar ratio ~~significantly increased from 1 to 2.7 (value of 1999 and 2017). As nitrate's fraction significantly elevated, particle pH was also found to increase in winter Beijing given sufficient ammonia (average concentration 7.1μg/m³, 12.9μg/m³ during pollution). During $PM_{2.5}$ pollution episodes, the particle pH predicted~~. The thermodynamic model (ISORROPIA-II) calculation results showed that during the $PM_{2.5}$ pollution episodes particle pH increased from 4.4 (moderate acidic) to 5.4 (~~near neutral) as nitrate to sulfate~~more neutralized) when the molar ratio of nitrate to sulfate increased from 1 to 5~~. It is found that the major H^+ contributor S(VI) was mostly in the form of sulfate~~, indicating that ~~anions~~aerosols were more neutralized as the nitrate content elevated. ~~In the final part,~~Based on the results of sensitivity tests, the future prediction ~~of~~for the particle acidity change was discussed ~~via sensitivity tests: On one hand,~~. We found that nitrate–rich particles ~~would~~in Beijing at low and moderate humid conditions (RH: 20%–50%) can absorb ~~more~~twice amount of water ~~compared to the~~than sulfate–rich particles~~. This absorption contrast doubles~~ , and the nitrate and ammonia with ~~low to moderate RH (20%~50%). On the other hand, increased level of nitrate and ammonia would~~higher levels have synergetic effects ~~leading to rapid elevation of~~, rapidly elevating particle pH to merely neutral (above 5.6). As moderate haze events might occur more frequently ~~with high~~under the abundant ammonia and ~~particulate~~ nitrate ~~concentration~~-dominated $PM_{2.5}$ conditions, the major chemical

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processes during haze events and the control target ~~shall~~should be re-evaluated to obtain the most effective control strategy.

1 Introduction

Severe haze ~~had~~ pollution has been causing serious environmental problems and harming public health in China over the past decades ~~(He et al., 2001;Wang et al., 2016b;Zhang et al., 2015b). Strong~~(He et al. 2001; Wang et al. 2016; Zhang et al. 2015b). Therefore, strong actions ~~were~~have been taken to ~~reverse~~improve the worsening atmospheric environment ~~situation~~, including cutting down the pollutants~~' emission~~ emissions with forced installation of catalytic converter on vehicles, ~~buildings of~~building clean-coal power generation system, ~~and prohibition~~ prohibiting open burning of crop residue ~~burning in~~during the harvest ~~season~~seasons, etc.~~(Chen et al., 2017;Zhang et al., 2012;Liu et al., 2016).~~. (Chen et al. 2017; Zhang et al. 2012; Liu et al. 2016). As a result, the $PM_{2.5}$ ~~pollutions were~~pollution is relieved to ~~a level that met~~meet the goals in ~~AIR POLLUTION PREVENTION AND CONTROL ACTION PLAN~~Air Pollution Prevention and Control Action Plain (issued by the ~~state council~~State Council of China, http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm, in Chinese). Among all the regions of interests, Beijing has achieved great success in $PM_{2.5}$ ~~controlling (~~reduction (the annual average $PM_{2.5}$ concentration of 2017 was 58 μg~~/m^3~~ m^{-3}). Yet, ~~compare to~~ $PM_{2.5}$ concentration in Beijing is still higher than that in most developed countries~~, this record was still high. Despite emission control, it is also important to elucidate the key processes in atmosphere pollutions in Beijing and across China~~.

~~The cause of $PM_{2.5}$ pollution in China was multivariate (Guo et al., 2014;Ding et al., 2013). One feature of $PM_{2.5}$ pollution across the country is significant high secondary formation of inorganic components (Huang et al., 2014a). Sulfate, nitrate and ammonium (SNA) comprised over 30% of the $PM_{2.5}$ mass, and SNA's fraction continues to increase during development of pollution episodes(Cao et al., 2012). While models could well predict the airborne particle pollutions in the U.S. or Europe, it is challenging to simulate the real atmospheric environment in China (Wang et al., 2014;Ervens et al., 2003). Previous modeling works showed that the simulated $PM_{2.5}$ concentrations were underestimated within current scheme, and suggested the importance of heterogeneous reactions in the SNA~~

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formation processes (Huang et al., 2014b;Herrmann et al., 2005). In Beijing, severe haze events occur with abundant nitrogen species (NO_x, NH_3, etc.) and high RH while photochemistry is often less active (Wang et al., 2016b;Cheng et al., 2016b). Field observations, chamber experiments, source apportionments and simulation works all suggests that the joint effect of NO_2, SO_2, and NH_3 is important in the sulfate formation processes in haze events (Cheng et al., 2016b;Wang et al., 2016b;He et al., 2018).Aqueous oxidation of SO_2 by NO_2 could be of major process of sulfate formation in winter Beijing, as well as transition metal ions (TMI) catalyzed oxidation (Wang et al., 2016b;Cheng et al., 2016b). Besides, though the photochemistry were less active during winter haze periods, extra radical provided by HONO might enhance the atmospheric oxidation capacity and thus leads to extra SNA formation (Tan et al., 2018). Since these reactions are all sensitive to particle acidity, adequate quantification of airborne particle's acidity is essential to elucidate the specific contribution.

Particle acidity has widely been studied due to its important roles in haze formation, and is widely implemented in major models (Yu et al., 2005;Robert et al., 2016). Since there was rarely practical method to direct measure the acidity of particles in real atmosphere (Wei et al., 2018;Freedman et al., 2019), calculation of the particle pH by thermodynamic models had been the most used method to quantify particle acidity. Most models (ISORROPIA II, E-AIM-IV, AIOMFAC, etc.) can predict H^+, ALWC, and partitioning of volatile/semi volatile components, such as ammonia (Fountoukis and Nenes, 2007;Clegg et al., 2008). These models' ability to describe physiochemical properties of airborne particles was validated by various studies (Weber et al., 2016;Guo et al., 2016;Shi et al., 2017;Tao and Murphy, 2019;Murphy et al., 2017). However, several publications using the same method gave different particle pH values in Beijing, and contradict conclusions were drawn on whether the sulfate formation by NO_2 oxidation could be important. Cheng et al. conducted modeling work and suggest that Beijing's $PM_{2.5}$ pH ranged from 5.4–6.2, which is favorable for aqueous NO_2 oxidation. Not only by modeling works, field observation and chamber study also support the NO_2 oxidation's major contribution and address the importance of high ALWC as well as sufficient ammonia (Wang et al., 2016a;Chen et al., 2019). Meanwhile, particle pH during winter of 2015 to 2016 simulated by Liu et al with the same method was lower (3.0–4.9, average 4.2) and it was suggested that the acidic particle did not favor the NO_2 oxidation mechanism. With averaged data from typical locations, Guo et al further concluded that high ammonia could not raise the particle pH high enough for the NO_2 oxidation. On the other side, Song et al suggested that the model (ISORROPIA II) might have coding error that predict pH values to be negative or above 7. However, with lab studies and field observations, Wang et al raised concern that whether it was appropriate to elucidate the chemical reactions by particle pH predicted with only inorganic compositions. In fact, since the real atmosphere was affected by uncountable factors, it is common that particle pH would have variation when simulated with ambient data. At least moderate acidic to near neutral acidity was reported in China, and airborne particles were more neutralized than those in the US., given the fact that the gaseous ammonia was still at a high level to particulate ammonium (Song et al., 2018).

There are many factors contributing to the $PM_{2.5}$ pollution in China (Guo et al. 2014; Ding et al. 2013). The

$PM_{2.5}$ pollution across the country is featured by significantly high secondary formation of inorganic components (Huang et al. 2014a). Sulfate, nitrate and ammonium (SNA) comprised over 30% of the $PM_{2.5}$ mass, and SNA's fraction continues to increase during the pollution evolution (Cao et al. 2012). While models could well predict the airborne particle pollution in the U.S. or Europe, it is challenging to simulate the real atmospheric pollution in China (Wang et al. 2014; Ervens et al. 2003). Previous modeling works showed that the simulated $PM_{2.5}$ concentrations were underestimated within the current scheme, which is related to the important role of heterogeneous reactions in the SNA formation processes (Huang et al. 2014b; Herrmann et al. 2005). It was reported that the classical formation mechanism of sulfate in the atmosphere was through oxidation by H_2O_2, but recent studies in China pointed out that non-classical H_2O_2 formation pathways, which are mentioned in text books, cannot be ignored. In Beijing, severe haze events occur with abundant nitrogen species (NO_x, NH_3, etc.), high relative humidity (RH) and less active photochemistry (Wang et al. 2016; Cheng et al. 2016). Field observations, chamber experiments, source apportionments and numerical simulation works all suggest that the joint effect of NO_2, SO_2, and NH_3 is important for the sulfate formation processes in haze events (Cheng et al. 2016; Wang et al. 2016; Wang et al., 2018; He et al. 2018, Xue et al., 2019). Aqueous oxidation of SO_2 by NO_2 could be a major process of sulfate formation in Beijing during winter, as well as the catalyzed oxidation by transition metal ions (TMI) (Wang et al. 2016; Cheng et al. 2016). Besides, although the photochemistry is less active during haze periods in winter, the extra OH radical provided by HONO might enhance the atmospheric oxidation capacity and lead to a rapid formation of SNA (Tan et al. 2018, Ge et al. 2019). Since these reactions are all sensitive to particle acidity, adequate quantification of airborne particles' acidity is essential for elucidating the specific contribution.

Particle acidity has been widely studied due to its important role in the haze formation, and has been widely implemented in major models (Yu et al. 2005; Robert et al. 2016). Since the practical method of directly measuring the particle acidity in real atmosphere is not available (Wei et al. 2018; Freedman et al. 2019),

thermodynamic models, which can calculate the particle pH, have been mostly used in quantifying the particle acidity. Most models (ISORROPIA II, E-AIM-IV, AIOMFAC, etc.) can predict H^+, aerosol liquid water content (ALWC) and the partitioning of volatile/semi volatile components, such as ammonia (Fountoukis and Nenes 2007; Clegg et al. 2008). These models' abilities to describe physiochemical properties of airborne particles have been validated in various studies (Weber et al. 2016; Guo et al. 2016; Shi et al. 2017; Tao and Murphy 2019; Murphy et al. 2017). However, several publications using the same method gave different particle pH values in Beijing, and contradictory conclusions were drawn on the importance of the sulfate formation by NO_2 oxidation. Cheng et al. (2016) conducted some modeling work and suggested that the $PM_{2.5}$ pH in Beijing ranges between 5.4 and 6.2, which is favorable for the aqueous NO_2 oxidation. The NO_2 oxidation's major contribution and the importance of high ALWC and sufficient ammonia are supported not only by modeling works, but also by field observation and chamber study (Wang et al. 2016; Chen et al. 2019). On the contrary, Liu et al. (2017) simulated the particle pH during the winter of 2015 and 2016 with the same method, and claimed that pH of the Beijing haze particles was lower (3.0–4.9, average 4.2) and unfavorable for the NO_2 oxidation mechanism. Based on the ISORROPIA-II model results , which assumed Chinese haze particles as a homogeneous inorganic mixture, Guo et al. (2017) further concluded that high ammonia cannot raise the particle pH enough for the aqueous oxidation of SO_2 by NO_2. Recently Song et al. (2018) reported that the thermodynamic model (ISORROPIA-II) has coding errors, which can lead to the predicted pH values negative or above 7. Furthermore, with lab studies and field observations, Wang et al. (2018) raised the concern that whether it is appropriate to elucidate sulfate production for the Beijing haze by using particle pH predicted only based on the inorganic compositions. In fact, since the real atmosphere is affected by uncountable factors, it is common that particle pH has variation when simulated with the ambient data. Although the pH predicted by the thermodynamic models are of uncertainty, it is widely believed that haze particles in China are moderate acidic and are more neutralized than those in the US., given that the gaseous ammonia is still at a high level relative to particulate ammonium(Song et al. 2018).

Air pollution control in China's ~~air pollution control~~ has entered the second phase~~: —~~ —further mitigation of the moderate haze pollution, which is ~~accompanied with high levels of NO_x and NH_3 (Liu et al., 2019;de Foy et al., 2016). With stronger control policies, the severe haze could be well controlled. But to meet the WHO standard, strategies to prevent moderate haze events are getting more important. The main scope of this article is~~ characterized by high levels of nitrate and ammonium and low level of sulfate (Liu et al. 2019; de Foy et al. 2016) due to the efficient SO_2 emission control. Such a change in chemical compositions could significantly alter physicochemical properties of the atmospheric aerosols in China. This paper aims to investigate ~~how~~ the variation of the particle acidity of $PM_{2.5}$ ~~would change as~~when the sulfur emission was well controlled in Beijing. First, ~~general information~~the compositions of ~~the atmospheric~~air pollutants, including inorganic components ~~including the inorganic composition~~ of $PM_{2.5}$ during the winter of 2017~~-~~ and 2018 ~~was~~, were analyzed and compared ~~to~~with previous studies; then, based on observations, the ~~respond~~response of particle acidity to the elevation of nitrate was studied by using the ISORROPIA II~~;~~ thermodynamic model; and finally, the possible changes in the future ~~were~~are discussed ~~with~~based on the sensitivity tests.

2 Sampling site and instrumentation ~~description~~

The observation was conducted at an urban site~~— —~~the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58′28″N, 116°22′16″E) in Beijing. All the instruments were ~~located~~ on the roof of a two-story building. The ~~main~~ local emissions are mainly ~~emitted~~ from the vehicles, ~~while~~and the industrial emission is ~~much less~~greatly reduced since the major factory/power plants ~~were~~are moved out of Beijing or phased out due to the emission control policy. Overall, this site represents ~~a normal~~the typical atmospheric environment of urban Beijing, ~~and~~from which the data obtained ~~from this site is applicable to compare to~~ can be compared with those from previous studies in ~~Beijing~~the city (Ji et al.~~,~~ 2018).

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A continuous online measurement of atmospheric components was conducted with a time resolution of 1 hour. Two ~~1405~~ TEOM™ continuous ambient ~~connected to either~~PM monitors using $PM_{2.5}$ or PM_{10} cyclone inlet (Metone) ~~was engaged~~were applied to obtain $PM_{2.5}$ and PM_{10} mass ~~concentration.~~concentrations. For trace gases (O_3, NO_2~~,~~ and SO_2), a series of gas monitors were used for the hourly measurement (Model 49i, 42i and 43i, respectively). Meteorology data, including ambient temperature, ~~relative humidity~~RH, wind speed, wind direction and total solar radiation, were measured with an automatic weather station (MILOS 520, VAISALA Inc., Finland) located in the middle of the ~~yard of the~~ observation site yard. Visibility data ~~from~~of Beijing ~~airport online data was obtained~~were downloaded from the website of https://gis.ncdc.noaa.gov/maps/ncei/cdo/hourly. ~~Besides~~Apart from these online monitors, a high volume sampler (TISCH ENVIRONMENTAL) with a $PM_{2.5}$ inlet was used to collect $PM_{2.5}$ samples on a day/night basis (daytime of 8:00–17:50 and nighttime of 18:00–7:50).

The inorganic water soluble components of $PM_{2.5}$ (SO_4^{2-}, NO_3^-, Cl^-, NH^{4+}, Na^+, Ca^{2+}, Mg^{2+}, and K^+) and ammonia gas were measured with an online-IC system: IGAC (In-situ Gases and Aerosol Composition monitor, Fortelice International Co., Ltd.). IGAC ~~is comprised~~comprises of ~~two major~~2 parts: sampling unit and ~~analysis unit(Young et al., 2016).~~analyzer unit (Young et al. 2016). A vertical wet annular denuder (WAD) ~~was engaged~~is used to collect the gas phase species prior to a scrub and impactor aerosol collector (SIC), while the latter part can efficiently collect ~~particle~~particles into liquid samples. During the campaign, 1mM H_2O_2 solution ~~was~~is used as the absorption liquid for the air samples. Under most atmospheric conditions, the absorption liquid ~~could~~can well absorb the ~~targeted~~target atmospheric components (e.g. SO_2). An ICS-5000$^+$ ion chromatograph ~~was engaged~~is used as the analyzer unit in this study. For anions, an AS18 column (~~2mm×250mm~~2 mm × 250 mm, Dionex™ IonPac™) ~~was~~is used while a CS-16 column (~~4mm×250mm~~4 mm × 250 mm, Dionex™ IonPac™) ~~was~~is chosen ~~for the analysis of~~to analyze major cations, both running with recommended eluent (solution of KOH for anion/ methane sulfonic acid for cation). The ~~behavior~~performance of the system ~~was~~has been tested and improved over recent years, and studies of $PM_{2.5}$ water-soluble ~~ions~~ion observations ~~were~~have been conducted by using ~~this~~

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instrumentit (Young et al., 2016;Song et al., 2018;Liu et al., 2017a).(Young et al. 2016; Song et al. 2018; Liu et al. 2017). A better sensitivity due to the advanced suppression technology of the system greatly enhancedenhances its ability to measure trace ions, such as sodium and magnesium, which could beis important in studies of particle ion balance studies. For details of the comparison between IGAC comparisons withand filter sampling results, please refer to supplementary materials (Fig. S1).

3. Results

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3.1 Major pollutants' levels

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We firstfirstly present the overall time series and statistics of major pollutants and meteorological parameters from Dec. 15th, 2017 to Feb. 25th, 2018. As shown fromin Fig.1, during the observation campaign, Beijing was relatively cold and dry. Due to the frequent occurrence of cold advection, air outbreaks, the average air temperature was around zero Celsius degree0°C, with a minimum of --10°C, and the relative humidityRH was low on average (20%–30%) with a maximum of 80%. The average total solar radiation was 254.3 w/m² m^{-2}, which is a typical measure in winter Beijing. Wind during winter. The wind usually blew from the north with an average speed of 1.9m/9 m s^{-1}, but the strong wind (speed over 5m/5 m s^{-1}) frequently occurred inon the clean days. BenefitBenefiting from the weather condition, Beijing'sthe atmospheric pollution levelin Beijing was much lower compare toweaker than that in the winter of 2013. Overall, the atmospheric environment improvement of the atmospheric environment was visible: with anthe average visibility was around 15km (15 km during the campaign and about 7.5km5 km during the pollution), sky was much clearer than before (e.g. 667m, in an extreme case, reported by Zhang et al. (2015a)). periods.

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With strict control actions, there were less $PM_{2.5}$ pollution occurred lessepisodes and theits concentration kept at a low level during the most of the time in the winter of 2017. The average concentrations of $PM_{2.5}$ and PM_{10} were

39.7 μg/m³ m⁻³ and 68.5 μg/m³ m⁻³, respectively. According to the $PM_{2.5}$ concentration, three conditions of the atmospheric environment were classified in this study : clean (the $PM_{2.5}$ was classified: Clean – below 35μg/m³; Transition – 35μg/m³ ~ 75μg/m³; Pollution – above 75μg/m³. From clean, μg m⁻³), transition to polluted condition(the $PM_{2.5}$ was between about 35 μg m⁻³ and 75 μg m⁻³) and pollution (the $PM_{2.5}$ was above 75 μg m⁻³). In the clean, transition and pollution periods, the average $PM_{2.5}$ concentration was concentrations were 13.0±7.8 μg/m³ m⁻³, 52.0±11.4 μg/m³ m⁻³ and 128.0±46.5μg/m³ μg m⁻³ , respectively (as showed in Table 1), indicating that there was still $PM_{2.5}$ pollutionspollution during thisthe winter (, with a maximum hourly $PM_{2.5}$ concentration was 298.0μg/m³). Average concentration of 298 μg m⁻³. The average ozone concentration was 18.5±12.8 ppbv, and the value decreased as $PM_{2.5}$ concentrations increased. AverageThe average SO_2 concentration (3.2±3.1ppbv1 ppbv) was almost 10 times lower than that of NO_2 (21.4±14.8ppbv). This8 ppbv). The significant contrast ofgap between SO_2 and NO_2 concentration couldconcentrations can be attributed to the sulfur emission control over recent years and the fast increase of gasoline vehicles in Beijing(Cheng et al., 2018;Wang et al., 2018b). (Cheng et al. 2018; Wang et al. 2018b). Both of the two gaseous pollutantpollutants showed an increasing trend as the $PM_{2.5}$ concentration increasesincreased during the haze episodes, but the elevationincrease of NO_2 level was much more significant, thus making it a more important role in the pollution processes.

NO_2 and SO_2 are the most important precursor gases for major secondary inorganic nitrate and sulfate in $PM_{2.5}$. Due to the emission control being effectively conducted, , the sulfur emission decreased significantly and thus led to , resulting in lower ambient SO_2 concentration. To better describe thisit, changes inof these the two precursor gases during winter wereare investigated by examining the data from 2014 –to 2016 in Beijing. Average values and the standard deviation wereare plotted in Fig. 2. SO_2 showed a significant decreasing trend in all the three conditionsperiods. In 2014, the concentrations of SO_2 in the three periods were 3.9, 10.0 and 16.9 ppbv in the three conditions., respectively. The SO_2 concentration differences between each stage were getting smaller.difference in different conditions was narrowing. Until 2017, the difference of SO_2 concentrations in

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between any two of three conditions had been all ~~three stages were~~ within ~~10ppbv~~10 ppbv. Meanwhile, NO_2 concentrations kept increasing after 2015 in clean and transition conditions, but ~~in~~ the NO_2 concentration during the pollution periods of 2017 ~~NO_2~~ was surprisingly lower than that in 2014. ~~Besides the fact that~~Although the dilution condition was much better than before, more quick and strong actions were taken to prevent the $PM_{2.5}$ pollution in 2017, such as construction prohibition, private vehicle restriction and vast shutting down of factories in ~~neighborhood~~neighboring regions ~~(Cheng et al., 2018). The significant drop of NO_2 proves the effectiveness of pollution control actions~~(Cheng et al. 2018). The significant drop of NO_2 proves the effectiveness of pollution control in 2017.

3.2 $PM_{2.5}$ chemical compositions

~~Similar~~ According to several previous reports, the chemical compositions of $PM_{2.5}$ during the winter of 2017 in Beijing changed significantly ~~(Shao et al., 2018;Elser et al., 2016;Ge et al., 2017;Huang et al., 2017;Wang et al., 2017).~~(Shao et al. 2018; Elser et al. 2016; Ge et al. 2017; Huang et al. 2017; Wang et al. 2017). The major inorganic ions of $PM_{2.5}$ in Beijing during ~~2017~~the winter ~~were~~of 2017 included ammonium (3.3±4.4 μg~~/m³~~ m^{-3}), nitrate (7.1±9.6 μg~~/m³~~ m^{-3}), sulfate (4.5±5.9 μg~~/m³~~ m^{-3}) and chloride (2.4±2.3 μg~~/m³). Increase~~ m^{-3}). Concentrations of ~~all~~ the major ~~compositions' concentration was observed~~components increased as the $PM_{2.5}$ concentration increased, but changes in the crustal ion (Na^+, Mg^{2+}~~,~~$^+$ and Ca^{2+}) concentrations were less ~~differed in different conditions. Potassium~~significant among the clean, transition and pollution periods. K^+ increased during the $PM_{2.5}$ ~~pollutions~~pollution episodes (average concentration: 2.3±5.1 μg~~/m³~~ m^{-3}), indicating the possible contribution ~~from~~of biomass burning sources or fireworks during Chinese New Year. ~~Chloride~~Cl^- in $PM_{2.5}$ has been used as a tracer for biomass burning and the coal consumption ~~tracer~~. The concentration of Cl^- in $PM_{2.5}$ chloride increased significantly as $PM_{2.5}$ ~~loading got higher,~~ increased, but the imbalance of chloride molar concentration ~~of chloride~~ to potassium suggests that biomass burning might not be the major source of $PM_{2.5}$

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chloride ~~in $PM_{2.5}$~~ other than the coal consumption ~~in Beijing's~~during the $PM_{2.5}$ pollution episodes in Beijing.

SNA greatly increased the $PM_{2.5}$ ~~pollutions~~pollution. Unlike the findings from some previous studies ~~(Wang et al., 2016b;Huang et al., 2014a;Ji et al., 2014)~~(Wang et al. 2016; Huang et al. 2014a; Ji et al. 2014), nitrate dominated the water-soluble ions (WSIs) in the winter of 2017. During pollution episodes, concentration of nitrate and sulfate were respectively 23.0±10.7 μg~~/m³~~ m^{-3} and 13.1±8.4 μg~~/m³~~ m^{-3}, with an average molar ratio of nitrate to sulfate ($Ratio_{N\text{-}to\text{-}S}$) around 3.3 ±1.4. Fig.3 ~~showed~~shows the correlation of nitrate and sulfate with the total water-soluble ions. Sulfate presented a lower fraction when total WSIs was below 65 μg~~/m³~~ m^{-3}, but the ~~slope~~fraction increases as WSIs exceeds 65 μg~~/m³~~ m^{-3}, showing an enhanced formation of sulfate during heavy pollution episodes. Interestingly, the ratio of nitrate to WSIs ~~ratio~~ remained the same throughout the campaign. ~~Considering~~As the concentrations of other components~~' concentration~~ also increased, this phenomenon indicated that the nitrate formation was enhanced in hazy days. ~~The concentration~~Besides, the concentrations of ammonium and ammonia both increased significantly (from 0.9 μg~~/m³~~ m^{-3} to 10.4 μg~~/m³~~ m^{-3}) from the clean to the pollution condition.

3.3 Comparison of major inorganic compositions during the early 21st century in Beijing

To illustrate the changes in chemical ~~composition~~compositions of $PM_{2.5}$ ~~during~~at the China's economy booming stage (1999-2017), nitrate, sulfate and ammonium ~~were~~are chosen for the comparison with ~~previous~~previously reported data during winter in Beijing (Fig. 4). Only winter-averaged ~~winter~~ observation data or representative pollution records ~~were chosen~~are selected to show the significant change of SIA ~~composition~~compositions. On average, ~~though~~although the concentration might be varied due to ~~emission~~different emissions and weather ~~condition variations~~conditions over the years, SIA ~~concentrations~~ concentration in the winter of 2017 ~~were~~was the lowest ~~compare to~~compared with the years before. Sulfate concentration varied from 4.5 μg~~/m³~~ m^{-3} to 25.4 μg~~/m³~~ m^{-3} and contributed the most $PM_{2.5}$ masses among SIA ~~compositions~~species during ~~pollutions~~the pollution episodes before 2015. The emission control of SO_2 started ~~at the year of~~in 2006 to prevent

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adverse atmospheric environment events such as acid rain and high particulate matter loading ~~(Wang et al., 2013;Wang et al., 2018b).~~(Wang et al. 2013; Wang et al. 2018b). As a ~~response,~~result, the sulfate concentration in winter ~~were decreasing~~ decreased gradually (see results of 1999, 2011, 2015-a and 2017), the average concentration in recent years ~~were~~has been much lower than that in the early 2000s ~~–~~(detailed literature comparison ~~could~~can be found ~~at Lang et al. (2017)).~~in Lang et al. (2017)). However, it was widely reported that sulfate still contributed the most ~~of~~to the $PM_{2.5}$ mass concentration during the severe haze ~~period~~periods, such as ~~in~~ the winter of 2013 ~~(Huang et al., 2014a;Guo et al., 2014;Ji et al., 2014). Heterogeneous~~(Huang et al. 2014a; Guo et al. 2014; Ji et al. 2014). The heterogeneous formation might be responsible for the enhanced ~~transfer~~conversion ratio ~~of~~from SO_2 to particulate sulfate, including the NO_2 ~~–~~promoted aqueous reaction and transition ~~–~~metal ~~–~~catalyzed oxidations ~~(Huang et al., 2014b;Xie et al., 2015a).~~(Huang et al. 2014b; Xie et al. 2015). On the other hand, the NO_x emission in ~~north~~North China significantly increased as the ~~amount of~~ power consumption and transportation kept increasing. Therefore, nitrate in $PM_{2.5}$ had been increasing since 2011. ~~Average~~The average concentration of nitrate ~~ranged~~rose from 7.1 μg~~/m³~~ m^{-3} to 29.1 μg~~/m³~~ m^{-3}. By ~~the year of~~ 2015, the nitrate concentration had exceeded the sulfate concentration, and the two equally contributed to PM mass ~~equally as sulfate in pollutions~~ in winter. pollution episodes. Although the nitrate~~'s~~ concentration during pollution ~~period~~periods decreased in 2017 (23.0 μg~~/m³~~ m^{-3}), the decrease was not ~~obvious~~significant and the concentration was still comparable to previous studies. ~~As for~~ The winter-averaged ammonium~~, the winter average~~ concentration reached the maximum (~20 μg~~/m³~~ m^{-3}) in ~~the year of~~ 2015, but decreased afterwards. ~~Taking the role~~ The decreasing trend of ammonium ~~as~~, which is the major neutralizer in the atmosphere of Beijing, ~~the decreasing trend~~ well represented the efficient pollution control of SNA ~~composition~~compositions during the winter of 2017. In a word, ~~nitrate~~ as the dominant composition~~-~~, high nitrate fraction has become one of the major features of $PM_{2.5}$ in Beijing during winter.

The ratio between major SIA ~~compositions could~~components can better represent the composition change

from data discussed above. As shown in figFig.5, the nitrate to sulfate molar ratio (Ratio $_N$Ratio$_{N\text{-to-}S}$) hadhas been increasing significantly from below 1.0 to 2.7 (1999 vs. 2017). Ratio $_N$Ratio$_{N\text{-to-}S}$ was around 1 before 2013 but then steadily increased after the year of 2013, same as previouslyprevious publications (Shao et al., 2018;Lang et al., 2017).(Shao et al. 2018; Lang et al. 2017). Interestingly, Ratio$_{N\text{-to-}S}$ during pollution episodes was lower than the winter average in 2015, but Ratio $_N$Ratio$_{N\text{-to-}S}$ during pollution episodes greatly exceeded the average value in 2017, showing that nitrate'sthe dominance inof nitrate in the present $PM_{2.5}$ pollutions nowadays.pollution. The rapid increase of NRatio$_{N\text{-to-}S}$ ratio from around 1 to nearly 3 was not only resulted from the result of sulfur emission control, itbut also indicates that from more nitrate was formed and enterpartitioning to the particle phase via partitioning.. Abundant ammonia in the Beijing's atmosphere wouldcan enhance the partitioning of nitric acid gas by forming ammonium nitrate. To identify whether the ammonia wasis sufficient, the ammonium to sulfate ratio (Ratio $_A$Ratio$_{A\text{-to-}S}$) wasis calculated with the published data as well. It is reported that North China Plain experienced ammonia insufficient situationinsufficiency during summer (Ammonium to sulfate rationRatio$_{A\text{-to-}S:}$ less than 1.5), thus limitlimiting the formation and partitioning of nitrate into particle phase (Pathak et al., 2009;Pathak et al., 2011).the particle phase (Pathak et al,. 2004; Pathak et al. 2009; Pathak et al. 2011). However, Ratio $_A$Ratio$_{A\text{-to-}S}$ in winter Beijing during winter was always above 1.5, the. The lowest value appeared in 1999 (averaged Ratio$_{A\text{-to-}S}$ averaged: 1.7), then the ratio reached higher levelincreased rapidly (above 3) after the year of 2011 (red bars in Fig.5). In recent years, the ammonium Ratio$_{A\text{-to-}S}$ sulfate ratio s has reached around 4. This value is typically observed in the eastern AmericanAmerica during winter, though the absolute concentration wasis much higher in Beijing (Shah et al., 2018).(Shah et al. 2018). To sum up, these results suggest that the effective sulfur emission control and ammonia -rich atmosphere providedprovide the favorable environment for nitrate formation, and eventually changingchange $PM_{2.5}$ in Beijing from sulfate-dominated to nitrate-dominated type.

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3.4 Aerosol pH's response to ~~$PM_{2.5}$ nitrate fraction~~ the elevation of nitrate fraction in $PM_{2.5}$

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~~The shift from sulfate dominant to nitrate dominant $PM_{2.5}$ will further influence the secondary chemical processes via changing physiochemical properties of aerosols, e.g. hygroscopicity and particle acidity. In a thorough study in the U.S, despite the emission of NO_x was well controlled, nitrate fraction in $PM_{2.5}$ didn't show a corresponding decreasing trend. This was caused by the elevated partitioning of nitric acid to particle phase in eastern America (Shah et al., 2018). Researchers implied that higher nitrate partition fraction could be attributed to increasing particle pH, which is contradictory to some publication focusing on the particle pH's trend in the U.S (Weber et al., 2016). The critical problem on particle pH was more controversial in China since its importance in elucidating the key atmospheric chemistry processes (Cheng et al., 2016b;Guo et al., 2016;Wang et al., 2016b;Weber et al., 2016;Guo et al., 2017a;Liu et al., 2017a). Therefore, it is necessary to study the response of particle acidity to the chemical composition changes based on high resolution observation dataset.~~

The shift from sulfate-dominated to nitrate-dominated $PM_{2.5}$ further influences the secondary chemical processes via changing physiochemical properties of aerosols, e.g. hygroscopicity and particle acidity. In a thorough study in the U.S, despite the well control of NO_x emission, the nitrate fraction in $PM_{2.5}$ didn't show a corresponding decreasing trend. It was caused by the elevated partitioning of nitric acid to the particle phase in the eastern America (Shah et al. 2018). Researchers implied that higher nitrate partition fraction is resulted from the increasing particle pH, while some studies showed that the particle pH was decreasing as particulate sulfate decreases in the U.S (Weber et al. 2016). Since the chemical composition of $PM_{2.5}$ changed significantly, it is necessary to study the relevant response of particle acidity based on high-resolution observation datasets.

In this study, ~~we calculated~~ the bulk particle pH is calculated with the thermodynamic model ISORROPIA II in forward mode with the assumption of aerosol in metastable state. The simulation ~~was~~ is limited to the data with the corresponding RH between 20%–90%, same as that in previous studies (Liu et al. 2017; Cheng et al. 2016). The analysis is further limited to data ~~when RH was between 20% – 90%, same as previous studies (Liu et al., 2017a;Cheng et al., 2016b). We further limit the analysis to data~~ with sufficient ~~aerosol liquid water (~~ALWC~~,~~ (above 5 μg~~/m³~~ m^{-3}) to avoid unrealistic pH values caused by false ~~prediction~~predictions of ALWC. To study the effect of the nitrate fraction's elevation on particle acidity, the ~~Ratio $_N$~~ $Ratio_{N\text{-}to\text{-}S}$ ~~was~~is compared to the bulk particle

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pH (Fig. 6). As the nitrate fraction ~~increased,~~increases, the particle pH ~~also increased~~increases. When the ratio is between 0~~–~~2, predicted pH ~~value was~~values are rather scattered (2.1~~~~~~6.2) with a median value of 4.4. As the ratio increases, pH values ~~became~~become less scattered and the median value ~~increased~~increases as well. When the ratio ~~was~~is around 4~~–~~6, the predicted pH ~~could~~values range from 4.9 to 5.6 with a median value of 5.4, which is ~~favorable for aqueous oxidation of SO_2 by NO_2 (Cheng et al., 2016a;Wang et al., 2016a;Xie et al., 2015b). The~~comparable with previous reported values in $PM_{2.5}$ pollutions (Cheng et al. 2016; Wang et al. 2016; Xie et al. 2015). There are several factors causing the chemistry nature of the pH increasing with higher $Ratio_{N\text{-}to\text{-}S}$ ~~could be attributed to several reasons:~~, including neutralization by ammonia, higher pH of ammonium nitrate in comparison with ammonium sulfate, and increased ALWC ~~led~~leading to dilution of predicted H^+ ~~(Hodas et al., 2014;Xue et al., 2014;Wang et al., 2018c).~~ (Hodas et al. 2014; Xue et al. 2014; Wang et al. 2018c). To confirm that the pH elevation ~~was~~is not caused by crustal ions, the simulation using data without crustal ions (input is set to ~~zeroes~~0) was conducted. It is shown that the exclusion of crustal ions in the simulation ~~could result~~can cause an overall lower pH, but the pH elevation ~~as~~with $Ratio_{N\text{-}to\text{-}S}$ ~~was~~is still observed~~. For details, please refer to~~ (detailed analysis can be found in the supplementary materials ~~(Fig.~~, Figs. S2~~ Fig.~~ and S3).

~~Less~~ In this study, fewer predicted H^+ ~~ion~~ions in aerosol liquid water ~~was~~were found to be the major cause of the higher pH with high nitrate fraction ~~in this study.~~ The correlation between H^+ and major anions (HSO_4^-, SO_4^{2-}, NO_3^-, Cl^-) ~~was~~is shown in Fig.7 to identify the acidity contribution of each anion. Sulfate and bisulfate ~~had~~have long been recognized as major ~~acid~~acidic components of atmospheric particles. Their concentrations have significant impact on the particle acidity ~~of particles (Weber et al., 2016;Liu et al., 2017a).~~(Weber et al. 2016; Liu et al. 2017). Therefore, the H^+ ion concentration was found to strongly ~~correlated~~correlate with sulfate as well as bisulfate (~~Fig.~~Figs. 7a ~~& Fig.~~and 7b). The ~~outliers might~~outlier data points can be attributed to the fireworks~~' effect~~ events during ~~spring festival~~the Chinese New Year (extreme data on ~~Spring Festival's eve were~~Chinese New Year's Eve are excluded). The average molar ratio of bisulfate to sulfate is 1.~~08x10~~08 × 10^{-6}, indicating that

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most of the sulfate ~~was~~is balanced by ammonium, same as ~~previous studies (Song et al., 2018).~~the results reported by previous studies (Song et al. 2018). The excess ammonium ~~was~~is then balanced by nitrate and chloride. The correlation between H^+ and nitrate ion ~~was~~is much different as ALWC ~~varied~~varies (Fig. 7c). ~~At~~Under the high ~~-~~ ALWC condition, the H^+ increases ~~as~~with the nitrate concentration ~~increase~~, which can be explained by the simultaneously ~~increased~~increasing sulfate fraction during several pollution episodes. ~~At~~Under the drier condition (ALWC < 10μg~~/m^3~~ m^{-3}), as NO_3^- increases, H^+ ~~was decreasing~~decreases, which implies that the weaker aerosol acidity ~~favored~~favors nitric acid partitioning to the particle phase. Since HCl is more volatile than nitric acid gas, ~~it's~~its occurrence in the particle phase is more sensitive to the particle acidity ~~of particles~~ (Fig. 7d). Therefore, the negative correlation with H^+ ~~was~~is much obvious when it ~~came~~comes to chloride, free of ALWC amount.

~~Discussions above showed that sulfate is the main particle acidity contributor in $PM_{2.5}$ in Beijing. Given excess H^+ in the liquid water, HSO_4^- would be formed as the equilibrium theory predicts. Therefore, HSO_4^- to SO_4^{2-} ratio could be a good indicator of aerosol's ability of excess H^+ formation. To understand the chemical nature of the elevation of pH with increasing $Ratio_{N\text{-}to\text{-}S}$, correlation between bisulfate/sulfate and $Ratio_{N\text{-}to\text{-}S}$ was investigated (Fig.8). The bisulfate/sulfate ratio significantly decreased when nitrate fraction increased, indicating that there were less free H^+ in ALWC when nitrate dominates the chemical composition of $PM_{2.5}$. From these results and the fact that moderate pH is more favorable for the partitioning of nitric acid gas to particle phase (Shah et al., 2018), the larger the fraction of nitrate in $PM_{2.5}$ is, the more balancing of anion by ammonium and less H^+ would be expected.~~

~~The low level of H^+, especially its negative correlation with $Ratio_{N\text{-}to\text{-}S}$ should be attributed to the neutralization by ammonia. Under most conditions, the excess of ammonia is an implicit prerequisite for SIA formation in Beijing, and the excessing level would affect the predicted particle acidity (Guo et al., 2017a;Weber et al., 2016). As an auxiliary evidence, the observed ammonia partition fraction (F_{NH4}) was investigated to quantify the ammonia excess and its relation with particle acidity. It could be easily seen that F_{NH4} exhibited a positive trend as $Ratio_{N\text{-}to\text{-}S}$ increases (Fig.9). The trend is divided into two branches colored by predicted pH: a more acidic (pH below 4.5) branch with $Ratio_{N\text{-}to\text{-}S}$ range between 1 to 3 and F_{NH4} ranges between 0.1 to 0.6; and another less acidic (pH above 5.5) branch with $Ratio_{N\text{-}to\text{-}S}$ range in 1 to 7 and F_{NH4} range between 0.1 to 0.4. When airborne particles exhibit higher acidity, it is more favorable for ammonia partitioning to particle phase. Also, sulfate could accommodate twice the ammonia than nitrate, making the higher F_{NH4} in the upper branch. On the other hand, increased particle pH would prevent ammonia from partitioning to particle phase (Guo et al., 2017a), and the decrease in $PM_{2.5}$ sulfate concentration might probably lead to higher ammonia concentration in the atmosphere according to recent study (Liu et al., 2018). Therefore, the elevation of F_{NH4} at high pH (5~6) along with increasing $Ratio_{N\text{-}to\text{-}S}$ (between 1 to 4) implied that the~~

~~nitrate formation was promoted by higher tropospheric ammonia concentration (Wang et al., 2013). When Ratio $_{N-to-S}$ was above 4, F_{NH4} decreased as pH increased. From above discussions, observation and model results showed that fine particle enriched in nitrate during winter in Beijing will lead to lower particle acidity.~~

The low level of H^+, especially its negative correlation with $Ratio_{N-to-S}$ should be attributed to the neutralization by ammonia via gas-particle partitioning. Under most conditions, the excess of ammonia is an implicit prerequisite for SIA formation in Beijing, and higher NH_3 concentration could increase the predicted particle pH (Guo et al. 2017; Weber et al. 2016). As an auxiliary evidence, ammonia partition fraction (F_{NH4}, calculated with observation data) exhibits a positive trend as $Ratio_{N-to-S}$ increases (Fig. 8), while ammonia concentration remains less varied in the same case (Fig.S4). The positive trend is divided into two parts: a more acidic (pH below 4.5) branch with $Ratio_{N-to-S}$ of 1–3 and F_{NH4} of 0.1–0.6 and the other less acidic (pH above 5.5) branch with Ratio $_{N-to-S}$ of 1–7 and F_{NH4} of 0.1–0.4. The overall higher F_{NH4} in the lower pH branch is reasonable since it is more favorable for ammonia partitioning to the particle phase when airborne particles exhibit higher acidity. Moreover, sulfate can accommodate twice amount of ammonia than nitrate and thus increase F_{NH4}. Yet, the highest value of F_{NH4} were observed with more nitrate (Ratio $_{N-to-S}$ ~2.5) and a slightly higher pH. By contrast, even though the high particle pH (5~6) can prevent ammonia from partitioning to the particle phase (Guo et al. 2017), the elevation of F_{NH4} with increasing Ratio $_{N-to-S}$ (1–4) is still observed with pH ranging 5 to 6 despite there were some outliers with lower F_{NH4} which is not caused by higher NH_3 concentration. Nitrate formation is observed to be enhanced in North China, either by heterogeneous formation (e.g. N_2O_5 hydrolysis) or with sufficient ambient NH_3 (Wang et al. 2013). The positive trend of F_{NH4} with $Ratio_{N-to-S}$ clearly shows that nitrate formation and partitioning have significant contribution to NH_3 partitioning process, and will lead to an enhanced neutralization with the help of more ammonia partitioning into the particle phase. Combining these analyses, we conclude that fine particles enriched in nitrate in Beijing during winter will lead to lower particle acidity.

4. Discussion: ~~Possible~~possible impacts of increasing fraction of nitrate in $PM_{2.5}$

So far, the effect of emission control~~'s effect~~ on SNA ~~composition~~compositions in Beijing's $PM_{2.5}$ pollution and the response of particle pH ~~was~~have been illustrated, but it is important to make ~~future~~ predictions with the ~~currently~~current knowledge for future better control strategy. In this section, sensitivity tests regarding to hygroscopicity and particle ~~-~~acidity change ~~were~~are conducted to help understand the possible changes of these properties in the future. ~~Aerosol liquid water content (ALWC) was~~ALWC is directly engaged in the calculation of particle pH and limited by several major parameters (~~relative humidity~~RH, hydrophilic composition ~~concentrations, temperatures~~concentration, temperature, etc.). During the campaign, the ALWC predicted by ISORROPIA II varied between 0.8 ~~to~~and 154.2 $\mu g/m^3$ m^{-3} with an average value of 6.4 $\mu g/m^3$ m^{-3}. As previously mentioned, the average value of $Ratio_{N\text{-}to\text{-}S}$ ~~was~~is around 2 during the haze ~~event~~events in the winter of 2017 in Beijing. The average ALWC in the haze events increased to 24.4 $\mu g/m^3$ m^{-3} accordingly. It has been reported that nitrate salts have ~~larger~~greater contribution to ALWC due to its lower deliquescence RH, and the elevated ALWC might ~~have~~has strong impact on ~~several~~water-soluble gas partitioning such as glyoxal, leading to ~~further secondary composition formation processes (Hodas et al., 2014;Xue et al., 2014).~~an enhanced SOA production (Hodas et al. 2014; Xue et al. 2014). As a matter of fact, the increase of hygroscopicity related to nitrate-rich fine particles ~~have~~has been observed in Beijing ~~(Wang et al., 2018c).~~ (Wang et al. 2018c). However, ~~though the possibly higher ALWC in nitrate rich particles might lead to dilution of H^+, it was~~ it is difficult to conclude that ~~the~~lower pH in nitrate ~~-~~rich particles ~~have~~is caused by the dilution of H^+ with higher ALWC with current data, since the higher nitrate fraction ~~was~~is usually observed with the moderate RH in pollution episodes in the winter of 2017.

~~Moving on now to consider the~~The possible enhancement of hygroscopicity in nitrate ~~-~~rich $PM_{2.5}$~~. For most~~ was investigated. Most single salts~~,~~ can only be deliquesced over a certain RH ~~it can be deliquesced, which often behaves in a way that~~ , thus the ALWC only exists when a certain RH is exceeded ~~(Wexler and Seinfeld, 1991;Mauer and Taylor, 2010). However, the atmospheric~~(Wexler and Seinfeld 1991; Mauer and Taylor 2010). In

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real atmosphere, aerosols ~~contain varieties of chemical compositions and thus making it a~~ are usually a mixture of salts~~,~~ and organics, which might ~~significantly reduce the deliquescence point.~~be easier to deliquesce. In addition, the deliquescence ~~behavior~~ of NH_4NO_3 is unique, and it becomes more complicated in the system of NH_4NO_3/$(NH_4)_2SO_4$. The NH_4NO_3 ~~only~~ system would ~~absorbs~~absorb water vapor even at an extreme low ~~relative humidity~~ RH (down to 10%%) ~~(Willeke et al., 1980;ten Brink and Veefkind, 1995).~~(Willeke et al. 1980; ten Brink and Veefkind 1995). The system comprised of NH_4NO_3/$(NH_4)_2SO_4$ ~~would have a~~has a higher deliquesce point when the sulfate content is higher ~~deliquesce point when sulfate content is higher~~ ($Ratio_{N\text{-}to\text{-}S}$ ~~<~~ <1), but ~~will~~ absorbs water even at low RH (~20%) when nitrate is dominant ($Ratio_{N\text{-}to\text{-}S}$ > 2) in $PM_{2.5}$ inorganic ions ~~(Wexler and Seinfeld, 1991;Ge et al., 1996, 1998).~~(Wexler and Seinfeld 1991; Ge et al. 1996, 1998). Inspired by these facts, we conducted ~~ALWC~~a sensitivity test of ALWC to RH by using the observation dataset to study the effect of nitrate fraction elevation on ALWC changes (the RH value ranging from 20% to 90%%, with 10% as interval). ~~Only data during transition or pollution period was analyzed here, since~~Concentrations of pollutants in the clean periods are relatively low and the data ~~during~~of the clean ~~period~~periods might be more influenced ~~more~~ by the observation artifacts. Thus, only the data obtained in the transition and pollution conditions were analyzed here. The ALWC changes ~~were~~are defined as Eq (1) ~~:~~).

$$Fraction_{change} = ALWC_{(RH+10\%)}/ALWC_{RH} \quad \text{~~Eq~~(1)).}$$

Then, we ~~limit~~choose the data with ~~two conditions: Ratio~~ $_N$$Ratio_{N\text{-}to\text{-}S}$ above 3 and $Ratio_{N\text{-}to\text{-}S}$ below 1. These values were both mentioned in previous lab studies ~~(Ge et al., 1998)~~(Ge et al. 1998) and are also typical values of nitrate ~~-~~rich or sulfate ~~-~~rich conditions in field observations. As shown in Fig.~~10~~ 9, $PM_{2.5}$ with higher ~~Ratio~~ $_N$$Ratio_{N\text{-}to\text{-}S}$ adsorbs more water than lower nitrate fraction as the RH increases~~. When the RH was low (20%-40%), the increase of ALWC was~~, which is more significant ~~compare to~~under lower RH (<50%) conditions compared with that uner higher RH ~~range~~ (50~~%-%~~70%). ~~Considering that at the starting stage of $PM_{2.5}$ pollutions, the relative~~

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humidity was%) conditions. As the RH is usually lower (30% – 50), the –50) at the beginning stage of $PM_{2.5}$ pollution development in Beijing, such a significant increase ofin hygroscopicity inof nitrate –rich particles mightcan greatly enhance the uptake of precursor gases or promote the haze formation under relatively dry conditions by enhancing the gas-to-particle partitioning of water-soluble compounds and the aqueous-phase formation of secondary formations or precursor uptake processes e.g.aerosols, e.g. ammonia partitioning and nitrate formation through partitioning or hydrolysis of N_2O_5 (Badger et al., 2006;Bertram and Thornton, 2009;Sun et al., 2018;Hodas et al., 2014;Shi et al., 2019)(Badger et al. 2006; Bertram and Thornton 2009; Sun et al. 2018; Hodas et al. 2014; Shi et al. 2019).

Particle pH's response to ammonia and sulfate changes was established in previous studies (Weber et al., 2016;Guo et al., 2017a;Murphy et al., 2017). The response of particle pH to ammonia and sulfate changes has been indicated in previous studies (Weber et al. 2016; Guo et al. 2017; Murphy et al. 2017). Here we further analyze the particle pH inunder the condition of elevated nitrate concentration with the increasing level of ammonia in the atmosphere, which areis expected to be the case for most of Chinese cities in the nextcoming years. Two versionskinds of pH sensitivity test weretests are conducted: one with fixed nitrate but varying sulfate and ammonia varies;and the other one with fixed sulfate input but varying nitrate and ammonia varies (Fig.11 10). In the test, crustal ions were all set to zeroas 0, while fixed chloride, sulfate and nitrate concentration concentrations were set with pollutionas the average data in pollution (see Table 2). To compare with previous publications (Guo et al., 2017a;Song et al., 2018)Compared with previous studies (Guo et al. 2017; Song et al. 2018), the RH was set toas 58% and the temperature was set toas 273.15K. Despite system errors due to the instability of the model at the extreme high -anion and low -NH_x condition (Song et al., 2018), the pH showed continuous changing as(Song et al. 2018), the pH shows continuously changing as the free variable changes. The significant sharp edge of pHpHs in both plot definedplots defines the ion balance condition. We selected observation inthe observations data obtained during the pollution conditionepisodes within the RH rangeranging

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from 50% to 70% to compare with the ~~result~~results of both sensitivity ~~test. Apart~~tests. As shown in Fig.10, apart from some data points (those with ~~less~~lower nitrate concentration but very high NH_x concentration), observation data ~~display was~~(triangle points) are quite well merged into the results of sensitivity ~~test results~~tests, and the pH values ~~were~~are generally higher than the test ~~result~~results due to the lack of crustal ions ~~as input in~~inputting the sensitivity simulation. Therefore, the result of sensitivity tests ~~could~~can well represent the pH change of the real atmosphere environment in Beijing.

Future ~~prediction of~~changes in particle pH ~~could~~can be found with ~~the result of~~ the sensitivity test results. Cutting down the sulfate concentration without reducing atmospheric ammonia (horizontally moving from right to left in Fig.~~11, Left~~ 10, left part) ~~would~~can lead to a significant increase of particle pH (up to 5). As ~~could~~can be seen from the right part of Fig.~~11~~10, the elevation of ~~particle pH might be enhanced with the help of more nitrate in $PM_{2.5}$. The effect of nitrate on~~ particle pH ~~rely~~ might be enhanced with the help of more nitrate in $PM_{2.5}$. The effect of nitrate on particle pH greatly relies on the ~~concentration of~~ NH_x concentration in the atmosphere. ~~Considering~~As the ammonia in the atmosphere ~~of~~over North China might still be increasing ~~(Liu et al., 2018)~~(Liu et al. 2018), and the sulfur content in the atmosphere might not be greatly ~~be further~~ reduced in the future, the particle pH shall increase in the path along the ion balance edge, which also implies a synergetic effect of increased nitrate and ammonia.

~~Together these~~ These results (lower acidity, higher hygroscopicity) provide insights into the possible effects of an elevated nitrate content on the physiochemical properties of particles~~: (1) Heterogeneous~~. First, heterogeneous reactions that don't need high acidity might ~~be of great contribution~~greatly contribute to the airborne particle chemistry, such as the NO_2 -induced oxidation of SO_2 mechanism ~~(Cheng et al., 2016b;Wang et al., 2016b).~~(Cheng et al. 2016; Wang et al. 2016). Reactions which rely greatly on acidified ~~particle~~particles might ~~have~~contribute less ~~contribution~~, such as the acid -catalyzed SOA formation from VOCs~~(Jang et al., 2002;Surratt et al., 2010). (2) The~~ (Jang et al. 2002; Surratt et al. 2010). Second, the uptake processes of gaseous compounds onto particles (carbonyl

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acids, for example) might be enhanced, and the uptake of alkaline ~~compound~~compounds could also be enhanced via the ALWC elevation ~~of ALWC. (3) Optical~~. Third, optical properties of particles ~~would~~will greatly ~~be varied:~~vary. On one hand, higher ALWC ~~would~~can increase the light scattering effect~~(Titos et al., 2014)~~ (Titos et al. 2014), while the light absorption ~~of~~by BrC would be enhanced ~~with higher pH(Phillips et al., 2017).~~at higher pH (Phillips et al. 2017). All these facts might add up ~~to~~ the difficulties to the control of moderate haze in Beijing, which usually ~~occurred~~occurs with lower RH and higher nitrate content as shown in this study. It is strongly suggested that the control strategy should be made accordingly based on thorough and scientific evaluation on both NO_x and ammonia ~~to be made accordingly~~.

5 Conclusions

~~This study firstly reported observation of~~Due to the strict emission controls, $PM_{2.5}$ ~~inorganic compositions as well as other common atmospheric components~~in Beijing during the winter of 2017~~. Due to the strict emission control actions, $PM_{2.5}$ concentrations~~, greatly decreased to a low level (39.7 μg~~/m³~~ in~~ m^{-3} for daily~~, on~~ average~~).~~ ~~But~~ concentration), but moderate haze episodes still frequently occurred ~~and~~in the ~~highest $PM_{2.5}$ concentration even reached 300 μg/m³. Combining~~city. With the observation and ~~historic~~historical data, we found that the SO_2 concentration decreased significantly while the NO_2 concentration far exceeded that of SO_2 and kept increasing in Beijing during winter ~~of Beijing~~. In ~~respond~~response to the emission control, the nitrate concentration exceeded the concentration of sulfate significantly and thus became the dominant SIA component in fine particles. The molar ratio of nitrate to sulfate kept increasing over the years and rose to 2.7 during $PM_{2.5}$ pollution episodes in the winter of 2017. The ammonium to sulfate ratio ~~was~~has always been above 1.5 in Beijing, and has exceeded 3 ~~ever~~ since ~~the year of~~ 2011~~, suggesting the~~. Such a sufficient ammonia is favorable ~~condition~~ for the nitrate formation ~~with sufficient ammonia in~~ in Beijing. During the campaign the ~~Beijing winter atmosphere.~~pH of $PM_{2.5}$ increased from 4.4 to 5.4 as the molar ratio of nitrate to sulfate increased from 1 to 5, which is firstly due to the less amount

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of sulfate that suppressed the formation of H^+ and secondly due to the ammonia neutralizing.

~~Secondly, what follows is an account of the chemical composition changes' effects on acidity of the particles, and it was examined using thermodynamic modeling. The pH of $PM_{2.5}$ predicted with observation data increased from 4.4 to 5.4 as molar ratio of nitrate to sulfate increased from 1 to 5. The cause of pH elevation with higher nitrate fraction was discussed in this study: Firstly, main acidity contributor- sulfate was found to be neutralized by ammonium, and the increase of nitrate to sulfate ratio will suppress the formation of H^+. Secondly, enhanced ammonia partitioning was found with nitrate fraction increase, indicating that the pH elevation was mainly due to the ammonia neutralizing.~~

~~Lastly, sensitivity test~~Sensitivity tests of particle hygroscopicity and acidity ~~was~~were conducted to investigate the possible changes ~~of~~in the physiochemical properties if ammonia and nitrate ~~were~~are not well controlled in China in the future. The results showed that the nitrate-rich particles ~~(Ratio $_{N.to.S}$) would~~can absorb more water than particles ~~that have~~with higher sulfate fractions ~~at~~under a moderate humid conditions (RH ~~(below <~~60~~%). On the other hand, %)~~, and the particle pH ~~would increase~~increases rapidly ~~with~~due to the synergetic effect of ammonia and nitrate ~~both increases~~, which ~~is~~will very likely occur in China ~~since~~in the following years, because both the pollutants are not well controlled yet. ~~These~~Those changes ~~would~~will enhance the uptake of gaseous ~~compound~~compounds, promote the chemical reactions which ~~favors~~favor lower acidity, and ~~might~~ also affect the optical properties of airborne particles in ~~winter Beijing. In conclusion~~China. Therefore, the processes and properties of haze particles during ~~nitrate~~ nitrated-dominated ~~$PM_{2.5}$ pollutions~~periods in the country need to be thoroughly investigated with more consideration on the more hygroscopic and neutralized particles.

Author contribution

~~YN.~~G.H. Wang conceived the study and designed the experiment. YN. Xie conducted the online IGAC-$PM_{2.5}$ chemical composition analysis and filter sampling in Beijing during the campaign. GQ. Tang, LL. Wang, YS. Wang and J. Gao provided other related observation data used in this article, including trace gases, PM mass concentrations, ~~meteorology~~meteorological data. G.H. Wang, XP. Wang, YB. Chen, GY. Xue and SS. Ge conducted the lab analysis of filters ~~as well as~~and the data QA/QC. YN. Xie ~~conducted the~~ , G.H. Wang and J.M.

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Chen performed the data analysis ~~of overall data QA/QC and thermodynamic modeling.~~. YN. Xie and ~~GH.~~G.H. Wang ~~prepare the manuscript with~~wrote the ~~help of JM.Chen on editing.~~paper. All the co-authors ~~contribute~~contributed to the data interpretation and discussion~~.~~

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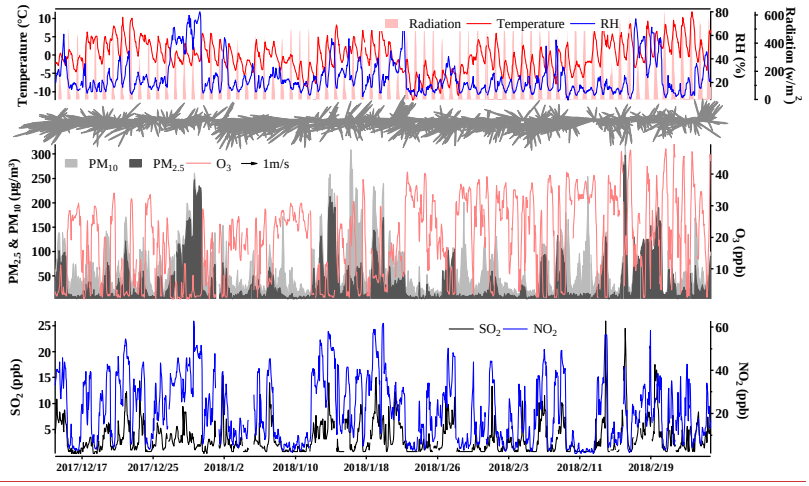

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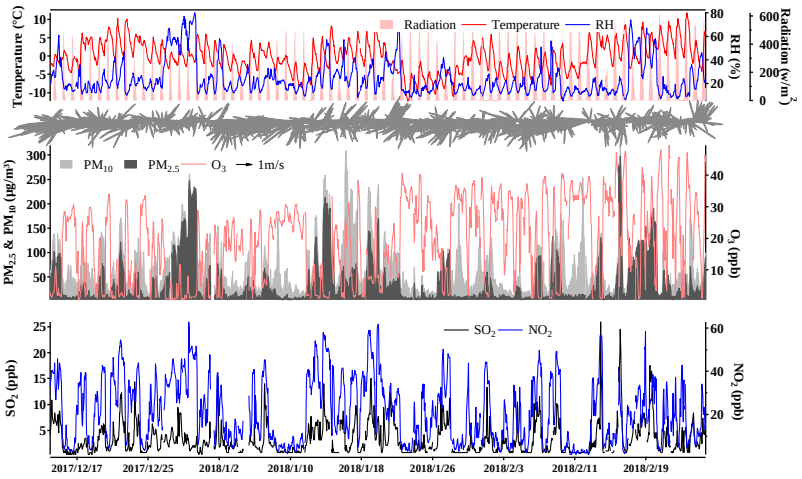

FIG. 1. Timeseries of major pollutants during the campaign. Upper panel: ~~Radiation~~radiation, temperature ~~and~~ RH~~,~~ and wind arrows ~~were draw~~(drawn below~~; Middle~~); middle panel: $PM_{2.5}$, PM_{10} and ~~Ozone~~ozone concentration~~. Lower;~~ lower panel: SO_2 and NO_2 concentrations.

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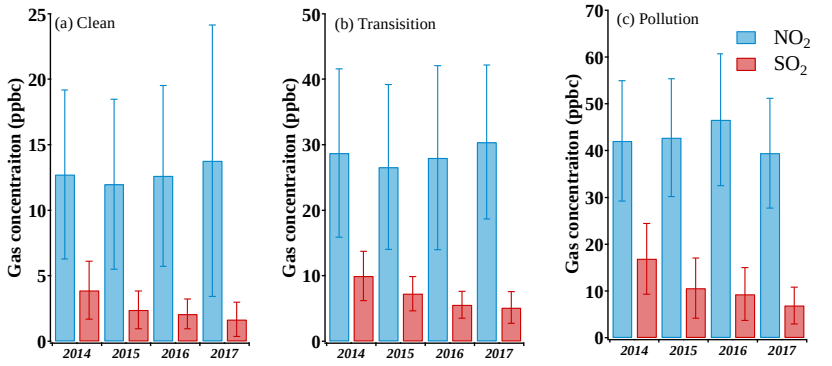

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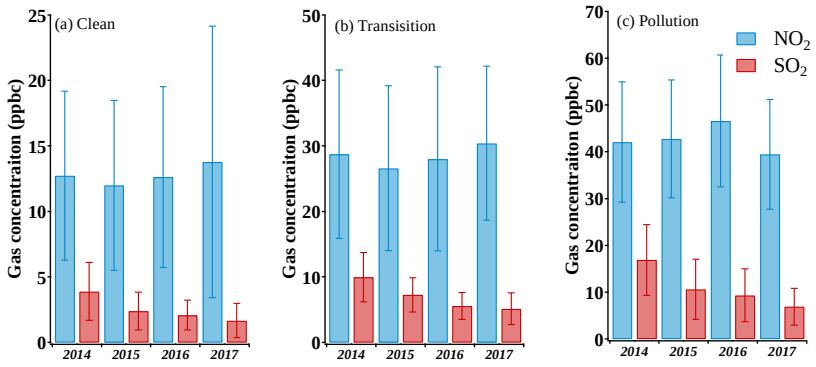
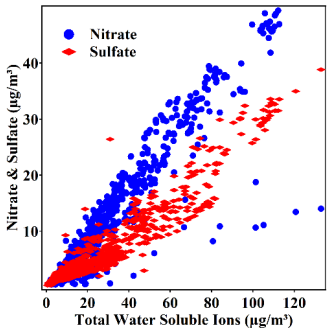


FIG. 2. Statistics plot of NO_2 and SO_2 measured in downtown of Beijing ~~in~~at different $PM_{2.5}$ levels during winter (December ~~–~~–February) for the past 4 years. ~~History~~Historical data (2014~~–~~2016) ~~were obtained~~are from air quality real-time publishing platform, China National Environmental Monitoring Center~~. Data~~, and data of 2017 ~~was~~is obtained during the campaign.



~~Figure.~~FIG. 3. Scatter ~~plot~~plots of nitrate and sulfate vs. WSIs during the campaign.

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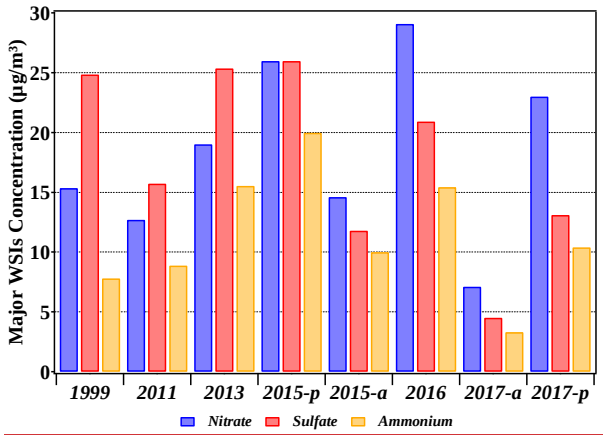

~~Figure.~~

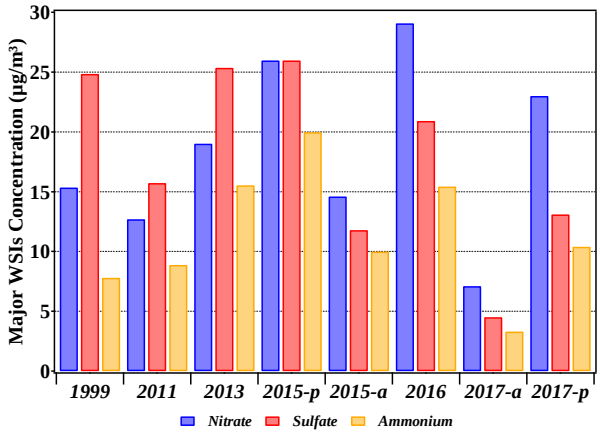

FIG. 4. Major inorganic compositions in $PM_{2.5}$ observed in Beijing during winter ~~in Beijing~~ from representative ~~research~~ articles. The ~~result~~results of 2017 denote the average concentration during haze ~~condition~~episodes in this study. For details of the reviewed literature, please refer to Table S1.

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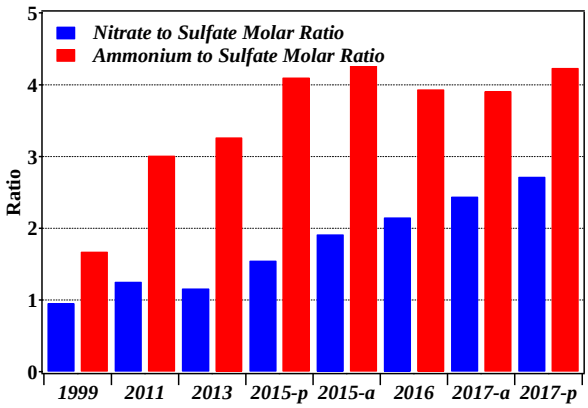
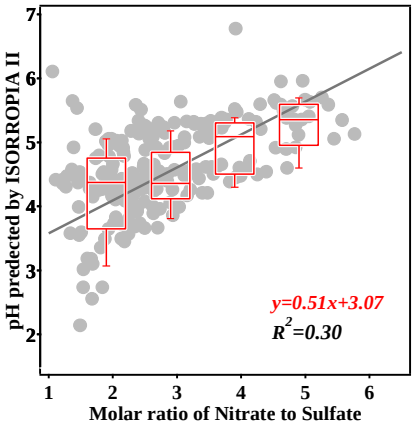


~~Figure.5 Molar ratio of nitrate to sulfate and molar ratio of ammonium to sulfate~~FIG. 5. $Ratio_{N\text{-}to\text{-}S}$ and $Ratio_{A\text{-}to\text{-}S}$ calculated from the averaged data reported in representative research articles. Only the data in pollution ~~condition was~~episodes is chosen for 2017.



~~Figure.~~FIG. 6. Scatter plot of simulated pH vs. ~~the molar ratio of nitrate to sulfate (~~$Ratio_{N\text{-}to\text{-}S}$~~).~~ Linear fitting and the

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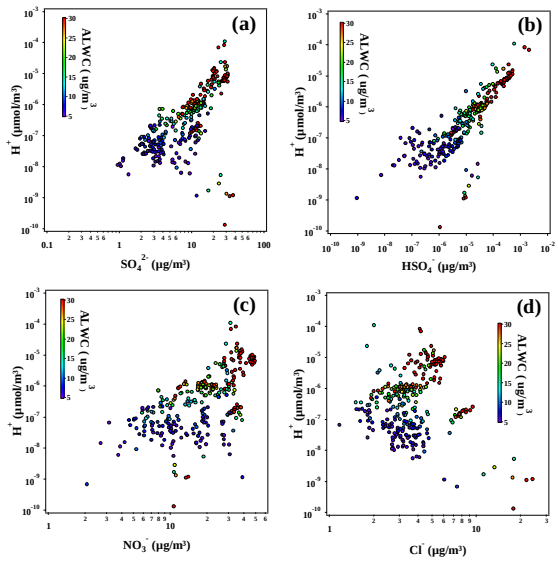
correlation coefficient ~~were~~are given ~~in the figure.~~. The box plot denotes the data points classified by ~~four~~4 different ranges of the Ratio$_{N\text{-}to\text{-}S}$: 0–2;2–3;3-~~4;~~4-~~;~~ and 4–6. Only the data ~~during~~ corresponding to the pollution ~~classification~~categories and with sufficient aerosol liquid water (above 5 μg~~/m^3) was~~ m^{-3}) is chosen and the data ~~from~~during Chinese New Year ~~was~~is excluded.



~~Figure.~~FIG. 7. Scatter ~~plot~~plots of simulated H^+ ion vs. major inorganic anions~~:~~, including (a) SO_4^{2-}, (b) HSO_4^-, (c)NO_3^- ~~;~~ and (d)Cl^-~~, note that~~ ; the coordinates are in logarithm.

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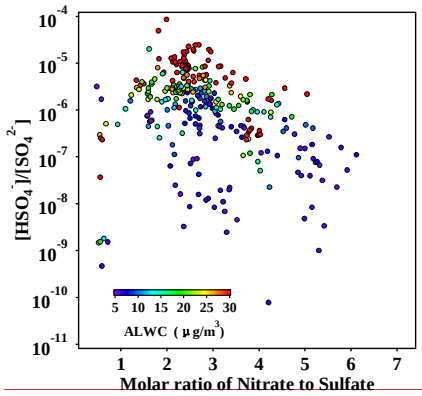
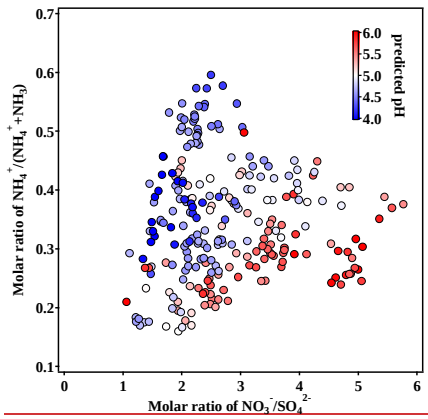


~~Figure.8 Scatter plot of $[HSO_4^-]/[SO_4^{2-}]$ vs. molar ratio of nitrate to sulfate.~~ **Only** the **data** ~~of ALWC above 5μg/m^3 were chosen~~corresponding to the pollution categories and with sufficient aerosol liquid water (above 5 μg m^{-3}) is chosen and the data during Chinese New Year is excluded.



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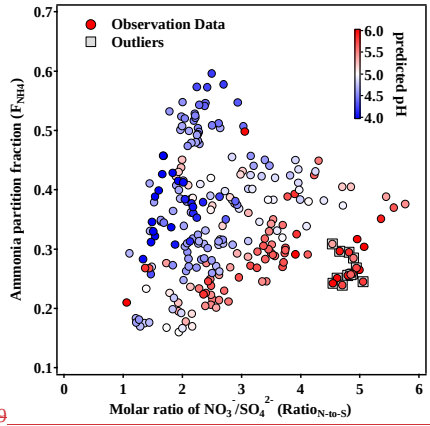
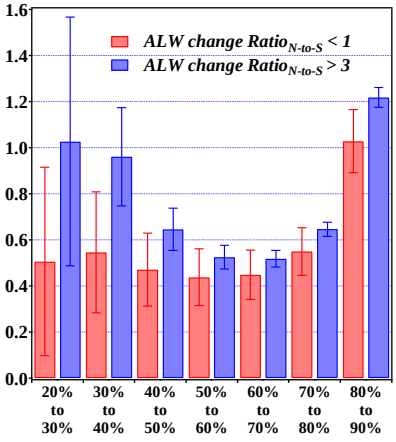


~~Figure.9~~

FIG. 8. Scatter plot of ~~conversion ratio of NH_3~~ F_{NH4} vs. the ~~molar ratio of nitrate~~ $Ratio_{N\text{-}to\text{-}sulfate\text{-}S}$ colored with predicted pH.



~~Figure.10 relative~~ Only the data corresponding to the pollution categories and with sufficient aerosol liquid water (above 5 μg m^{-3}) is chosen and the data during Chinese New Year is excluded. Note that the grey frame depicts the outliers which have lower F_{NH4} and lower Ammonia concentration.

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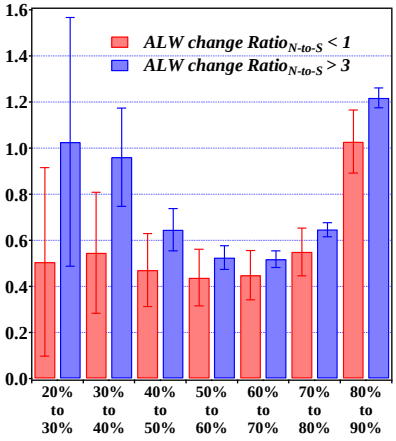

855 **FIG. 9. Relative ALWC change due to the RH elevation ~~of RH in~~at different ~~nitrate to sulfate molar ratio.~~Ratio$_{N\text{-}to\text{-}S}$. Bars represent the relative change amount, and whiskers depict the standard deviation.**

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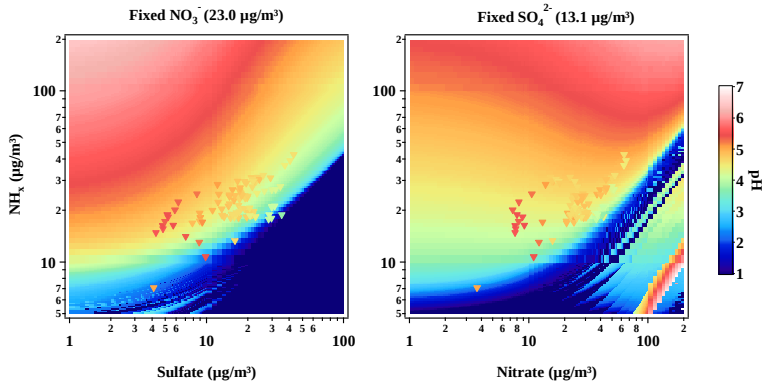

~~Fig.11~~FIG. 10. Sensitivity ~~test~~tests of pH's ~~responding~~response to ~~Sulfate~~sulfate or ~~Nitrate~~nitrate change with inputting given NH$_x$ ~~as input~~, simulated by ISORROPIA II. ~~Selected~~Field measurement data ~~was~~(triangles) were drawn upon the

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simulation data and colored with predicted pH, respectively. ~~Simulation was~~The simulation is conducted with fixed RH (58%) and temperature (273.~~15K~~15 K).

Table ~~.~~ 1. Visibility and concentrations of major pollutants in Beijing during the ~~2017~~ winter ~~campaign.~~ of 2017

	Average	Clean	Transition	Pollution
Visibility	~~15007±10227~~15±10	~~20278±9499~~20±9.5	~~11728±8259~~12±8.3	~~7467±6570~~7.5±6.6
$PM_{2.5}$	39.7±47.1	13.0±7.8	52.0±11.4	128.~~0~~±46.5
PM_{10}	68.5±53.9	42.2±27.9	99.2±43.3	153.3±52.1
O_3	18.5±12.8	23.6±11.2	10.6±10.0	8.4±10.3
SO_2	3.2±3.1	1.7±1.3	5.1±2.5	6.9±1.3
NO_2	21.4±14.8	13.8±10.4	32.8±9.6	39.8±11.6

Table ~~.~~ 2 ~~Gases &~~. Concentrations(μg/m^3) of ammonia and inorganic ~~components~~ions of $PM_{2.5}$ measured by IGAC during the campaign.~~.~~

~~Unit :μg/m^3~~	Average	Clean	Transition	Pollution
NH_3	7.1±5.9	4.3±3.3	9.5±4.9	12.9±7.4
Na^+	0.3±0.3	0.2±0.4	0.4±0.2	0.5±0.2
NH_4^+	3.3±4.4	0.9±0.8	3.7±2.4	10.4±4.8
K^+	0.7±2.4	0.2±0.3	0.7±0.9	2.3±5.1
Mg^{2+}	0.2±0.5	0.2±0.6	0.2±0.1	0.4±0.7
Ca^{2+}	0.5±0.5	0.4±0.6	0.5±0.4	0.5±0.2
Cl^-	2.4±2.3	0.9±0.8	2.3±0.8	4.6±2.9
NO_3^-	7.1±9.6	1.7±1.4	7.9±3.2	23.0±10.7
SO_4^{2-}	4.5±5.9	1.8±1.6	4.2±2.2	13.1±8.4

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