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Discussions

Observation of nitrate dominant $PM_{2.5}$ and particle pH elevation in urban Beijing during the winter of 2017

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Abstract. Particle acidity is crucial to understand secondary formation processes in pollution events since acidity has substantial impacts 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 mechanisms 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 pollution control actions, average $PM_{2.5}$ concentration reduced to a low level (39.7μg/m^3) in urban Beijing during winter of 2017. Compare to history record (2014-2017), SO_2 gradually decreased to a low level (3.2ppbv in 2017 winter) while NO_2 kept increasing (21.4ppbv in 2017 winter). As a response, nitrate's contribution (23.0μg/m^3) to $PM_{2.5}$ become dominant over sulfate (13.1μg/m^3) during $PM_{2.5}$ pollution episodes. The 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/m^3, 12.9μg/m^3 during pollution). During $PM_{2.5}$ pollution episodes, the particle pH predicted increased from 4.4 (moderate acidic) to 5.4 (near neutral) as nitrate to sulfate molar ratio 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 were more neutralized as nitrate content elevated. In the final part, future prediction of particle acidity change was discussed via sensitivity tests: On one hand, nitrate rich particles would absorb more water compared to the sulfate rich particles. This absorption contrast doubles with low to moderate RH (20%~50%). On the other hand, increased level of nitrate and ammonia would have synergetic effects leading to rapid elevation of particle pH to merely neutral (above 5.6). As moderate haze might occur more frequently with high ammonia and particulate nitrate concentration, the major chemical processes during haze events and the control target shall be re-evaluated to obtain the most effective control strategy.

1 Introduction

Severe haze had been causing 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 actions were taken to reverse the worsening atmospheric environment situation, including cutting down the pollutants' emission with forced installation of catalytic converter on vehicles, buildings of clean-coal power generation system, and prohibition of crop residue burning in harvest season, etc.(Chen et al., 2017;Zhang et al., 2012;Liu et al., 2016). As a result, $PM_{2.5}$ pollutions were relieved to a level that met the goals in AIR POLLUTION PREVENTION AND CONTROL ACTION PLAN (issued by the state council of China, http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm, in Chinese). Among all the regions of interests, Beijing achieved great success in $PM_{2.5}$ controlling (annual average $PM_{2.5}$ concentration of 2017 was 58μg/m^3). Yet, compare to 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 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

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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).

China's air pollution control has entered the second phase: further mitigation 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 to investigate how the particle acidity of $PM_{2.5}$ would change as sulfur emission was well controlled in Beijing. First, general information of the atmospheric components including the inorganic composition of $PM_{2.5}$ during winter of 2017-2018 was analyzed and compared to previous studies; then, based on observations, the respond of particle acidity to the elevation of nitrate was studied using ISORROPIA II; finally, the possible changes in the future were discussed with 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 mainly emitted from the vehicles, while the industrial emission is much less since the major factory/power plants were moved out of Beijing or phased out due to emission control policy. Overall, this site represents a normal atmospheric environment of urban Beijing, and data obtained from this site is applicable to compare to previous studies in Beijing (Ji et al., 2018).

A continuous online measurement of atmospheric components was conducted with a time resolution of 1-hour. Two 1405 TEOM™ continuous ambient connected to either $PM_{2.5}$ or PM_{10} cyclone inlet (Metone) was engaged to obtain $PM_{2.5}$ and PM_{10} mass concentration. For trace gases (O_3, NO_2, 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, 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. Visibility data from Beijing airport online data was obtained from https://gis.ncdc.noaa.gov/maps/ncei/cdo/hourly. Besides 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 8:00 – 17:50 and nighttime 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+}, 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 of two major parts: sampling unit and analysis unit(Young et al., 2016). A vertical wet annular denuder (WAD) was engaged to collect the gas phase species prior to a scrub and impactor aerosol collector (SIC), while the latter part can efficiently collect particle into liquid samples. During the campaign, 1mM H_2O_2 solution was used as absorption liquid for the air samples. Under most atmospheric conditions, the absorption liquid could well absorb the targeted atmospheric components (e.g. SO_2). An ICS-5000$^+$ ion chromatograph was engaged as analyzer unit in this study. For anions, an AS18 column (2mm×250mm, Dionex™ IonPac™) was used while a CS-16 column (4mm×250mm, Dionex™ IonPac™) was chosen for the analysis of major cations, both running with recommended eluent (solution of KOH for anion/ methane sulfonic acid for cation). The behavior of the system was tested and improved over recent years, and studies of $PM_{2.5}$ water-soluble ions observations were conducted using this instrument (Young et al., 2016;Song et al., 2018;Liu et al., 2017a). A better sensitivity due to advanced suppression technology of the system greatly enhanced its ability to measure trace ions, such as sodium and magnesium, which could be important in particle ion balance studies. For details of the IGAC comparisons with filter sampling results, please refer to supplementary materials (Fig.S1).

3. Results

3.1 Major pollutant levels

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

With strict control actions, $PM_{2.5}$ pollution occurred less and the 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 39.7μg/m^3 and 68.5μg/m^3, respectively. According to $PM_{2.5}$ concentration, three conditions of the atmospheric environment in this study was classified: Clean – below 35μg/m^3; Transition –35μg/m^3 ~ 75μg/m^3; Pollution – above 75μg/m^3. From clean, transition to polluted condition, the average $PM_{2.5}$ concentration was 13.0±7.8μg/m^3, 52.0±11.4μg/m^3 and 128.0±46.5μg/m^3 (as showed in Table 1), indicating that there was still $PM_{2.5}$ pollutions during this winter (maximum hourly $PM_{2.5}$ concentration was 298.0μg/m^3). Average concentration of ozone was 18.5±12.8 ppbv, and the value decreased as $PM_{2.5}$ concentrations increased. Average SO_2 concentration (3.2±3.1ppbv) was almost 10 times lower than NO_2 (21.4±14.8ppbv). This significant contrast of SO_2 and NO_2 concentration could be attributed to the sulfur emission control over recent years and fast increase of gasoline vehicles in Beijing(Cheng et al., 2018;Wang et al., 2018b). Both of the two gaseous pollutant showed increasing trend as $PM_{2.5}$ concentration increases during the haze episodes, but the elevation of NO_2 level was 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, sulfur emission decreased significantly and thus led to lower ambient SO_2 concentration. To better describe this, changes in these the two precursor gases during winter were investigated by examining data from 2014 – 2016 in Beijing. Average values and the standard deviation were plotted in Fig.2. SO_2 showed significant decreasing trend in all three conditions. In 2014, the concentrations of SO_2 were 3.9, 10.0 and 16.9 ppbv in the three conditions. The SO_2 concentration differences between each stage were getting smaller. Until 2017, the difference of SO_2 concentrations in all three stages were within 10ppbv. Meanwhile, NO_2 concentrations kept increasing after 2015 in clean and transition conditions, but in 2017 NO_2 was surprisingly lower than 2014. Besides the fact that the dilution condition was much better than before, more quick and strong actions were taken to prevent $PM_{2.5}$ pollution in 2017, such as construction prohibition, private vehicle restriction and vast shutting down of factories in neighborhood regions (Cheng et al., 2018). The significant drop of NO_2 proves the effectiveness of pollution control actions in 2017.

3.2 $PM_{2.5}$ chemical compositions

Similar to several previous reports, the chemical compositions of $PM_{2.5}$ during 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). The major inorganic ions of $PM_{2.5}$ in Beijing during 2017 winter were ammonium (3.3±4.4μg/m^3), nitrate (7.1±9.6μg/m^3), sulfate (4.5±5.9μg/m^3) and chloride (2.4±2.3μg/m^3). Increase of all the major compositions' concentration was observed as $PM_{2.5}$ concentration increased, but the crustal ion (Na^+, Mg^{2+}, Ca^{2+}) concentrations were less differed in different conditions. Potassium increased during $PM_{2.5}$ pollutions (average concentration 2.3±5.1μg/m^3), indicating the possible contribution from biomass burning sources or fireworks during Chinese New Year. Chloride in $PM_{2.5}$ has been used as a biomass burning and coal consumption tracer. The concentration of $PM_{2.5}$ chloride increased significantly as $PM_{2.5}$ loading got higher, but the imbalance of molar concentration of chloride to potassium suggests that biomass burning might not be the major source of chloride in $PM_{2.5}$ other than coal consumption in Beijing's $PM_{2.5}$ pollution.

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

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

To illustrate the changes in chemical composition of $PM_{2.5}$ during the China's economy booming stage (1999 - 2017), nitrate, sulfate and ammonium were chosen for the comparison with previous reported data during winter in Beijing (Fig.4). Only averaged winter observation data or representative pollution records were chosen to show the significant change of SIA composition. On average, though the concentration might be varied due to emission and weather condition variations over the years, SIA concentrations in the winter of 2017 were the lowest compare to the years before. Sulfate concentration varied from 4.5μg/m^3 to 25.4μg/m^3 and contributed the most $PM_{2.5}$ masses among SIA compositions during pollutions before 2015. The emission control of SO_2 started at the year of 2006 to prevent adverse atmospheric environment events such as acid rain and high particulate matter loading (Wang et al., 2013;Wang et al., 2018b). As a response, sulfate concentration in winter were decreasing gradually (see results of 1999, 2011, 2015-a and 2017), the average concentration in recent years were much lower than the early 2000s (detailed literature comparison could be found at Lang et al. (2017)). However, it was widely reported that sulfate still contributed the most of $PM_{2.5}$ mass concentration during the severe haze period, such as in the winter of 2013 (Huang et al., 2014a;Guo et al., 2014;Ji et al., 2014). Heterogeneous formation might be responsible for the enhanced transfer ratio of 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). On the other hand, NO_x emission in 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 concentration of nitrate ranged from 7.1μg/m^3 to 29.1μg/m^3. By the year of 2015, nitrate concentration exceeded sulfate and contributed to PM mass equally as sulfate in pollutions in winter. Although nitrate's concentration during pollution period decreased in 2017 (23.0μg/m^3), the decrease was not obvious and the concentration was still comparable to previous studies. As for ammonium, the winter average concentration reached maximum (~20μg/m^3) in the year of 2015, but decreased afterwards. Taking the role of ammonium as the major neutralizer in the atmosphere of Beijing, the decreasing trend well represented the efficient pollution control of SNA composition during the winter of 2017. In a word, nitrate as dominant composition has become one of the major features of $PM_{2.5}$ in Beijing during winter.

The ratio between major SIA compositions could better represent the composition change from data discussed above. As shown in fig.5, the nitrate to sulfate molar ratio (Ratio $_{N\text{-}to\text{-}S}$) had been increasing significantly from below 1.0 to 2.7 (1999 vs. 2017). Ratio $_{N\text{-}to\text{-}S}$ was around 1 before 2013 but then steadily increased after the year of 2013, same as previously publications (Shao et al., 2018;Lang et al., 2017). Interestingly, Ratio$_{N\text{-}to\text{-}S}$ during pollution was lower than the winter average in 2015, but Ratio $_{N\text{-}to\text{-}S}$ during pollution greatly exceeded average value in 2017, showing that nitrate's dominance in $PM_{2.5}$ pollutions nowadays. The rapid increase of N-to-S ratio from around 1 to nearly 3 was not only the result of sulfur emission control, it also indicates that more nitrate was formed and enter particle phase via partitioning. Abundant ammonia in Beijing's atmosphere would enhance the partitioning of nitric acid gas by forming ammonium nitrate. To identify whether the ammonia was sufficient, the ammonium to sulfate ratio (Ratio $_{A\text{-}to\text{-}S}$) was calculated with the published data as well. It is reported that North China Plain experienced ammonia insufficient situation during summer (Ammonium to sulfate ration less than 1.5), thus limit the formation and partitioning of nitrate into particle phase (Pathak et al., 2009;Pathak et al., 2011). However, Ratio $_{A\text{-}to\text{-}S}$ in winter Beijing was always above 1.5, the lowest value appeared in 1999 (Ratio$_{A\text{-}to\text{-}S}$ averaged 1.7), then the ratio reached higher level rapidly (above 3) after the year of 2011 (red bars in Fig.5). In recent years, the ammonium to sulfate ratio reached around 4. This value is typically observed in eastern American during winter, though the absolute concentration was much higher in Beijing (Shah et al., 2018). To sum up, these results suggest that the effective sulfur emission control and ammonia rich atmosphere provided favorable environment for nitrate formation and eventually changing $PM_{2.5}$ in Beijing from sulfate-dominated to nitrate-dominated type.

3.4 Aerosol pH's response to $PM_{2.5}$ nitrate fraction elevation

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.

In this study, we calculated the bulk particle pH with thermodynamic model ISORROPIA II in forward mode with the assumption of aerosol in metastable state. The simulation was 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 $5\mu g/m^3$) to avoid unrealistic pH values caused by false prediction of ALWC. To study the effect of nitrate fraction elevation on particle acidity, the Ratio $_{N\text{-}to\text{-}S}$ was compared to bulk particle pH (Fig.6). As nitrate fraction increased, particle pH also increased. When the ratio is between 0-2, predicted pH value was rather scattered (2.1 ~ 6.2) with a median value of 4.4. As the ratio increases, pH values became less scattered and the median value increased as well. When the ratio was around 4-6, the predicted pH could 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 chemistry nature of the pH increasing with higher $Ratio_{N\text{-to-}S}$ could be attributed to several reasons: neutralization by ammonia, higher pH of ammonium nitrate in comparison with ammonium sulfate, and increased ALWC led dilution of predicted H^+ (Hodas et al., 2014;Xue et al., 2014;Wang et al., 2018c). To confirm the pH elevation was not caused by crustal ions, simulation using data without crustal ions (input set to zeroes) was conducted. It is shown the exclusion of crustal ions in the simulation could result an overall lower pH, but the pH elevation as $Ratio_{N\text{-to-}S}$ was still observed. For details, please refer to the supplementary materials (Fig.S2-Fig.S3).

Less predicted H^+ ion in aerosol liquid water was 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 shown in Fig.7 to identify the acidity contribution of each anion. Sulfate and bisulfate had long been recognized as major acid components of atmospheric particles. Their concentrations have significant impact on the acidity of particles (Weber et al., 2016;Liu et al., 2017a). Therefore, the H^+ ion concentration was found to strongly correlated with sulfate as well as bisulfate (Fig.7a & Fig.7b). The outliers might be attributed to the fireworks' effect during spring festival (extreme data on Spring Festival's eve were excluded). The average molar ratio of bisulfate to sulfate is $1.08\text{x}10^{-6}$, indicating that most of the sulfate was balanced by ammonium, same as previous studies (Song et al., 2018). The excess ammonium was then balanced by nitrate and chloride. The correlation between H^+ and nitrate ion was much different as ALWC varied (Fig.7c). At high ALWC condition, the H^+ increases as nitrate concentration increase, which can be explained by the simultaneously increased sulfate fraction during several pollution episodes. At drier condition (ALWC < 10μg/m^3), as NO_3^- increases, H^+ was decreasing, which implies the weaker aerosol acidity favored nitric acid partitioning to particle phase. Since HCl is more volatile than nitric acid gas, it's occurrence in particle phase is more sensitive to the acidity of particles (Fig.7d). Therefore, the negative correlation with H^+ was much obvious when it came 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 $Ratio_{N\text{-to-}S}$, correlation between bisulfate/sulfate and $Ratio_{N\text{-to-}S}$ 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 $Ratio_{N\text{-to-}S}$ 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 $F_{\text{-}NH4}$ 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 $F_{\text{-}NH4}$ 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 $_{N\text{-}to\text{-}S}$ 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.

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

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

Moving on now to consider the possible enhancement of hygroscopicity in nitrate rich $PM_{2.5}$. For most single salts, only over a certain RH it can be deliquesced, which often behaves in a way that the ALWC only exists when a certain RH is exceeded (Wexler and Seinfeld, 1991;Mauer and Taylor, 2010). However, the atmospheric aerosols contain varieties of chemical compositions and thus making it a mixture of salts, organics, which might significantly reduce the deliquescence point. 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 water vapor even at extreme low relative humidity down to 10% (Willeke et al., 1980;ten Brink and Veefkind, 1995). The system comprised of $NH_4NO_3/(NH_4)_2SO_4$ would have a 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 in $PM_{2.5}$ inorganic ions (Wexler and Seinfeld, 1991;Ge et al., 1996, 1998). Inspired by these facts, we conducted ALWC sensitivity test to RH using the observation dataset to study the effect of nitrate fraction elevation on ALWC changes (RH value from 20% to 90% with 10% as interval). Only data during transition or pollution period was analyzed here, since the data during clean period might be influenced more by the observation artifacts. The ALWC changes were defined as Eq(1) :

$$Fraction_{change} = ALWC_{(RH+10\%)}/ALWC_{RH} \qquad Eq(1)$$

Then, we limit the data with two conditions: Ratio $_{N\text{-}to\text{-}S}$ above 3 and below 1. These values were both mentioned in previous lab studies (Ge et al., 1998) and are also typical values of nitrate rich or sulfate rich conditions in field observations. As shown in Fig.10, $PM_{2.5}$ with higher Ratio $_{N\text{-}to\text{-}S}$ adsorbs more water than lower nitrate fraction as RH increases. When the RH was low (20%-40%), the increase of ALWC was more significant compare to higher RH range (50%-70%). Considering that at the starting stage of $PM_{2.5}$ pollutions, the relative humidity was usually lower (30% - 50), the significant increase of hygroscopicity in nitrate rich particles might greatly enhance the uptake of precursor gases or promote secondary formations or precursor uptake processes 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).

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). Here we further analyze the particle pH in the condition of elevated nitrate concentration with increasing level of ammonia in the atmosphere, which are expected to be the case for most of Chinese cities in the next years. Two versions of pH sensitivity test were conducted: one with fixed nitrate but sulfate and ammonia varies; the other one with fixed sulfate input but nitrate and ammonia varies (Fig.11). In the test, crustal ions were all set to zero, while fixed chloride, sulfate and nitrate concentration were set with pollution average data (see Table 2). To compare with previous publications (Guo et al., 2017a;Song et al., 2018), the RH was set to 58% and the temperature was set to 273.15K. Despite system errors due to the instability of the model at extreme high anion and low NH_x condition (Song et al., 2018), the pH showed continuous changing as free variable changes. The significant sharp edge of pH in both plot defined the ion balance condition. We selected observation in pollution condition within the RH range from 50% to 70% to compare with the result of both sensitivity test. Apart from some data points (those with less nitrate concentration but very high NH_x), observation data display was quite well merged into the sensitivity test results and the pH values were generally higher than the test result due to the lack of crustal ions as input in the sensitivity simulation. Therefore, the result of sensitivity tests could well represent the pH change of the real atmosphere environment in Beijing.

Future prediction of particle pH could be found with the result of the sensitivity test. Cutting down sulfate concentration without reducing atmospheric ammonia (horizontally moving from right to left in Fig.11, Left part) would lead to significant increase of particle pH (up to 5). As could be seen from the right part of Fig.11, 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 greatly on the concentration of NH_x in the atmosphere. Considering the ammonia in the atmosphere of North China might still be increasing (Liu et al., 2018), and the sulfur content in the atmosphere might not greatly be further reduced, 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 results (lower acidity, higher hygroscopicity) provide insights into the possible effects of an elevated nitrate content on the physiochemical properties of particles: (1) Heterogeneous reactions that don't need high acidity might be of great contribution to airborne particle chemistry, such as the NO_2 induced oxidation of SO_2 mechanism (Cheng et al., 2016b;Wang et al., 2016b). Reactions which rely greatly on acidified particle might have less contribution, such as the acid catalyzed SOA formation from VOCs(Jang et al., 2002;Surratt et al., 2010). (2) The uptake processes of gaseous compounds onto particles (carbonyl acids, for example) might be enhanced, and the uptake of alkaline compound could also be enhanced via the elevation of ALWC. (3) Optical properties of particles would greatly be varied: On one hand, higher ALWC would increase the light scattering effect(Titos et al., 2014), while the light absorption of BrC would be enhanced with 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 with lower RH and higher nitrate content as shown in this study. It is strongly suggested that the control strategy based on thorough and scientific evaluation on both NO_x and ammonia to be made accordingly.

5 Conclusions

This study firstly reported observation of $PM_{2.5}$ inorganic compositions as well as other common atmospheric components during the winter of 2017. Due to the strict emission control actions, $PM_{2.5}$ concentrations greatly decreased to a low level (39.7μg/m^3 in daily, on average). But moderate haze episodes still frequently occurred and the highest $PM_{2.5}$ concentration even reached 300 μg/m^3. Combining the observation and historic data, we found that SO_2 concentration decreased significantly while NO_2 concentration exceeded that of SO_2 and kept increasing in winter of Beijing. In respond to the emission control, nitrate concentration exceeded 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 in the winter of 2017.The ammonium to sulfate ratio was always above 1.5 in Beijing, and exceeded 3 ever since the year of 2011, suggesting the favorable condition for nitrate formation with sufficient ammonia in the Beijing winter atmosphere.

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 of particle hygroscopicity and acidity was conducted to investigate the possible changes of the physiochemical properties if ammonia and nitrate were not well controlled in China in the future. The nitrate-rich particles ($Ratio_{N\text{-}to\text{-}S}$) would absorb more water than particles that have higher sulfate fractions at a moderate RH (below 60%). On the other hand, the particle pH would increase rapidly with the synergetic effect of ammonia and nitrate both increases, which is very likely in China since the both pollutants are not well controlled yet. These changes would enhance the uptake of gaseous compound, promote the chemical reactions which favors lower acidity and might also affect the optical properties of airborne particles in winter Beijing. In conclusion, the processes and properties during nitrate dominated $PM_{2.5}$ pollutions need to be thoroughly investigated with more consideration on the more hygroscopic and neutralized particles.

Author contribution

YN.Xie conducted the $PM_{2.5}$ chemical composition 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 data. XP.Wang, YB.Chen, GY.Xue and SS.Ge conducted the lab analysis of filters as well as data QA/QC. YN.Xie conducted the analysis of overall data QA/QC and thermodynamic modeling. YN.Xie and GH.Wang prepare the manuscript with the help of JM.Chen on editing. All the co-authors contribute to the data interpretation and discussion.

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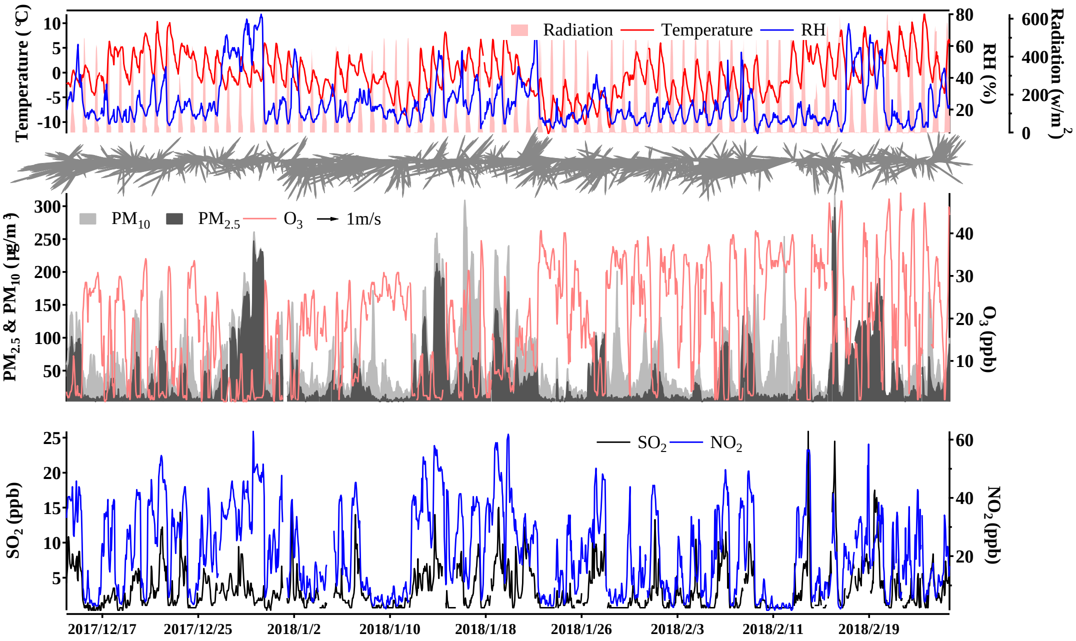


Figure.1 Timeseries of major pollutants during the campaign. Upper panel: Radiation, temperature and RH, wind arrows were draw below; Middle panel: PM$_{2.5}$, PM$_{10}$ and Ozone concentration. Lower panel: SO$_2$ and NO$_2$ concentrations.

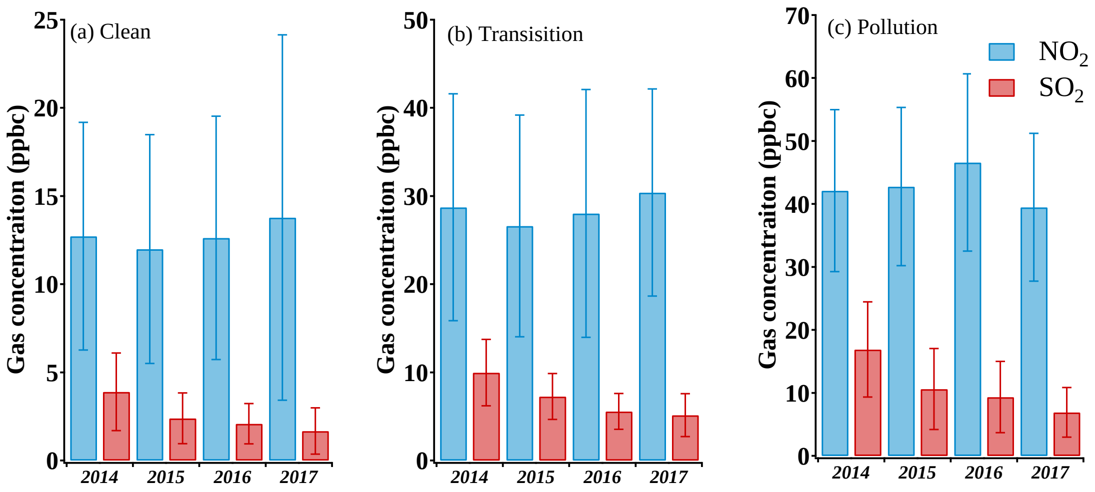
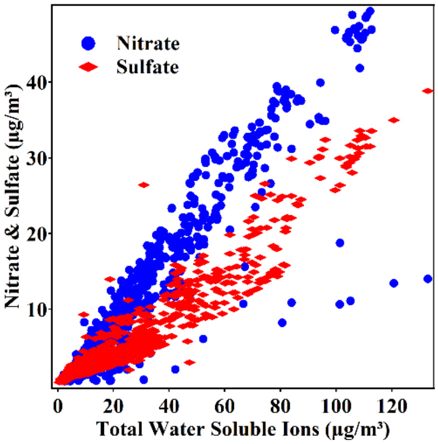


Figure.2 Statistics plot of NO$_2$ and SO$_2$ measured in downtown Beijing in different PM$_{2.5}$ levels during winter (December - February) for the past 4 years. History data (2014-2016) were obtained from air quality real-time publishing platform, China National Environmental Monitoring Center. Data of 2017 was obtained during the campaign.



645 **Figure.3 Scatter plot of nitrate and sulfate vs. WSIs during the campaign.**

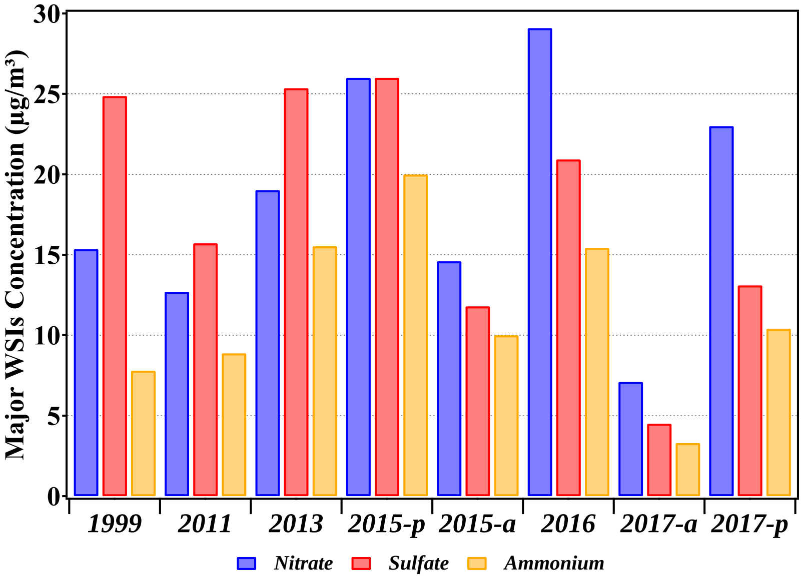


Figure.4 Major inorganic compositions in $PM_{2.5}$ observed during winter in Beijing from representative research articles. The result of 2017 denote the average concentration during haze condition in this study. For details of the reviewed literature, please refer to Table S1.

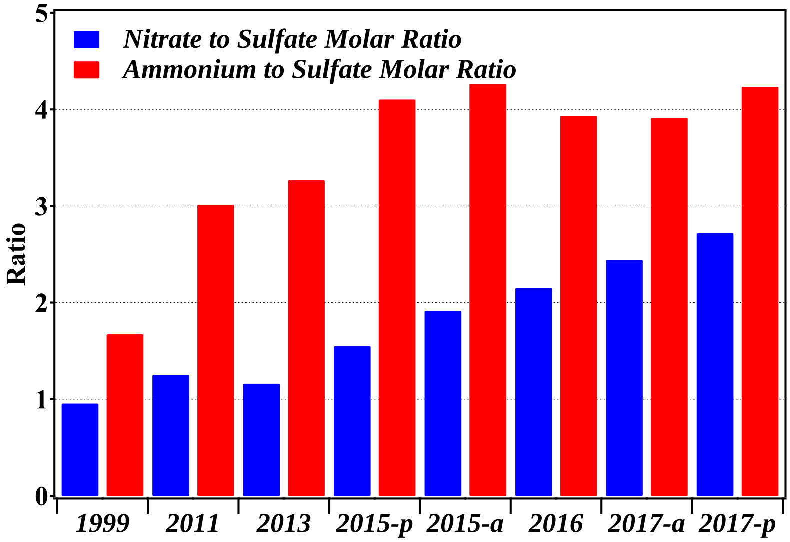


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Figure.5 Molar ratio of nitrate to sulfate and molar ratio of ammonium to sulfate calculated from averaged data reported in representative research articles. Only data in pollution condition was chosen for 2017.

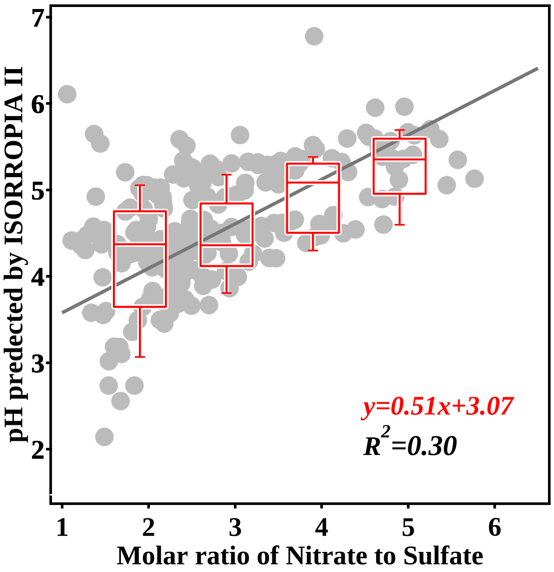


Figure.6 Scatter plot of simulated pH vs. the molar ratio of nitrate to sulfate (Ratio$_{\text{N-to-S}}$). Linear fitting and the correlation coefficient were given in the figure. The box plot denotes the data points classified by four different ranges of the Ratio$_{\text{N-to-S}}$: 0-2;2-3;3-4;4-6. Only the data during pollution classification and with sufficient aerosol liquid water (above 5μg/m^3) was chosen and the data from Chinese New Year was excluded. 655

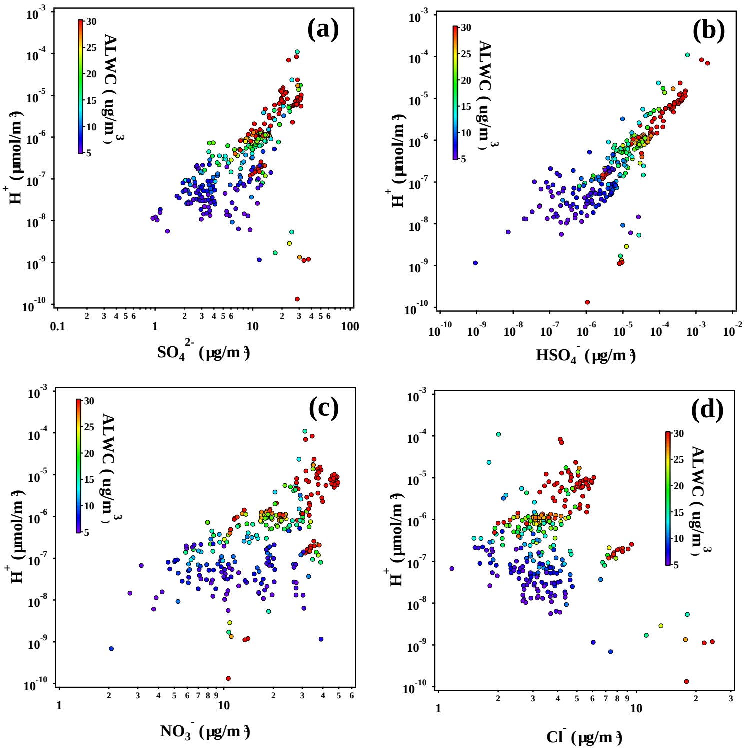


Figure.7 Scatter plot of simulated H^+ ion vs. major inorganic anions: (a) SO_4^{2-}, (b) HSO_4^-, (c)NO_3^-, (d)Cl^-, note that coordinates are in logarithm.

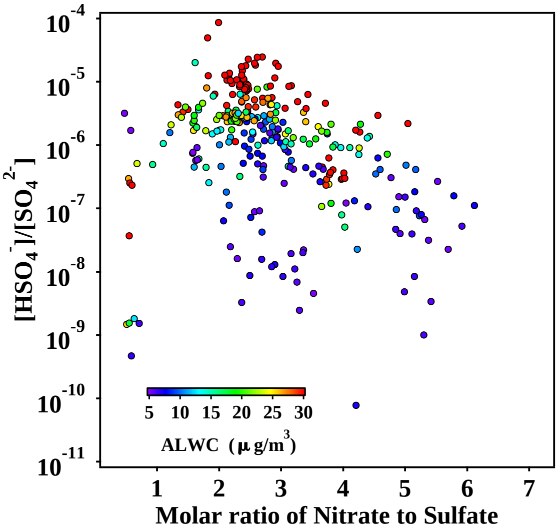
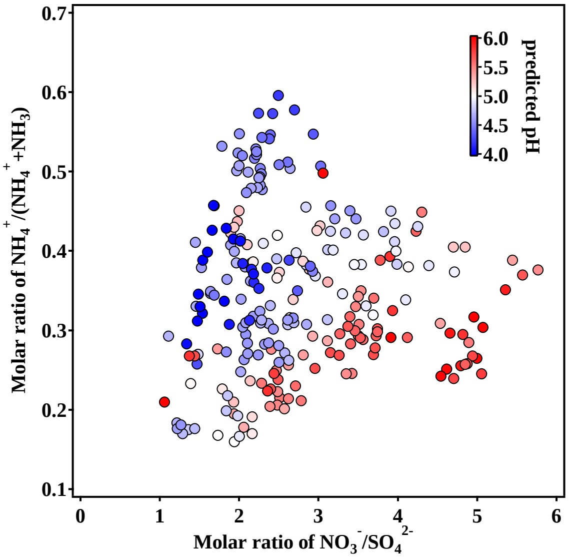


Figure.8 Scatter plot of $[HSO_4^-]$ /$[SO_4^{2-}]$ vs. molar ratio of nitrate to sulfate. Only data of ALWC above 5μg/m^3 were chosen.



665 **Figure.9 Scatter plot of conversion ratio of NH3 vs. the molar ratio of nitrate to sulfate colored with predicted pH.**

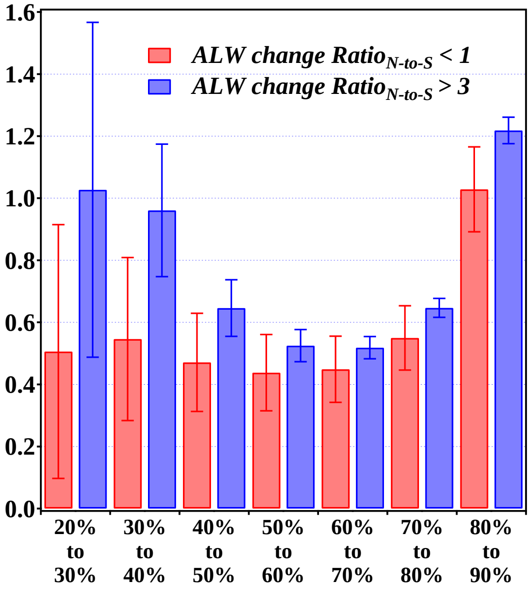


Figure.10 relative aerosol liquid water change due to elevation of RH in different nitrate to sulfate molar ratio. Bars represent the relative change amount, whiskers depict the standard deviation.

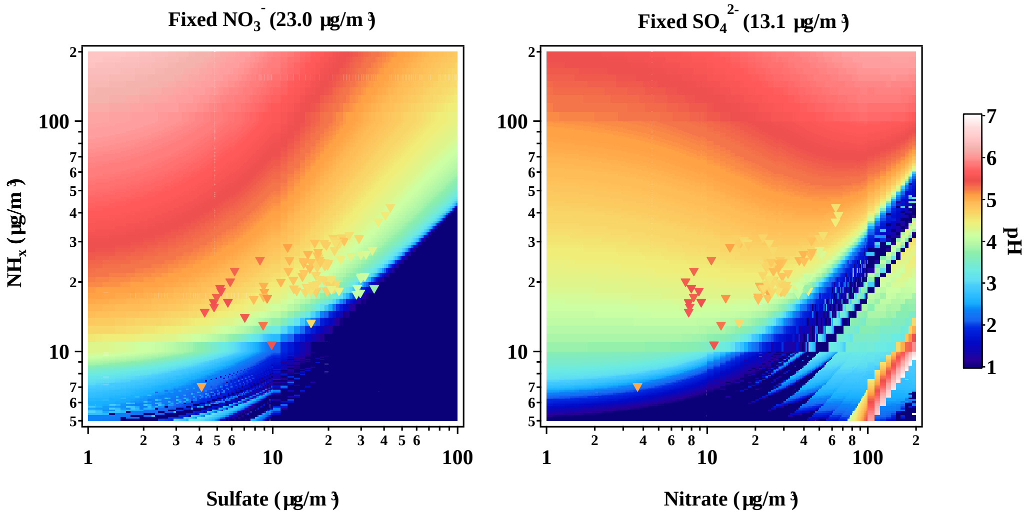


Fig.11 Sensitivity test of pH's responding to Sulfate or Nitrate change with given NH_x as input, simulated by ISORROPIA II. Selected measurement data was drawn upon the simulation data and colored with predicted pH, respectively. Simulation was conducted with fixed RH (58%) and temperature (273.15K).

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

	Average	Clean	Transition	Pollution
Visibility (m)	15007 ±10227	20278 ±9499	11728 ±8259	7467 ±6570
$PM_{2.5}$ (μg/m^3)	39.7 ±47.1	13.0 ±7.8	52.0 ±11.4	128.0 ±46.5
PM_{10} (μg/m^3)	68.5 ±53.9	42.2 ±27.9	99.2 ±43.3	153.3 ±52.1
O_3 (ppbv)	18.5 ±12.8	23.6 ±11.2	10.6 ±10.0	8.4 ±10.3
SO_2 (ppbv)	3.2 ±3.1	1.7 ±1.3	5.1 ±2.5	6.9 ±1.3
NO_2 (ppbv)	21.4 ±14.8	13.8 ±10.4	32.8 ±9.6	39.8 ±11.6

Table.2 Gases & inorganic components 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