Dear Editor,

We are truly grateful for your and other reviewers' second-round comments, which are very helpful for us to highlight our work. Substantial changes were made in this version of manuscript, and most sections of this manuscript were re-examined and reorganized. The revision was mainly aimed at the language editing, the reorganization of key points in discussions, and the refinement of conclusions.

1) We refined the **Abstract** and **Conclusions** to highlight the key points. And the language and figures are re-edited as recommended.

2) We re-adjusted the structure of **Introduction** to make the logic and purpose of this work more clear.

3) In Section 3.4 and 3.6 in the revised manuscript, we simplified the discussions of sensitivity tests, focusing on the factors affecting $PM_{2.5}$ pH and gas-particle partitioning, which is helpful to understand the driving factors of aerosol acidity in the North China Plain and provide the idea of controlling nitrate in the particles.

4) We seriously revised the parts of the paper that were not clear enough and not necessary. In addition, we asked a professional English editing website to revise our paper. The certificate is attached at the end of this document.

Thank you very much for your concerning.

Best regards.

Sincerely yours,

Pusheng Zhao & Jing Ding

Anonymous Referee #1

Substantial changes were made to the first draft of this paper based on the comments from the reviewers. The paper still has substantial problems. First, the analysis is largely not novel; the paper seems to essentially copy the work of published papers, where the only main difference is the work was done in a different location. I suggest the authors try to add more insight to their work. Second, the paper is hard to follow and understand. The language usage and grammar is very poor; the paper needs substantial editing. The figures largely do not make sense with multiple types of plots on the same figure and no explanation in the figure caption. Third, many of the explanations for the observed sensitivities do not make sense, or are not explained in a logical way. Much of this is new text added after the first round of review. The authors might want to explain why they discuss sensitivity of Hair+ (i.e., why is Hair+ important). As the sensitivity analysis section is largely very difficult to follow, the authors may wish to completely remove it from the paper. Instead the focus could be on the bulk predicted pH when both gas and particle MARGA data are available (including it's validation, issues with RH, etc) and the MOUDI size-resolved pH.

Response: We would like to express our gratitude for your comments, which are very important to help us highlight our work. In this work, the thermodynamic model ISORROPIA-II was utilized to predict aerosol pH in Beijing based on a long-term online high-temporal resolution dataset and a size-resolved offline dataset. Additionally, a sensitivity analysis was conducted to identify the key factors affecting aerosol pH and gas-particle partitioning. The main purposes of this work are to 1) obtain the PM2.5 pH level based on long-term online aerosol samples, contributing towards a global pH dataset; 2) investigate the size-resolved aerosol pH, providing useful information for understanding the formation processes of secondary aerosols; and 3) explore the main factors affecting aerosol pH and gas-particle partitioning, which can help explain the possible reasons for pH divergence in different works and provide a basis for controlling secondary aerosol generation.

As you suggested, substantial changes were made in this version of manuscript, we

simplified the paper and summarized the key points of our work, including:

1) In 2016-2017, the mean $PM_{2.5}$ pH (at RH > 30%) over four seasons was 4.5±0.7 (winter) > 4.4±1.2 (spring) > 4.3±0.8 (autumn) > 3.8±1.2 (summer), showing moderate acidity. According to the size-resolved aerosol pH, the particles in coarse mode were neutral in most cases. However, on heavily polluted days, more secondary ions accumulated on the coarse particles, leading to a change in the acidity of the coarse particles from neutral to weakly acidic. Sensitivity tests demonstrated Ca^{2+} and Mg^{2+} played an important role in aerosol pH.

2) In the North China Plain (NCP), the common driving factors affecting $PM_{2.5}$ pH variation in all four seasons were SO_4^{2-}, TNH_3 (total ammonium (gas+aerosol)), and temperature, while the unique factors were Ca^{2+} in spring and RH in summer. Elevated SO_4^{2-} levels can enhance aerosol acidity due to the stronger ability of SO_4^{2-} to provide hydrogen ions. The decreasing SO_4^{2-} and increasing NO_3^- mass fractions in $PM_{2.5}$ as well as excessive NH_3 in the atmosphere in the NCP in recent years are the reasons why aerosol acidity in China is lower than that in Europe and the United States. The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicated that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was still acidic.

3) Gas-particle partitioning sensitivity tests revealed that the typical high RH values and low temperatures during haze events in the NCP are conducive to the formation of secondary particles. Given that ammonia was excessive in most cases, a decrease in nitrate would occur only if TNH_3 were greatly reduced. Therefore, in terms of controlling the generation of nitrate, a reduction in NOx emissions is more feasible than a reduction in NH_3 emissions.

In brief, the revision is mainly aimed at the language editing, the reorganization of key points in discussions, and the refinement of conclusions.

1) We refined the **Abstract** and **Conclusions** to highlight the key points. And the language and figures are re-edited as recommended.

2) We re-adjusted the structure of **Introduction** to make the logic and purpose of this work more clear.

3) After careful consideration, we still believe that the sensitivity tests are important

for understanding the causes of pH changes. In the revised manuscript, we rewrote this part and simplified the discussions of sensitivity tests, mainly focusing on the factors affecting $PM_{2.5}$ pH and gas-particle partitioning. Please see section 3.4 and 3.6.

4) We seriously revised the parts of the paper that were not clear enough and not necessary.

Specific Comments.

Lines 226 to 228: Provide numbers to support the statement that ALWC could be off in regions of high OA fractions. That is, give some idea how high the OA fraction would need to be for it to matter. Published typical hygroscopicity parameters for OA could be assumed.

Response: Thanks for your important comment. In our manuscript, we indeed notice that both inorganic and part of organic species in particles are hygroscopic. According to the literatures, the organic matter-induced aerosol water in some studies conducted in China could be negligible compared to the inorganic matter-induced particle water (Guo et al., 2015, 2016; Liu et al., 2017). In the southeastern United States, a large fraction of the PM2.5 (~70 %) was organic matter, and the corresponding ALWCo is on average 29% to 39 % of total aerosol water, $PM_{2.5}$ pH increased by 0.15 to 0.23 units when ALWCo is included. In the North China Plain, particularly in recent years, the fraction of organic matter was 20%~25% in $PM_{2.5}$, which is much lower than that in southeastern United States. In contrast, more than 50% of PM2.5 are inorganic ions in the North China Plain (Huang et al., 2017; Zhang et al., 2018; Zhang et al., 2019). The results in Liu et al., (2017) showed that the mass fraction of organic matter-induced particle water accounted for only 5% of total ALWC, indicative of a negligible contribution to aerosol acidity. Hence, the aerosol pH can be fairly predicted by ISORROPIA-II with measurements of inorganic species in most cases.

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Zhang, H., Cheng, S., Li, J., Yao, S., and Wang, X.: Investigating the aerosol mass and chemical components characteristics and feedback effects on the meteorological factors in the Beijing-Tianjin-Hebei region, China, Environ Pollut, 244, 495-502, 10.1016/j.envpol.2018.10.087, 2019.

Zhang, Y., Lang, J., Cheng, S., Li, S., Zhou, Y., Chen, D., Zhang, H., and Wang, H.: Chemical composition and sources of PM1 and PM2.5 in Beijing in autumn, Sci Total Environ, 630, 72-82, 10.1016/j.scitotenv.2018.02.151, 2018.

Line 258 to 260. Explain how gas denuder artifacts would result in the model greatly over-predicting HNO3 or HCl. Artifacts associated with particles deposited in the denuder would seem to result in measured values larger than predicted, opposite what is shown.

Response: The precision and accuracy performance of MARGA was assessed by the US EPA (Rumsey et al., 2014). Precision of MARGA was evaluated by calculating the median absolute relative percent difference between paired hourly results from duplicate MARGA units. The accuracy of the MARGA was evaluated by calculating the median absolute relative percent difference for each MARGA unit relative to the

average of the duplicate denuder/filter pack concentration. The results demonstrated that the MARGA performed moderately well in measuring HNO_3 and NH_3. The measured HNO_3 and NH_3 by MARGA were lower than the denuder concentrations. The performance of the MARGA in measuring HNO_3 and NH_3 was likely influenced by the adsorption of HNO_3 and NH_3 onto the sampling tubing and inlet since the HNO_3 and NH_3 are all "sticky" gases, which may also apply to HCl. Thus, it is reasonable that the measured values of gas phase HNO_3 were lower than the predicted values in the results of this study.

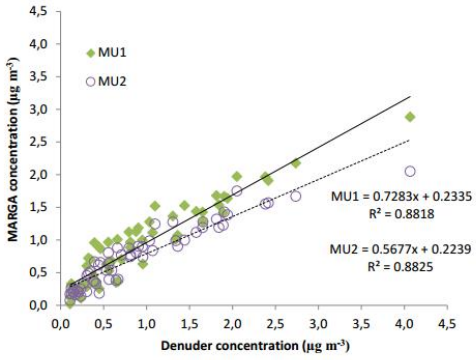

Figure 12. Regression analysis of MARGA HNO_3 concentrations against denuder HNO_3 concentrations.

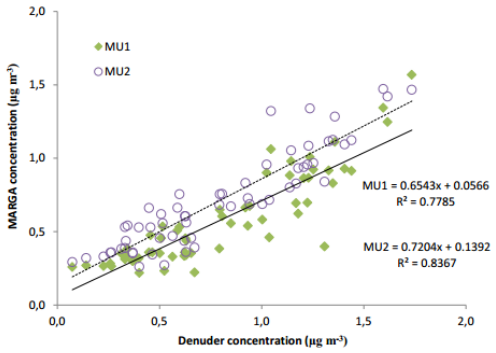

Figure 22. Regression analysis of MARGA NH_3 concentrations against denuder NH_3 concentrations.

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The figures largely do not make sense. In Figs 2, 3, 4… there are two sets of plots, which is very confusing. Either make separate figures or somehow integrate them better and explain the plots in the Fig captions. Eg, in Fig. 2 the difference between the top set of plots and the bottom set is not clear. Was one set deleted but not indicated in this edited version? The axis and the meaning of the polar plots of Fig 3 (and other polar plots) is not clear. What is the point of these plots?, Fig 4?....

Response: Thanks for your advice. We checked all the problems of figures you pointed out. In the revised manuscript, the figure captions are clear to understand.

There are many issues with explanations from the sensitivity tests. Overall, the discussion is just a laundry list of how things vary with season. What is the point to this

discussion? The manuscript would be greatly improved if it be simplified or somehow focused more. The discussion of RH, H+ and LWC is very confusing and simplistic; details in the logic are missing. I do not understand the T discussion. Basically all the added text in the second version of the paper is hard to follow.

Response: Thanks for your comments to improve our work. The discussion about factors affecting ALWC, H_{air}^{+}, $PM_{2.5}$ pH, and gas-particle partitioning (Section 3.4 in the manuscript) are simplified, more focusing on the factors affecting $PM_{2.5}$ pH, and gas-particle partitioning, which helps to understand the role of aerosol acidity in secondary particle formation. For example, Cheng et al. (2016) and Wang et al. (2016) proposed that SO_2 could oxidized by NO_2 to form sulfate, whereby high reaction rates are sustained by the high neutralizing capacity of the atmosphere in northern China. However, many studies show that the aerosol pH in North China Plain is moderately acidic (Liu et al., 2017; Shi et al., 2017; Tan et al., 2018), which means the new pathways for sulfate production in China proposed by Cheng et al. (2016) and Wang et al. (2016) should be revisited. Therefore, the sensitivity analysis is aimed to identify the crucial factor affecting aerosol pH and gas-particle portioning, which may explain the differences of aerosol acidity level of these studies. Moreover, the discussion of gas-particle portioning helps to provide an idea on controlling the secondary aerosol formation.

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Aerosol pH and its ~~influencing~~driving factors in Beijing

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Abstract

~~The acidity or pH is an important feature of ambient aerosol. At present, the aerosol pH in the North China Plain, either seasonal variation or size-resolved characteristics, need to be further studied. In addition, it is also worthy of discussion about what factors have a greater impact on pH and how these factors affect pH. In view of these, the hourly water soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) of $PM_{2.5}$ and trace gases (HCl, HNO_3, HNO_2, SO_2, and NH_3) were online measured by a MARGA system in four seasons during 2016 and 2017 in Beijing. Furthermore, the size-resolved aerosol was also sampled by a MOUDI sampler and analyzed for the chemical compositions of different sizes. On the basis of these data, the particle hydronium ion concentration per volume air (H_{air}^+), aerosol liquid water content (ALWC), and $PM_{2.5}$ pH were calculated by using ISORROPIA-II. Moreover, the sensitivities of H_{air}^+, ALWC, aerosol pH to all the main influencing factors were discussed. In Beijing, the $PM_{2.5}$ pH over four seasons showed moderately acid. The $PM_{2.5}$ acidity in NCP was both driven by aerosol composition and particle water. The sensitivity analysis revealed that SO_4^{2-}, T, NH_4^T, and RH (only in summer) are crucial factors affecting the $PM_{2.5}$ pH. The SO_4^{2-} had a key role for aerosol acidity, especially in winter and spring. The impact of NO_3^- on $PM_{2.5}$ pH was different in four seasons. Although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral, which mainly attributed to the limited ALWC. Elevated Ca^{2+} concentration could increase the aerosol pH because of the buffering capacity of Ca^{2+} to the acid species and the weak water solubility of $CaSO_4$. The sensitivity analysis also implied that decreasing NO_3^T could reduce the $\varepsilon(NH_4^+)$ effectively. In contrast, the nitrate response to NH_4^T control was highly nonlinear. According to the size resolved results, the pH for coarse mode, which was near or even higher than 7, was much higher than that for fine mode. It must be noted that the aerosol pH in coarse mode showed a marked decrease when under heavily polluted condition.**

Aerosol acidity plays a key role in secondary aerosol formation. The long-term high-temporal resolution $PM_{2.5}$ pH and size-resolved aerosol pH in Beijing were calculated with ISORROPIA-II. In 2016-2017, the mean $PM_{2.5}$ pH (at relative humidity (RH) > 30%) over four seasons was 4.5±0.7 (winter) > 4.4±1.2 (spring) > 4.3±0.8 (autumn) > 3.8±1.2 (summer), showing moderate acidity. In coarse-mode aerosols, Ca^{2+} and Mg^{2+} played an important role in aerosol pH. Under heavily polluted conditions, more secondary ions accumulated on the coarse particles, leading to a change in the acidity of the coarse particles from neutral to weakly acidic. Sensitivity tests also demonstrated the significant contribution of crustal ions to $PM_{2.5}$ pH. In the North China Plain (NCP), the common

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driving factors affecting $PM_{2.5}$ pH variation in all four seasons were SO_4^{2-}, TNH_3 (total ammonium (gas+aerosol)), and temperature, while the unique factors were Ca^{2+} in spring and RH in summer. Elevated SO_4^{2-} levels can enhance aerosol acidity due to the stronger ability of SO_4^{2-} to provide hydrogen ions. The decreasing SO_4^{2-} and increasing NO_3^- mass fractions in $PM_{2.5}$ as well as excessive NH_3 in the atmosphere in the NCP in recent years are the reasons why aerosol acidity in China is lower than that in Europe and the United States. The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicated that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was still acidic, which might be attributed to the limited aerosol liquid water content (ALWC) and hydrolysis of ammonium salts. Elevated RH values can enhance water uptake and promote gas-to-particle conversion. Therefore, the specific impact of RH on $PM_{2.5}$ pH needs to be determined by the degrees of change in H_{air}^+ and ALWC. Gas-particle partitioning sensitivity tests revealed that the typical high RH values and low temperatures during haze events in the NCP are conducive to the formation of secondary particles. To reduce nitrate by controlling ammonia, the amount of ammonia must be greatly reduced below excessive quantities.

Key words: Aerosol pH, ISORROPIA-II, Influencing factors, Beijing

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1. Introduction

~~Acidity or pH, which drives many processes related to particle composition, gas-aerosol partitioning and aerosol secondary formation, is an important aerosol property (Jang et al., 2002; Eddingsaas et al., 2010; Surratt et al., 2010). The aerosol~~ Aerosol acidity has a significant effect on ~~the aerosol~~ secondary aerosol formation through the gas-aerosol partitioning of semi-volatile and volatile species (Eddingsaas et al., 2010; Surratt et al., 2010; Pathak et al., 2011a; Guo et al., 2016). ~~Recent studies~~Studies have shown that aerosol acidity ~~could~~can promote the generation of secondary organic ~~aerosol~~aerosols by affecting ~~the~~ aerosol acid-~~catalyzed~~catalysed reactions (Rengarajan et al., 2011). Moreover, metals can become soluble by acid dissociation under ~~lower~~low aerosol pH (Shi et al., 2011; Meskhidze et al., 2003) or by forming ~~a ligand~~ligands with organic species, such as oxalate, at higher pH (Schwertmann et al., 1991). In addition, ~~higher~~high aerosol acidity can lower the ~~acidification~~ buffer capacity and ~~affects~~affect the formation of acid rain. The investigation of aerosol acidity is conducive to better ~~understand~~understanding the important role of aerosols in acid deposition and atmospheric chemical reactions.

~~The hygroscopic components in the aerosols include water-soluble inorganic ions and part of organic acid~~ Aerosol ~~(Peng, 2001; Wang et al., 2017). The deliquescence relative humidity (DRH) for the mixed-salt is lower than that of any single component (Seinfeld and Pandis, 2016), hence the ambient aerosols are generally droplets containing liquid water. The aerosol pH actually is the pH of the aerosol liquid water. The aerosol~~ acidity is frequently estimated by the charge balance of measurable cations and anions ~~in the aerosol liquid phase~~. A net negative balance is correlated with ~~an~~ acidic ~~aerosol~~aerosols and vice versa (Zhang et al., 2007; Pathak et al., 2011b; Zhao et al., 2017). Generally, a larger ~~value of the~~ ion balance value implies ~~a~~ stronger acidity or stronger ~~alkaline~~alkalinity. Nevertheless, ~~an~~ ion balance ~~or~~and other similar proxies fail to represent the ~~true~~in situ aerosol pH because ~~they~~such metrics cannot accurately predict the H^+ concentration in the aerosol liquid phase ~~accurately~~ (Guo et al., 2015~~), which could be calculated by~~). To better understand the in situ aerosol pH, the aerosol liquid water content (ALWC) and hydrogen ion concentration per volume air (H_{air}^+) ~~and the aerosol liquid water content (ALWC).~~

~~It is critical to obtain the ALWC in calculating aerosol acidity. One way to calculate the ALWC is based upon the assumption that the volume of ALWC is equal to subtracting the volume of dry aerosol particles from that of wet particles~~should be determined (Guo et al., 2015).

Most inorganic ions and some organic acids in aerosols are water soluble (Peng, 2001; Wang et al., 2017). ~~; Bian et al. 2014; Engelhart et al. 2011). Under this assumption, ALWC could be calculated by the size-resolved~~ Since the deliquescence relative humidity (DRH) of mixed salts is

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lower than that of any single component, ambient aerosols are generally in the form of droplets containing liquid water (Seinfeld and Pandis, 2016). ALWC can be derived from hygroscopic growth factors ~~(*g*(D, RH)) combining particle size distribution (PNSDs) or by the hygroscopic growth factor of aerosol scattering coefficient (*f*(RH)) (Bian et al.~~or calculated by ~~2014; Guo et al., 2015; Kuang et al., 2017a). The *g*(D, RH), defined as the ratio of the diameter of the wet particle at a certain relative humidity to the corresponding diameter at dry conditions, can be measured by a H-TDMA (Hygroscopic Tandem Differential Mobility Analyzer) (Liu et al., 1978; Swietlicki et al., 2008; Liu et al., 2011). The *f*(RH) can be observed by the wet & dry nephelometer system (Covert et al., 1972; Rood et al. 1985; Yan et al., 2009; Kuang et al., 2016, 2017b).~~

~~Another way to calculate the ALWC is based on the aerosol chemical components with~~ thermodynamic models, ~~such as ISORROPIA-II, AIM, ADDEM etc. (Nenes et al., 1998; Fountoukis~~ and ~~Nenes, 2007, Clegg et al., 1998, Topping et al., 2005a, b). Based on the aerosol chemical components as well as temperature and relative humidity, the aerosol thermodynamic models can output both ALWC and H_{air}^{+}, which offers a more precise approach to acquire aerosol pH (Pye et al., 2013). Among these thermodynamic models, ISORROPIA and ISORROPIA-II are widely used owing to its rigorous calculation and performance on computational speed. ISORROPIA simulates the gas-particle partitioning in the H_2SO_4, NH_3, HNO_3, HCl, Na^+, H_2O system, while its second version, ISORROPIA-II, adds Ca^{2+}, K^+, Mg^{2+} and the corresponding salts to the simulated particle components in thermodynamic equilibrium with water vapor and gas-phase precursors.~~

~~Comparisons were made in some studies to investigate the consistency of calculated ALWC derived from the above methods. In the North China Plain (NCP), Bian et al. (2014) found that the ALWC calculated using size-resolved hygroscopic growth factors and the PNSD agreed well with that calculated using ISORROPIA-II at higher relative humidity (>60%). Relatively good consistency was also found in the study of Engelhart et al. (2011) in the USA based on the similar method. Guo et al. (2015) compared the ALWC calculated by *f*(RH) with the total predicted water by organics and inorganics. The total predicted water was highly correlated and on average within 10 % of the *f*(RH) measured water. Though~~ good consistencies in ALWC ~~were~~have been found among these methods (Engelhart et al., 2011; Bian et al., 2014; Guo et al., 2015~~, the H_{air}^{+} could~~).

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However, H_{air}^+ can only be obtained by ~~the~~ thermodynamic models, which ~~had been applied~~offer a more precise approach to ~~predict~~determine aerosol ~~acidity in many studies~~pH (Nowak et al., 2006; Fountoukis et al., 2009; Weber et al., 2016; Fang et al., 2017).

~~The characteristics of aerosol chemical components are different among multiple size ranges. Among inorganic ions, SO_4^{2-}, NO_3^-, Cl^-, K^+, NH_4^+ mainly concentrate in fine mode except for the dust days (Meier et al.,~~ Among these thermodynamic models, ISORROPIA-II is widely used owing to its rigorous calculation, performance, and computational speed (Guo et al., 2015; Fang et al., ~~2009; Pan et al., 2009; Tian et al., 2014), whereas Mg^{2+}, Ca^{2+} are abundant in coarse mode (Zhao et al.,~~ 2017; Liu et al., 2017; Galon-Negru et al., 2018). ~~). The aerosol acidity is affected by coupling among many variables. Therefore, it could be expected that the aerosol pH is also diverse under different particle size. The gas precursor (NH_3, HNO_3, and HCl) of main water-soluble ions, as well as ambient temperature and relative humidity, are also important factors affecting the aerosol acidity. In some countries where particle matter concentration is very low, the pH diurnal variation was mainly driven by meteorological conditions (Guo et al.,~~

The North China Plain (NCP)~~2015, 2016; Bougiatioti et al., 2016). In China, however, the annual average $PM_{2.5}$ concentration in some megacities was ~2 times higher than the national standard value (35 μg m^{-3}) and the inorganic ions accounted for 40%–50% to $PM_{2.5}$, especially in the North China Plain (Zou et al., 2018; Huang et al., 2017; Gao et al., 2018). Hence it can be expected that the aerosol composition is also a crucial factor on pH, which cannot be ignored.~~

~~The North China Plain~~ is the region with the most severe aerosol pollution in China. Nitrate and sulfate are the major contributors to haze, and their secondary formation processes are determined in large part by aerosol pH (Zou et al., 2018; Huang et al., 2017; Gao et al., 2018). ~~Nevertheless, only a few studies have focused on aerosol pH~~Therefore, understanding the aerosol pH level in this region~~.~~ is extremely important and has recently become a trending topic. Some studies conducted in the NCP showed that the aerosol acidity was close to neutral~~, while in some other studies the fine particles showed moderately acidic~~ (Cheng et al., 2016; Wang et al., 2016; Chi et al., 2017), while in some other studies, fine particles showed moderate acidity (Liu et al., 2017; Shi et al., 2017). These results ~~were~~ all indicated significantly higher pH values than ~~that~~those found in the United States or Europe, where aerosols ~~were~~are often highly acidic with a pH lower than 3.0 (Guo et al., 2015, 2016; Bougiatioti et al., 2016; Weber et al., 2016; Young et al., 2013). The differences in aerosol pH in the NCP ~~mainly resulted~~arise from ~~the~~1) different methods ~~(ion balance & thermodynamic equilibrium models)~~ or different ~~data sets. Moreover, the variation of~~model settings, 2) variations in $PM_{2.5}$ chemical composition in the NCP in recent years ~~also contributed to the~~, 3) the levels of gas precursors of the main water-soluble ions (NH_3, HNO_3, and HCl), and 4) differences in ambient temperature and relative humidity (RH). In some countries where the particulate matter concentration is very low, pH diurnal variations are mainly driven by meteorological conditions

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(Guo et al., 2015, 2016; Bougiatioti et al., 2016). In the NCP, a comprehensive understanding of the impacts of these factors on aerosol pH is still poor.

Additionally, most studies on aerosol pH focus on PM_1 or $PM_{2.5}$. Knowledge regarding size-resolved aerosol pH is still rare. Aerosol chemical compositions are different among multiple size ranges. Among inorganic ions, SO_4^{2-}, NO_3^-, Cl^-, K^+, and NH_4^+ are mainly concentrated in the fine mode except on dusty days (Meier et al., 2009; Pan et al., ~~. The observations in previous studies exploring aerosol acidity in NCP were almost conducted before 2015. In the recent three years, the chemical composition of $PM_{2.5}$ in Beijing has undergone tremendous changes. Nitrate has replaced sulfate and is dominant in inorganic ions in most cases (Zhao et al.,~~ 2009; Tian et al., 2014), whereas Mg^{2+} and Ca^{2+} are abundant in the coarse mode (Zhao et al., ~~2017; Huang et al., 2017; Ma et al.,~~ 2017). ~~Moreover, studies about seasonal variation of aerosol~~Aerosol pH ~~and size-resolved aerosol pH~~can be expected to be diverse among different particle sizes; pH ~~are rare in NCP, and the key factors affecting aerosol acidity are still not well understood~~levels at different sizes may be associated with different formation pathways of secondary aerosols.

~~In~~To better understand the driving factors of aerosol acidity, in this work, the thermodynamic model ISORROPIA-II ~~with the forward mode~~ was utilized to predict ~~ALWC and~~ aerosol pH in Beijing~~.~~ based on a long-term online high-temporal resolution dataset and a size-resolved offline dataset. The hourly measured $PM_{2.5}$ inorganic ions and precursor gases in four seasons ~~during~~from 2016 to 2017 were used to ~~analyze~~analyse the seasonal and diurnal ~~variation of aerosol acidity, and the sensitivity analysis was conducted to identify the key factors that affecting the aerosol pH. In our previous studies, the~~variations in aerosol acidity; samples collected by multi-stage cascade impactors (MOUDI-120) were used ~~for size-resolved aerosol sampling from 2013 to 2015. The actual relative humidity inside the impactors was calculated, and the size distributions of water-soluble ions, organic carbon, and elemental carbon in three seasons were discussed (Zhao et al., 2017; Su et al~~to estimate the pH variations among 10 ~~, 2018). Based on these size-resolved results, the pH for aerosol in~~ different size ranges ~~could also be predicted~~. Additionally, a sensitivity analysis was conducted to identify the key factors affecting aerosol pH and gas-particle partitioning. The main purposes of this work are to 1) obtain the $PM_{2.5}$ pH level based on long-term online aerosol samples, contributing towards a global pH dataset; 2) investigate the size-resolved aerosol pH, providing useful information for understanding the formation processes of secondary aerosols; and 3) explore the main factors affecting aerosol pH and gas-particle partitioning, which can help explain the possible reasons for pH divergence in different works and provide a basis for controlling secondary aerosol generation.

2. Data Collection and Methods

2.1 Site

The measurements were performed at the Institute of Urban Meteorology in the Haidian district of Beijing (39°56'N, 116°17'E). The ~~sampling~~ site ~~was~~is located next to a high-density residential area, without significant nearby air pollution emissions ~~around the site.~~ Therefore, the observation

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data ~~could~~ represent the air quality levels of the urban area of Beijing.

2.2 Online data collection

Water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) ~~of~~in $PM_{2.5}$ and ~~trace gases~~gaseous precursors (HCl, HNO_3, HNO_2, SO_2, and NH_3) in ~~the~~ ambient air were measured by an online ~~analyzer~~analyser (MARGA) ~~at~~with hourly temporal resolution during ~~the~~ spring (April and May ~~in~~ 2016), winter (February ~~in~~ 2017), summer (July and August ~~in~~ 2017~~)~~), and autumn (September and October ~~in~~ 2017). ~~The more~~More details about MARGA can be found ~~at ten Brink~~in Rumsey et al. ~~(2007).~~(2014) and Chen et al. (2017). The $PM_{2.5}$ and PM_{10} mass concentrations (TEOM 1405DF), ~~the~~ hourly ambient temperature and ~~relative humidity~~RH were also synchronously ~~attained.~~

~~Hourly~~obtained. The hourly concentrations of $PM_{2.5}$, PM_{10}, and ~~water-soluble~~major secondary ions (SO_4^{2-}, NO_3^-, and NH_4^+) in $PM_{2.5}$, as well as meteorological parameters during the ~~observation~~observations, are shown in Figure 1. In the spring, two dust events occurred (~~21-22,~~ April 21 and ~~5-6,~~ May~~). During the first dust events, the wind came predominantly from the north with mean wind speed 3.5 m s^{-1}. The PM_{10} concentration reached 425 μg m^{-3} while the $PM_{2.5}$ concentration was only 46 μg m^{-3} on the peak hour. Similarly, the second dust event resulted from the strong wind coming from the northwest direction.~~ 6). In the following pH analysis based on MARGA data, it was assumed that the particles were internally mixed~~, and the chemical compositions were the same for particles of different sizes in $PM_{2.5}$. Hence~~; hence, these two dust events were excluded from this analysis.

Figure 1

2.3 ~~size~~Size-resolved chemical ~~compositions~~composition

A ~~Micro-Orifice Uniform Deposit Impactor~~micro-orifice uniform deposit impactor (MOUDI-120) was used to collect size-resolved aerosol samples with ~~the~~ calibrated 50% cut sizes of 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.1, 6.2, 9.9 and 18 μm. Size-resolved sampling was conducted ~~during~~ July 12-18, 2013; January 13-19, 2014; July 3-5, 2014; October 9-20, 2014; and January 26-28, 2015. Fifteen, fourteen, and eighteen sets of samples were obtained ~~for the~~in summer, autumn, and winter, respectively. Except for two sets of samples, all the samples were collected in daytime (from 08:00 to 19:00) and nighttime (from 20:00 to 7:00 the next day~~), respectively.~~). One hour of preparation time was ~~set~~allowed for filter changing and washing the nozzle plate ~~washing~~ with ethanol. The water-soluble ions ~~were analyzed from~~in the samples were analysed by using ~~an~~ ion chromatography (DIONEX ICS-1000). ~~The detailed~~Detailed information about the features of MOUDI-120~~,~~ and the procedures of sampling, pre-treatment, and laboratory chemical analysis (including ~~the~~ quality assurance & quality control) were described in our previous papers (Zhao et al., 2017; Su et al., 2018). ~~It should be noted that there was no observation of gas~~Gas precursors were not observed during the periods of MOUDI sampling.

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2.4 Aerosol pH prediction

~~As mentioned in the Introduction,~~Aerosol pH ~~of ambient aerosols~~ can be predicted by ~~the~~ thermodynamic ~~model~~models such as AIM and ISORROPIA~~,~~ (Clegg et al., 1998; Nenes et al., 1998). AIM is considered ~~as~~ an accurate benchmark model, while ISORROPIA has been optimized for use in chemical transport models. Currently, ISORROPIA-II, ~~adding~~with the addition of K^+, Mg^{2+}, and Ca^{2+} (Fountoukis and Nenes, 2007), can calculate the equilibrium H_{air}^+ ~~(particle hydronium ion concentration per volume air)~~ and ALWC with reasonable accuracy by ~~taking~~using the water-soluble ~~ions~~ion, mass concentration, temperature~~,~~ (T), and ~~relative humidity~~RH as input. ~~The~~ H_{air}^+ and ALWC were then used to predict aerosol pH by ~~the~~ Eq. (1).

~~$pH = -\log_{10} H_{aq}^+ \cong -\log_{10} \frac{1000 H_{air}^+}{ALWC_i}$~~ $pH = -\log_{10} H_{aq}^+ \cong -\log_{10} \frac{1000 H_{air}^+}{ALWC_i}$ (1)

~~Where~~where H_{aq}^+ (mole L^{-1}) is the hydronium ion concentration in the ambient particle liquid water. H_{aq}^+ can also be ~~deemed to be the~~calculated as H_{air}^+ (μg m^{-3}) divided by the concentration of ALWC associated with inorganic species, $ALWC_i$ (μg m^{-3}). Both the inorganic species and part of the organic species in particles are hygroscopic. However, ~~the~~ pH prediction is not highly sensitive to ~~the~~ water uptake by organic species ($ALWC_o$) (Guo et al., 2015, 2016). ~~The similar result~~In recent years, the fraction of organic matter in $PM_{2.5}$ in the NCP was ~~also found~~20%~25%, which is much lower than that in the United States (Guo et al., 2015). In contrast, approximately 50% of $PM_{2.5}$ in the NCP is inorganic ions (Huang et al., 2017; Zhang et al., 2018; Zhang et al., 2019). The results obtained by Liu et al. (2017) in Beijing ~~in Liu et al. (2017). Hence the~~ showed that the mass fraction of organic matter-induced particle water accounted for only 5% of total ALWC, indicating a negligible contribution to aerosol pH~~ could~~. Hence, aerosol pH can be fairly well predicted by ISORROPIA-II with ~~just~~only measurements of inorganic species in most cases. However, ~~it should be noted that the~~ potential ~~error could~~errors can be incurred by ignoring $ALWC_o$ in regions where hygroscopic organic species ~~has~~have a relatively high contribution to fine particles.

In ISORROPIA-II, forward and reverse ~~mode~~modes are provided to predict ALWC and H_{air}^+. In forward mode, T, RH, and the total (*i.e.*~~,~~ gas+aerosol) concentrations of NH_3, H_2SO_4, HCl, and HNO_3 need to be input. ~~Reverse~~In reverse mode ~~calculates the~~ equilibrium partitioning is calculated given only the concentrations of ~~only~~ aerosol ~~compositions together with~~components, RH, and T as input. In this work, the online ion chromatography system MARGA was used to measure both inorganic ions ~~of~~in $PM_{2.5}$ and ~~precursor gases.~~gaseous precursors. Moreover, ~~several studies had shown that the ion balance and reverse mode calculations of thermodynamic equilibrium models were not applicable to interpret the aerosol acidity (Hennigan et al., 2015; Liu et al. 2017; Song et al., 2018). The forward mode was also~~the forward mode has been reported to be less sensitive to measurement error than the reverse mode (Hennigan et al., 2015; Song et al., 2018). Hence, ISORROPIA-II was run in ~~the~~ "forward mode" for aerosols in the metastable ~~condition~~conditions in this study.

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When using ISORROPIA-II to calculate the $PM_{2.5}$ acidity, all particles were assumed to be internally mixed, and the bulk properties were used, without considering the variability ~~of~~in chemical ~~compositions~~composition with particle size. In the ambient atmosphere, the aerosol chemical composition is complicated~~.~~; hence, the ~~deliquescent~~deliquescence relative humidity (DRH) of ~~aerosol~~aerosols is generally low (Seinfeld and Pandis, 2016~~)~~), and ~~the~~ particles usually exist in the form of droplets, which makes the assumption that the particles are in a liquid state (metastable condition) reasonable. However, when ~~the~~ particles are exposed to a ~~quite~~substantially low RH, the state of the particles may change. Figure 2 and Figure S1-S4 ~~exhibit the~~show comparisons between the predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$ ($NH_4^+/(NH_3+NH_4^+)$, mol/mol), $\varepsilon(NO_3^-)$ ($NO_3^-/(HNO_3+NO_3^-)$, mol/mol)), and $\varepsilon(Cl^-)$ ($Cl^-/(HCl+Cl^-)$, mol/mol) based on real-time ion chromatography data~~, which~~; all results are ~~all colored by~~ coloured with the corresponding RH. ~~It can be seen that agreements between~~The predicted and measured NH_3, NH_4^+, NO_3^-, and Cl^- values are ~~pretty well,~~in good agreement; the R^2 values of linear regressions are all higher than 0.94, and the slopes are ~~around~~approximately 1. Moreover, the agreement between the predicted and measured $\varepsilon(NH_4^+)$ is better ~~when compared with~~ than those of $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$. The slope of the linear regression between the predicted and measured $\varepsilon(NH_4^+)$ was 0.93, 0.91, 0.95, and 0.96 and ~~the~~ R^2 ~~is~~was 0.87, 0.93, 0.89, and 0.97 in spring, winter, summer, and autumn, respectively. However, the measured and predicted partitioning of HNO_3 and HCl show significant discrepancies (R^2 values of 0.28 and 0.18, respectively), which may ~~attribute~~be attributed to the much lower gas concentrations ~~compared with the~~than particle concentrations, as well as the ~~gas denuder~~HNO_3 and HCl measurement uncertainties from ~~particle collection artifacts (Guo~~MARGA (Rumsey et al., ~~2018). Obviously~~2014). Clearly, more scatter points deviate from the 1:1 line when ISORROPIA-II ~~runs~~is operated at RH≤30%, which is ~~much~~highly evident in winter and spring. For data with RH ≤ 30%, the predictions are significantly improved when assuming ~~aerosol~~the aerosols are in stable mode (solid + liquid) (Figure S5-S6~~). However,~~) and the aerosol liquid water ~~was~~is almost zero and cannot be used to predict aerosol pH. ~~It~~This behaviour reveals that it is not reasonable to predict ~~the~~ aerosol pH using the thermodynamic model when the RH is relatively low. Consequently, we only ~~discussed~~determined the $PM_{2.5}$ pH for data with RH values higher than 30% in this work.

Figure 2

Running ISORROPIA-II in the forward mode with only aerosol component concentrations as input may result in a bias in predicted pH due to repartitioning of ammonia in the model, leading to a lower predicted pH when gas-phase data are not available (Hennigan et al., 2015). In this work, ~~since~~ no gas phase was available for ~~the~~ size-resolved pH prediction. We determined aerosol pH through an iteration procedure that used the measured particulate species and ISORROPIA-II to predict gas species~~, the detailed~~. Detailed information ~~could~~can be found in Fang et al. (2017) and Guo et al. (2016). ~~As a brief~~In summary, the predicted NH_3, HNO_3, and HCl concentrations from the i-~~1~~1th run were applied to the ith iteration, until the gas concentrations converged. Based on

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these iterative gas–phase concentrations, the ion concentrations ~~from~~of samples collected by ~~the~~ MOUDI as well as the ~~averaged~~average RH and T during each sampling period were used to determine the aerosol pH for different size ranges. ~~Just like~~Similar to calculating the ~~pH of~~ $PM_{2.5}$ pH, it was ~~also~~ assumed that all the particles ~~at~~in each size bin were internally mixed and had the same pH.

~~The comparisons~~Comparisons of the iterative and predicted NH_3, HNO_3, and HCl as well as the measured and predicted NO_3^-, NH_4^+, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ for ~~data from~~ MOUDI samples are ~~showed~~shown in Figure 3. ~~The~~A previous study showed that coarse–mode particles ~~were very difficult to~~could not easily reach equilibrium with ~~the~~ gaseous precursors due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000). Assuming that coarse–mode particles are in equilibrium with the gas phase could result in a large bias between the measured and predicted NO_3^- and NH_4^+ in coarse–mode particles (Fang et al., 2017). ~~We also find that~~ Additionally, in this work, ~~it can be clearly seen that~~ assuming that coarse–mode particles are in equilibrium with the gas phase could ~~overpredict~~over-predict NO_3^- and Cl^- and underestimate NH_4^+ in the coarse mode (~~the~~ blue scatters), which could subsequently underestimate the coarse–mode aerosol pH. ~~Compared with~~ In contrast to the coarse–mode particles, the measured and predicted NO_3^-, NH_4^+, and Cl^- agreed very well in fine–mode particles. Considering the kinetic limitations and nonideal gas-particle partitioning in coarse–mode particles, the aerosol pH in the coarse mode was determined by ignoring the gas phase.

Figure 3

2.5 ~~Sensitivities~~Sensitivity of ~~aerosol~~$PM_{2.5}$ pH to SO_4^{2-}, ~~NO_3^T, NH_4^T, Cl^T,~~ TNO_3, TNH_3, Ca^{2+}, RH, and T

~~In the real ambient air, the thermodynamic process of the aerosol is complicated, it is not easy to tell the effect of one factor~~To explore the major influencing factors on ~~the aerosol pH. The ALWC, H_{air}^+, aerosol pH, $c(NH_4^+)$, $c(NO_3^-)$, and $c(Cl^-)$ are all the output of ISORROPIA-II. Together, they reflect an objective state of particles. Considering the relative independence between input parameters, it is reasonable to discuss the influence of input variables on output parameters with the results of ISORROPIA-II. Thus, in this paper, we focus on the~~aerosol pH, sensitivity ~~analysis of single-factor variation, which can reflect the variation tendency of aerosol pH caused by the change of each variable.~~

~~In the ISORROPIA-II, the input parameters include SO_4^T (total sulfate (gas+aerosol) expressed as equivalent H_2SO_4), NO_3^T~~tests were performed. In the sensitivity analysis, SO_4^{2-}, TNO_3 (total nitrate (gas+aerosol) expressed as equivalent HNO_3), ~~NH_4^T~~TNH_3 (total ammonium (gas+aerosol) expressed as equivalent NH_3), ~~Cl^T (total chloride (gas+aerosol) expressed as equivalent HCl), Na^+, Ca^{2+}, K^+, Mg^{2+}, RH, and T. After running, the gas and aerosol phase of NO_3^T, NH_4^T, and Cl^T would be reapportioned and output. In view of this, it is more reasonable to analyze the impact of NO_3^T,~~

~~NH_4^+, and Cl^- on aerosol pH, rather than the impact of a single gas or aerosol phase of NO_3^-, NH_4^+, and Cl^- on aerosol pH. In addition, the mass concentration of K^+ and Mg^{2+} was low, so the variables in the sensitivity analysis were determined as SO_4^{2-}, NO_3^-, NH_4^+, Cl^-,~~ Ca^{2+}, RH, and T. ~~When assessing~~ were selected as the variables since SO_4^{2-} and NO_3^- are major anions in aerosols, NH_4^+ and Ca^{2+} are major cations in aerosols, and Ca^{2+} is generally considered representative of crustal ions. To assess how a variable affects ~~ALWC, H_{air}^+, and aerosol~~ $PM_{2.5}$ pH, the real-time measured values of this variable and the ~~averaged~~average values of other variables in each season were input into ISORROPIA-II. The magnitude of the relative standard deviation (RSD) of the calculated aerosol pH can reflect the impact of ~~one~~ variable variations on ~~the~~ aerosol acidity. The higher the RSD is, the greater the impact, and vice versa. The average value and variation range for each variable in ~~all~~the four seasons are listed in Table S1~~ and Figure S7~~.

The sensitivity analysis in this work was only aimed at ~~the~~ $PM_{2.5}$ (~~i~~*i.e.*, fine particles) ~~because~~since the MARGA system equipped with a $PM_{2.5}$ ~~components in four seasons were available and~~inlet had a high temporal resolution (~~1h~~1 h). In addition, the data set had a wide range, covering different levels of haze events. ~~Noted that the~~The sensitivity analysis in this work only reflected the characteristics during the observation periods, and further work is needed to determine whether the sensitivity analysis is valid in other environments.

3. Results and Discussion

3.1 Overall summary of $PM_{2.5}$ pH over four seasons

The ~~averaged $PM_{2.5}$~~ average mass concentrations ~~were 62±36, 60±69, 39±24,~~ of $PM_{2.5}$ and ~~59±48~~ ~~μg m^{-3} for observation periods of spring, winter, summer, and autumn, respectively (~~major inorganic ions in the four seasons are shown in Table 1~~).~~ Among all the ions measured, NO_3^-, SO_4^{2-}, and NH_4^+ were the three most dominant species, accounting for 83% ~ 87% of the total ~~ions. Compared with other seasons, the averaged concentration~~ion content. The average concentrations of primary inorganic ions (Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}) ~~was~~were higher in spring~~. The aerosol~~ than in other seasons. $PM_{2.5}$ in Beijing showed ~~the~~ moderate acidity, with $PM_{2.5}$ pH values of 4.~~04~~±1.~~02~~, 4.5±0.7, 3.8±1.2, and 4.3±0.8 for spring, winter, summer, and autumn ~~observation~~observations, respectively (data at RH ≤30% were excluded). The overall winter $PM_{2.5}$ pH was comparable to the result (4.2) found in Beijing~~, 4.2 from~~ by Liu et al. (2017) and that (4.5 ~~from~~) found by Guo et al. (2017), but lower than that (4.9, winter and spring) in Tianjin (Shi et al., 2017), another mega city ~~about~~approximately 120 km away from Beijing. The $PM_{2.5}$ pH in summer ~~$PM_{2.5}$ pH~~ was lowest among all four seasons. The seasonal variation ~~of~~in $PM_{2.5}$ pH in this work was similar to the ~~result from~~results in Tan et al. (2018~~)~~), except for spring, ~~which was~~and followed the trend winter (4.11 ± 1.37) > autumn (3.13 ± 1.20) > spring (2.12 ± 0.72) > summer (1.82 ± 0.53).~~ Noted that the observation in Tan et al. (2018) was conducted in Beijing in 2014, the distinction in the aerosol compositions was probably responsible for the lower $PM_{2.5}$ pH in their work.~~

Table 1~~.~~

To further investigate the $PM_{2.5}$ pH ~~performance~~level under different pollution ~~levels~~conditions

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over four seasons, the $PM_{2.5}$ concentrations were classified into three groups ~~with:~~ 0~75 μg m^{-3}, 75~150 μg m^{-3}, and >150 μg m^{-3}, representing ~~the~~ clean, polluted, and heavily polluted conditions, respectively. The relationship between $PM_{2.5}$ concentration and ~~its~~ pH is shown in Figure ~~S8~~S7. The $PM_{2.5}$ pH under clean ~~condition~~conditions spanned 2~7, while ~~the $PM_{2.5}$ pH~~those under polluted and heavily polluted conditions was mostly concentrated ~~in~~from 3~5. Table 1 shows that as the air quality deteriorated, the aerosol ~~components~~component concentration, as well as ALWC and H_{air}^+, all increased ~~for~~in each season~~, but the differences in $PM_{2.5}$ pH for three pollution levels were not statistically significant. In terms of the averaged values, the~~. The average $PM_{2.5}$ pH under ~~the~~ clean ~~condition~~conditions was the highest (Table 1), ~~then~~ followed by polluted and heavily polluted conditions in spring, summer, and autumn. In winter, however, the ~~averaged~~average pH under polluted ~~condition~~conditions (4.8±1.0) was the highest~~, then followed by clean (4.5±0.6) and heavily polluted conditions (4.4±0.7).~~

~~Time series of mass fraction of NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, and crustal ions (Mg^{2+} and Ca^{2+}) in total ions, as well as pH in all four seasons, are showed in Figure 4. It can be seen that on~~ On clean days, ~~high~~a higher $PM_{2.5}$ pH (>6) was generally ~~companied~~accompanied by ~~high~~a higher mass fraction of crustal ions~~, (Mg^{2+} and Ca^{2+})~~, while ~~the relatively low~~a lower $PM_{2.5}$ pH (<3) was ~~companied~~accompanied by ~~high~~a higher mass fraction of SO_4^{2-} and ~~low~~lower mass fraction of crustal ~~ion, which was~~ions; such conditions were most obvious in summer (~~large part of $PM_{2.5}$ pH with RH<30%~~Figure 4). Under polluted and heavily polluted conditions, the mass fractions of major chemical components were ~~excluded in spring and winter). On polluted and heavily polluted days,~~ similar, and the difference in $PM_{2.5}$ pH between these two conditions was also small. All of these results indicated that the aerosol chemical composition ~~was similar, mainly dominated by NO_3^-, hence the differences of $PM_{2.5}$ pH on polluted and heavily polluted days were small. Compared with the mass concentration of $PM_{2.5}$, the different aerosol chemical compositions~~ might be the ~~essence~~essential factor that ~~drove~~drives aerosol acidity. The impact of aerosol ~~compositions~~composition on $PM_{2.5}$ pH is discussed in Section 3.4.

Figure 4~~.~~

~~Beijing is surrounded by mountains on three sides. Haze episodes usually occur with southwest and southeast winds as well as calm winds in Beijing. The industry is mainly concentrated in the south of Beijing, leading to the higher $PM_{2.5}$ concentration in Beijing by the regional transport and accumulation. Wind dependence of $PM_{2.5}$, NO_3^-, SO_4^{2-}, NH_4^+ and the averaged $PM_{2.5}$ pH are shown in Figure 5 and Figure S9. In~~ In spring, summer, and autumn, the pH of $PM_{2.5}$ ~~pH in~~from the northern direction ~~were~~was generally higher than that ~~in~~from the southwest direction, but the ~~high~~higher pH in summer also occurred with ~~southwest~~ strong southwest winds (wind speed >3 m s^{-1}) (Figure 5). Generally, ~~the northerly~~northern winds ~~usually~~ occur with cold ~~-~~front systems, which ~~could~~can sweep away air pollutants but ~~raised~~raise dust in which the crustal ion species (Ca^{2+}, Mg^{2+}) ~~were~~are

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higher. In winter, the $PM_{2.5}$ pH was distributed relatively evenly in ~~each~~all wind ~~direction~~directions, but we surprisingly found that the pH in northerly winds ~~is~~could be as low as 3~4, which was consistent with the high mass fraction of SO_4^{2-} on ~~the~~ clean days caused by the ~~northerly~~northern winds.

Figure 5

3.2 Diurnal variation ~~of~~in ALWC, H_{air}^+, and $PM_{2.5}$ pH

~~The~~ Obvious diurnal variation was observed based on the long-term online dataset, as shown in Figure 6. To understand the factors that can drive changes in $PM_{2.5}$ pH, the diurnal variations of NO_3^-, SO_4^{2-}, ALWC, and H_{air}^+ were investigated and ~~$PM_{2.5}$ pH~~ are exhibited in Figure 6. ~~The diurnal variations for ALWC, H_{air}^+, and pH was similar over four seasons.~~ Generally, ~~nighttime mean~~ ALWC was higher during nighttime than daytime and reached a peak ~~at~~ near 04:00 ~ 06:00 (local time). After sunrise, the increasing ~~temperatures~~temperature resulted in a rapid drop in RH, leading to ~~the obvious~~a clear loss of particle water, and ALWC reached the lowest level in the afternoon. H_{air}^+ was highest in the afternoon ~~and then~~, followed by nighttime, and H_{air}^+ was relatively low in the ~~forenoon~~morning. The low ALWC and high H_{air}^+ values in the afternoon resulted in the minimum pH ~~in the afternoon~~at this time. The ~~averaged~~average nighttime pH ~~is~~was 0.3~0.4 ~~unit~~units higher than that ~~on~~during daytime. ~~Noted that the~~The diurnal variations ~~of~~in $PM_{2.5}$ pH described here were determined for the cases with an RH higher than 30%. ~~If the data at RH≤30% were included, the diurnal variations of H_{air}^+, pH, and SO_4^{2-} in winter were changed (Figure S10). H_{air}^+ and SO_4^{2-} were both higher at nighttime since the nocturnal boundary layer height was generally low in winter and easily resulted in the accumulation of SO_4^{2-}, hence leading to a lower pH at the night.~~

The ~~diurnal variation of~~ correlation between NO_3^- ~~in winter and spring agreed well with the aerosol acidity. Nevertheless, in summer and autumn, the agreement~~concentration and $PM_{2.5}$ pH was ~~not well.~~ weakly positive at low ALWC, and $PM_{2.5}$ pH was almost independent of the NO_3^- mass concentration at higher ALWC values (Figure ~~S11 shows the relationship between mass concentrations of SO_4^{2-} and NO_3^- and $PM_{2.5}$ pH at different ALWC levels for all four seasons. At the relatively low ALWC, the~~S8). In contrast, at a low ALWC level, increasing SO_4^{2-} ~~could decrease~~decreased the pH ~~obviously~~; at ~~the relatively~~a high ALWC~~, the~~ level, a negative correlation still existed between SO_4^{2-} mass concentration and $PM_{2.5}$ pH. ~~On the contrary, a weak positive correlation was found between NO_3^- and pH at the relatively low ALWC and the $PM_{2.5}$ pH was almost invariable with the NO_3^- mass concentration at the relatively high ALWC. Compared with the NO_3^-, the~~ SO_4^{2-} had a greater effect than NO_3^- on $PM_{2.5}$ pH. ~~When the ALWC was high enough (for example, higher than 100 μg m^{-3}), the impact of dilution of ALWC to the H_{air}^+ was more significant.~~

Figure 6

~~Guo et al. (2015) found that the ALWC diurnal variation was significant, and the diurnal pattern in pH was mainly driven by particle water dilution. However, in this work,~~ From the above

discussion, we found that both H_{air}^+ and ALWC had significant diurnal variations, ~~and the~~ indicating that aerosol acidity ~~variation agreed well with sulfate, indicating the aerosol acidity in~~ in the NCP was driven by both ~~driven by~~ aerosol composition and particle water. ~~For example, in the winter of NCP~~This trend is slightly different from the situation from the US: Guo et al. (2015) found that the ALWC diurnal variation was significant and the diurnal pattern in pH was mainly driven by the dilution of aerosol water. Specifically, in winter, the $PM_{2.5}$ mass concentration in Beijing was several ~~to~~ times or even dozens of times higher than that in the US, and the RH was generally low, which means there ~~are~~were more seeds in the limited particle water~~, and the RH was generally low, hence~~. Hence, the dilution of H_{air}^+ by aerosol liquid water ~~to H_{air}^+ doesn't work at all, the diurnal variation of aerosol components~~ was ~~more important.~~

~~**3.3 Gas-particle separation**~~

~~Table 2 exhibits the measured c(NH_4^+), c(NO_3^-), and c(Cl^-) at different RH levels. The measured c(NH_4^+), c(NO_3^-), and c(Cl^-) increased with the elevated RH in all four seasons, indicating more NH_4^T, NO_3^T, and Cl^T were partitioned into particle phase at higher RH. In~~ quite limited in winter ~~and spring, NO_3^T and Cl^T were dominated by particle phases, c(NO_3^-) and c(Cl^-) was higher than 65%. Whereas in summer and autumn, the lower RH generally companied by higher ambient temperature, more than half of the NO_3^T and Cl^T were partitioned into the gaseous phase. When the RH reached above 60%, more than 90% of NO_3^T and 70% of Cl^T were in the particle phase for all four seasons. Compared with c(NO_3^-) and c(Cl^-), the c(NH_4^+) was pretty lower. In spring, summer, and autumn, the average c(NH_4^+) was still lower than 0.3 even when the RH >60%, which might attribute to the higher NH_3 mass concentration in the atmosphere. The averaged NH_3 was 21.5±8.7 μg m^{-3}, 19.6±6.4 μg m^{-3}, and 16.8±8.0 μg m^{-3} in spring, summer, and autumn, respectively. In winter, the average c(NH_4^+) were much higher than that in other seasons with the relatively lower NH_3 mass concentration (4.9±2.8 μg m^{-3}).~~

~~**Table 2.**~~

3.43 Factors affecting ~~ALWC, H_{air}^+,~~ $PM_{2.5}$ pH~~, and gas-particle partitioning~~

~~As mentioned above, the aerosol chemical composition has a non-negligible effect on $PM_{2.5}$ pH. In~~ In this work, the effects of ~~SO_4^{2-}, NO_3^T, NH_4^T, Cl^T~~SO_4^{2-}, TNO_3, TNH_3, Ca^{2+}, RH, and T on $PM_{2.5}$ pH were ~~performed~~determined through a four-season sensitivity analysis ~~over four seasons.~~

~~As shown in Table 3, for ALWC, the largest relative standard deviation (RSD) was observed when RH was taken as the evaluated factor, then followed by SO_4^{2-} or NO_3^-, which means the RH had the greatest influence on ALWC, and SO_4^{2-} and NO_3^- were major hygroscopic components in the aerosol.~~

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~~The SO_4^{2-}, RH, NO_3^-, and NH_4^+ were all important influential factors for H_{air}^+, especially SO_4^{2-}. The SO_4^{2-} and T were two crucial~~. The common important driving factors affecting ~~the $PM_{2.5}$ pH variation. The $PM_{2.5}$ pH was also sensitive to NH_4^+ when it was in a lower range and sensitive to RH only in summer. The relationship between pH and NH_4^+ was nonlinear, the impact of NH_4^+ on pH weakened as NH_4^+ increased. In spring, the crucial factor for the $PM_{2.5}$ pH variation was SO_4^{2-}~~ $PM_{2.5}$ pH variations in all four seasons were SO_4^{2-}, TNH_3, and T (Table 2), while ~~it was SO_4^{2-}~~ the unique influencing factors were Ca^{2+} in spring and ~~NH_4^+~~RH in ~~winter. In~~ summer. For ALWC, the most important factor ~~affecting $PM_{2.5}$ pH was RH, then followed by NH_4^+ and SO_4^{2-}. In autumn, the effect of NH_4^+ on $PM_{2.5}$ pH was considerable, SO_4^{2-} and T were also important.~~was RH, followed by SO_4^{2-} or NO_3^-. Figure 7~~9~~ and ~~S12-S17~~Figure S9-S16 show how these factors ~~affecting the ALWC, H_{air}^+, and aerosol acidity over four seasons. The~~ affect the $PM_{2.5}$ pH, ALWC, and H_{air}^+ over all four seasons.

Table 2

Theoretically, elevated TNO_3 can reduce $PM_{2.5}$ pH since the $HNO_3 \rightarrow NO_3^-$ conversion process can release H^+. However, in the sensitivity tests, we found that only the $PM_{2.5}$ pH in winter and autumn decreased significantly with elevated TNO_3 (Figure 7, S16). In spring and summer, $PM_{2.5}$ pH changed little with elevated TNO_3. Moreover, when the TNO_3 concentration was low, $PM_{2.5}$ pH even increased with elevated TNO_3 (Figure 7, S13). The phenomenon was mainly due to the rich-ammonia condition in the NCP (Figure S18). The sensitivity tests showed that elevated TNH_3 could consume H_{air}^+ swiftly and increase the $PM_{2.5}$ pH. In this work, the lower TNH_3 mass concentration in winter and higher TNO_3 mass concentration in autumn (Table S1) resulted in decreased $PM_{2.5}$ pH with elevated TNO_3. In spring and summer, excessive NH_3 could continuously buffer the increasing TNO_3, leading to the minimal changes in $PM_{2.5}$ pH. Changes in TNH_3 in the lower concentration range had a significant impact on $PM_{2.5}$ pH, and changes in TNH_3 at higher concentrations could only generate limited pH changes (Figure 7, S13, S16). The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicates that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral, which might be attributed to the limited ALWC. Compared to the liquid water content in clouds and precipitation, the ALWC was much lower; hence, the dilution of H_{air}^+ by aerosol liquid water was limited. Moreover, the hydrolysis of ammonium salts contributes to the release of hydrogen ions.

Figure 7

Compared with NO_3^-, SO_4^{2-} has a key role in aerosol acidity due to its stronger ability to provide H^+ during the $H_2SO_4 \rightarrow SO_4^{2-}$ conversion process (Figure S9, S11, S14). Hence, elevated SO_4^{2-} is crucial in the increase of H_{air}^+. In this work, $PM_{2.5}$ pH was lowest in summer but highest in winter, which was consistent with the SO_4^{2-} mass fraction with respect to the total ion content. The SO_4^{2-} mass fraction was highest in summer among the four seasons, with a value of 32.4%±11.1%, but lowest in winter, with a value of 20.9%±4.4%. In recent years, the SO_4^{2-} mass fraction in $PM_{2.5}$ in

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Beijing has decreased significantly due to the strict emission control measures for SO_2; in most cases, NO_3^- dominates the inorganic ions (Zhao et al., 2013, 2017; Huang et al., 2017; Ma et al., ~~sensitivity analysis for ALWC and H_{air}^+ were similar over four seasons, while the sensitivity of $PM_{2.5}$ pH to RH and NO_3^- in four seasons were different from each other. In this study, winter and summer were chosen for a detailed discussion of sensitivity analysis because more heavy pollution episodes happened in winter while the photochemical reaction was relatively strong in summer.~~

~~**Table 3**~~

~~**Figure 7**~~

~~**Figure 8**~~

2017), which could reduce aerosol acidity. A study in the Pearl River Delta of China showed that the in situ acidity of $PM_{2.5}$ significantly decreased from 2007-2012; the variation in acidity was mainly caused by the decrease in sulfate (Fu et al.,2015). The excessive NH_3 in the atmosphere and the high NO_3^- mass fraction in $PM_{2.5}$ may be the reason why the aerosol acidity in China is lower than that in Europe and the United States. In addition, the DRH of NH_4NO_3 is lower than that of $(NH_4)_2SO_4$ (Seinfeld and Pandis, 2016); hence, the particles dominated by NH_4NO_3 can deliquesce at lower RH, which may result in the increase in ALWC.

Ca^{2+} is an important crustal ion; in the output of ISORROPIA-II, Ca exists mainly as $CaSO_4$ (slightly soluble). Elevated Ca^{2+} concentrations can increase $PM_{2.5}$ pH by decreasing H_{air}^+ and ALWC (Figure 7 and Figure S9-S16). As discussed in Section 3.1, on clean days, $PM_{2.5}$ pH reached 6~7 when the mass fraction of Ca^{2+} was high; hence, the role of crustal ions on $PM_{2.5}$ pH cannot be ignored in areas or seasons (such as spring) in which mineral dust is an important particle source. Due to the strict control measures for road dust, construction sites, and other bare ground, the crustal ions in $PM_{2.5}$ decreased significantly in the NCP, especially on polluted days.

In addition to the particle chemical composition, meteorological conditions also have important impacts on aerosol acidity. RH had a different impact on $PM_{2.5}$ pH in different seasons. Elevated RH can enhance water uptake and promote gas-to-particle conversion. In winter, the H_{air}^+ increase caused by elevated RH was much larger than the increase in ALWC; hence, elevated RH could reduce $PM_{2.5}$ pH. However, an opposite tendency was observed in summer due to the lower mass concentration of chemical components, and the dilution effect of ALWC on H_{air}^+ was obvious only in summer (Figure 7). In spring and autumn, RH had little impact on $PM_{2.5}$ pH due to the synchronous variation in H_{air}^+ and ALWC (Figure S13, S16). The different impacts of RH on $PM_{2.5}$ pH indicated that the higher RH during severe haze may increase aerosol acidity. Temperature can alter the $PM_{2.5}$ pH by affecting gas-particle partitioning. At higher ambient temperatures, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ all showed a decreased tendency (Figure 8). The volatilization of ammonium nitrate and ammonium chloride can result in a net increase in particle H^+ and lower pH (Guo et al.,

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2018). Moreover, a higher ambient temperature tends to lower ALWC, which can further decrease $PM_{2.5}$ pH.

Figure 8

3.4 Size distribution of aerosol pH values

Inorganic ions in particles present clear size distributions, and the size-resolved chemical composition can change at different pollution levels (Zhao et al., 2017; Ding et al., 2017; Ding et al., 2018), which may result in variations in aerosol pH. Thus, we further investigated the size-resolved aerosol pH at different pollution levels. According to the average $PM_{2.5}$ concentration during each sampling period, all the samples were also classified into three groups (clean, polluted, and heavily polluted) according to the rules described in Section 3.1. A severe haze episode occurred during the autumn sampling period; hence, there were more heavily polluted samples in autumn than in other seasons. Figure 9 shows the average size distributions of PM components and pH under clean, polluted, and heavily polluted conditions in summer, autumn, and winter. NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, K^+, OC, and EC were mainly concentrated in the size range of 0.32~3.1 μm, while Mg^{2+} and Ca^{2+} were predominantly distributed in the coarse mode (>3.1 μm). During haze episodes, the sulfate and nitrate in the fine mode increased significantly. However, the increases in Mg^{2+} and Ca^{2+} in the coarse mode were not as substantial as the increases in NO_3^-, SO_4^{2-}, and NH_4^+, and the low wind speed made it difficult to raise dust during heavily polluted periods. More detailed information about the size distributions for all analysed species during the three seasons is given in Zhao et al. (2017) and Su et al. (2018).

Figure 9

~~**RH:** RH had a different impact on $PM_{2.5}$.~~The aerosol pH in ~~different seasons. In winter, the $PM_{2.5}$ pH decreased with the increasing RH, whereas the $PM_{2.5}$ pH increased with the increasing RH in summer. In spring and autumn, the RH between 30~83% had little impact on $PM_{2.5}$ pH. The explanation for this is that the increased RH actually diluted the solution and promoted ionization, releasing H_{air}^+ and increasing ALWC as well, but the gradient was different. In winter, variation in H_{air}^+ caused by RH changes was much larger than variation in ALWC, whereas it showed an opposite tendency in summer. In autumn and spring, variation in H_{air}^+ caused by RH changes was slightly higher than the variation in ALWC. The different impact of RH on $PM_{2.5}$ pH indicated that the dilution effect of ALWC on H_{air}^+ was obvious only in summer, the high RH during the severe haze in winter could increase the aerosol acidity.~~

~~**T:** At high ambient temperature, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ all showed a decreased tendency (Figure 10 and S19). The procedure of $NH_4^+ \rightarrow NH_3$ releases one H^+ to particle phase, whereas the~~

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procedure of NO_3^-→HNO_3 or Cl^-→HCl both need one H^+ from the particle phase. Compared with the loss of NO_3^- from NH_4NO_3 as well as Cl^- from NH_4Cl, greater loss of NH_4^+ from NH_4NO_3, NH_4Cl, and $(NH_4)_2SO_4$ resulted in a net increase in particle H^+ and lower pH. In addition, the molality-based equilibrium constant (H^*) of NH_3-NH_4^+ partitioning decreased faster with increasing temperature when compared with that of HNO_3-NO_3^- partitioning, resulting in a net increase in particle H^+ (Guo et al., 2018). Moreover, higher ambient temperature tends to lower ALWC, which further decreases the $PM_{2.5}$ pH. The wide range of ambient temperature in autumn made a significant impact on $PM_{2.5}$ pH in the sensitivity analysis.

Figure 10

SO_4^{2-}: SO_4^{2-} had a key role in aerosol acidity, especially in winter and spring (Figure 9, S14, S17). In the sensitivity test, the $PM_{2.5}$ pH decreased by about 1.6 (4.1 to 2.5), 4.9 (5.1 to 0.2), 1.0 (3.6 to 2.6), and 0.9 (4.0 to 3.1) unit with SO_4^{2-} concentration went up from 0 to 40 μg m^{-3} in spring, winter, summer, and autumn, respectively. In spring and winter, the ALWC was low, the variation of SO_4^{2-} mass concentration could generate dramatic changes in H_{air}^+. In section 3.1, the $PM_{2.5}$ pHthe fine mode and coarse mode was lowest in summer whereas highest in winter, which was consistent with the SO_4^{2-} mass faction in total ions. The SO_4^{2-} mass faction in total ions in summer was highest among four seasons with 32.4%±11.1%, whereas it was lowest in winter with 20.9%±4.4%.

NO_3^T: The impact of NO_3^- on $PM_{2.5}$ pH was also different, which was related to the averages of input NH_4^T in different seasons. In winter, the $PM_{2.5}$ pH decreased with increasing NO_3^T concentration, whereas little impact was found in summer (Figure 9). In spring and autumn, the $PM_{2.5}$ pH increases first and then dropped with the increasing NO_3^T concentration (Figure S14, S17). In winter, the NH_4^T mass concentration was relatively low. As NO_3^T increases, all NH_3 could be converted into NH_4^+ ($\varepsilon(NH_4^+)$ ≈1). However, if HNO_3 continued to dissolve and released H_{air}^+, it would result in the decrease of $PM_{2.5}$ pH. In summer, the averages of NO_3^T and Cl^T was relatively low but the NH_4^T was excessive, the highest $\varepsilon(NH_4^+)$ was only 0.6 with the corresponding highest NO_3^T. The excessive NH_3 could provide continuous buffering to the increasing NO_3^T, together with a significant dilution of ALWC on H_{air}^+, leading to the little changes in $PM_{2.5}$ pH. In spring and autumn, the increasing pH with elevated NO_3^T in lower range attributed to the dilution of ALWC to H_{air}^+. H_{air}^+ concentration increased exponentially with elevated NO_3^T concentration, especially at

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higher NO_3^T concentrations, whereas the ALWC increased linearly with elevated NO_3^T concentration (Figure S12-S17), hence ALWC played a dominant role when the NO_3^T concentration was low. With the further increase of NO_3^T, the variation in H_{air}^+ caused by NO_3^T addition was larger than the variation in ALWC, leading to the decrease of $PM_{2.5}$ pH. Besides, the relationship between NO_3^T and $\varepsilon(NH_4^+)$ in the sensitivity analysis showed that decreasing NO_3^T could lower the $\varepsilon(NH_4^+)$ effectively (Figure 11 and S20), which helped NH_3 maintain in the gas phase.

Figure 11

NH_4^T: The relationship between $PM_{2.5}$ pH and NH_4^T was nonlinear. NH_4^T in lower range had a significant impact on the $PM_{2.5}$ pH (Table S2), and higher NH_4^T generated limited pH change (Figure 9, S14, S17). Elevated NH_4^T could reduce H_{air}^+ exponentially and slightly increase ALWC when the other input parameters were held constant. As the NH_4^T increased, H_{air}^+ was consumed swiftly during the dissolution of NH_3 and the further reaction with SO_4^{2-}, NO_3^-, and Cl^-. The elevated NH_4^T increased the $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$ when NO_3^T and Cl^T were fixed (Figure 11 and S20), which means the elevated NH_4^T altered the gas-particle partition and shifted more NO_3^T and Cl^T into particle phase, leading to the deliquescence of additional nitrate and chloride and an increase of ALWC. It seems that NH_3 emission control is a good way to reduce NO_3^-. However, the relationship between NH_4^T and $\varepsilon(NO_3^-)$ in the sensitivity analysis (Figure 11 and S20) showed that the $\varepsilon(NO_3^-)$ response to NH_4^T control was highly nonlinear, which means the decrease of nitrate would happen only when the NH_4^T was greatly reduced. The same result was also obtained from a study of Guo et al (2018).

The ratio of [TA]/2[TS] provides a qualitative description for the ammonia abundance, where [TA] and [TS] are the total (gas + aqueous + solid) molar concentrations of ammonia and sulfate. The rich-ammonia is defined as [TA] > 2[TS], while if the [TA] ≤ 2[TS], then it is defined as poor-ammonia (Seinfeld and Pandis, 2016). In this work, the ratio of [TA]/2[TS] was much higher than 1 and belonged to rich-ammonia (Figure. S21). Although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral, which might attribute to the limited ALWC. Compared to the liquid water content in clouds and precipitation, ALWC was much lower, hence the dilution of aerosol liquid water to H_{air}^+ was weak.

Cl^T: Cl^T had a relatively larger impact on the $PM_{2.5}$ pH in winter and spring compared to summer

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and autumn. Except for winter, the Cl^- mass concentration was generally lower than 10 μg m^{-3}, which accounted for the little impact on $PM_{2.5}$ pH. On account of the low level of Cl^-, the dilution of ALWC on H_{air}^+ played a dominant role, generating the $PM_{2.5}$ pH increase with elevated Cl^-. However, similar to NO_3^-, higher Cl^- could decrease the $PM_{2.5}$ pH.

Ca^{2+}: In fine particles, Ca^{2+} mass concentration was generally low. In the output of ISORROPIA-II, Ca existed as $CaSO_4$ (slightly soluble). Elevated Ca^{2+} concentration could increase the $PM_{2.5}$ pH by decreasing H_{air}^+ and ALWC (Figure S18), the decreased H_{air}^+ resulted from the buffering capacity of Ca^{2+} to the acid species, while the decreased ALWC resulted from the weak water solubility of $CaSO_4$. As discussed in Section 3.1, on clean conditions, the $PM_{2.5}$ pH could reach 6~7 when the mass fraction of Ca^{2+} was high, hence the role of mineral ions on $PM_{2.5}$ pH could not be ignored in seasons (such as spring) or regions where mineral dust was an important source of fine particles. Due to the strict control measures for road dust, construction sites, and other bare ground, the nonvolatile cations in $PM_{2.5}$ decreased significantly in NCP.

3.5 Size distribution of aerosol components and pH

According to the average $PM_{2.5}$ concentration during every sampling periods, all the samples were also classified into the three groups (clean, polluted, heavily polluted) with the same rule described in Section 3.1. A severe haze episode occurred during the autumn sampling, hence there were more heavily polluted samples for autumn than that in other seasons. Figure 12 shows the averaged size distributions of PM components and pH on clean, polluted, and heavily polluted conditions in summer, autumn, and winter, respectively. The NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, K^+, OC, and EC mainly concentrated in the size range with aerodynamic diameters between 0.32~3.1μm, while Mg^{2+} and Ca^{2+} predominantly distributed in the coarse mode. As shown in Figure 12, the concentration levels for all chemical components increased with the increasing pollution. During the haze episodes, the sulfate and nitrate in the accumulated mode increased significantly. However, the increase of Mg^{2+} and Ca^{2+} in the coarse mode were not as obvious as secondary ions, mainly due to the low wind speed and calm atmosphere which made it more difficult to raise dust during the heavy pollution. More detailed information about size distributions of mass concentration for all analyzed species during three seasons is shown in Zhao et al. (2017) and Su et al. (2018). As

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~~mentioned in section 2.4, assuming coarse mode particles in equilibrium with the gas phase could overpredict NO_3^- and Cl^- and underestimate NH_4^+ in the coarse mode (Figure 3), which subsequently underestimated the coarse mode aerosol pH. Thus, the gas phase was ignored for pH calculation of the coarse particles (>3.1μm).~~

~~**Figure 12**~~

~~The aerosol pH for both fine mode and coarse mode in summer was lowest among three seasons, then~~seasons, followed by autumn and winter. The seasonal variation ~~of~~in aerosol pH derived from MOUDI data was consistent with that derived from the real-time $PM_{2.5}$ ~~chemical components measurement.~~dataset. In summer, the predominance of sulfate in the fine mode and high ambient temperature resulted in a low pH, ranging ~~between~~from 1.8 ~~and~~to 3.9. ~~Aerosol pH for~~ The fine ~~particles~~-mode aerosol pH in autumn and winter was in the range of 2.4 ~ 6.3 and 3.5 ~ 6.5, respectively. ~~The~~ In the fine mode, the difference ~~of~~in aerosol pH ~~between~~among size bins ~~in fine mode~~ was not significant, probably owing to the excessive NH_3 (Guo et al., 2017).

~~As for coarse particles~~ Additionally, the ~~predicted pH was approximately near or even higher than 7 for all of the three seasons in this work, which mainly attributed to the buffering capacity of the coarse mode mineral dust. Simulations with extreme cases that Ca^{2+} and Mg^{2+} were removed from the input files were conducted. The results showed that the presence of Ca^{2+} and Mg^{2+} had a crucial effect on coarse mode aerosol pH (Figure S22), the difference of aerosol pH (with and without Ca^{2+} and Mg^{2+}) for particles larger than 1 μm increased with the increasing particle size. For particles smaller than 1 μm, the removal of Ca^{2+} and Mg^{2+} had little effect on aerosol pH.~~

~~The aerosol pH in coarse mode decreased significantly when under the heavily polluted condition, especially in autumn and winter. For example, the pH in stage 3 (3.1 6.2 μm) declined from 7.8 under the clean condition to 4.5 under the heavily polluted condition in winter, implying that the aerosols in coarse mode during severe hazy days would become weak acid from neutral. The obvious increase of nitrate in coarse mode might responsible for this. Moreover, the significant decrease of mass ratios of Ca^{2+} and Mg^{2+} resulted in the loss of coarse mode buffering capacity.~~

~~The~~ size distributions of aerosol pH ~~and all analyzed chemical components~~ in the daytime and nighttime were explored and are illustrated in Figure ~~S23. For~~S19. In summer and autumn, the pH in the daytime was lower than that in the nighttime ~~was higher than that in the daytime. The diurnal variation for aerosol pH based on MOUDI data was consistent with the online data. Whereas~~, while

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in winter, the pH was higher in the daytime. ~~In~~During the winter~~, the averaged RH during the~~ sampling ~~period was relatively low, leading to a low ALWC, but the~~periods, SO_4^{2-} and NO_3^- ~~in the nighttime~~ were obviously higher ~~due~~and led to ~~the lower boundary layer height. Therefore, H_{air}^+ was more~~ abundant H_{air}^+ in the nighttime ~~while the low ALWC had little effect on pH.~~

~~5. Summary and conclusions~~

~~On the basis of online measurements, the measured and predicted NH_3, NH_4^+, NO_3^-, Cl^-, and $\varepsilon(NH_4^+)$ by using~~ The abundance of Ca^{2+} and Mg^{2+} in the coarse mode led to a predicted coarse particle pH approximately at or higher than 7 for all three seasons. The difference in aerosol pH (with and without Ca^{2+} and Mg^{2+}) increased with increasing particle size above 1 μm (Figure S20). Moreover, the coarse-mode aerosols during severely hazy days shifted from neutral to weakly acidic, especially in autumn and winter. As shown in Figure 9, the pH in stage 3 (3.1-6.2 μm) declined from 7.8 (clean) to 4.5 (heavily polluted) in winter. The significant decrease in the mass ratios of Ca^{2+} and Mg^{2+} in the coarse mode on heavily polluted days resulted in the loss of acid-buffering capacity. Furthermore, the different size-resolved aerosol acidity levels may be associated with different generation pathways of secondary aerosols. According to Cheng et al. (2017) and Wang et al. (2017), the aqueous oxidation of SO_2 by NO_2 is key in sulfate formation under a high RH and neutral conditions. However, it is speculated that dissolved metals or HONO may be more important for secondary aerosol formation under acidic conditions.

3.5 Factors affecting gas-particle partitioning

Gas-particle partitioning can be directly affected by the concentration levels of gaseous precursors and meteorological conditions. In this work, sensitivity tests showed that decreasing TNO_3 lowered $\varepsilon(NH_4^+)$ effectively, which helped maintain NH_3 in the gas phase. Elevated TNH_3 can increase $\varepsilon(NO_3^-)$ when TNO_3 is fixed, which means that the elevated TNH_3 altered the gas-particle partitioning and shifted more TNO_3 into the particle phase, leading to an increase in nitrate (Figure 8 and S17). Controlling the emissions of both NO_x (gaseous precursor of NO_3^-) and NH_3 are efficient ways to reduce NO_3^-. However, the relationship between TNH_3 and $\varepsilon(NO_3^-)$ in the sensitivity tests (Figure 8 and S17) showed that the $\varepsilon(NO_3^-)$ response to TNH_3 control was highly nonlinear, which means that a decrease in nitrate would happen only when TNH_3 is greatly reduced. The same result was also obtained from a study by Guo et al. (2018). The main sources of NH_3 emission are agricultural fertilization, livestock, and other agricultural activities, which are all associated with people's livelihoods. Therefore, in terms of controlling the generation of nitrate, a reduction in NO_x emissions is more feasible than a reduction in NH_3 emissions.

RH and temperature can also alter gas-particle partitioning. The equilibrium constants for solutions of ammonium nitrate or ammonium chloride are functions of T and RH. The measurement data also showed that lower T and higher RH contribute to the conversion of more TNH_3, TNO_3, and TCl into the particle phase (Table 3). When the RH exceeded 60%, more than 90% of TNO_3 was in the particle phase for all four seasons. In summer and autumn, lower RH was generally accompanied by higher ambient temperature, and more than half of the TNO_3 and TCl were

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partitioned into the gaseous phase. In contrast, in winter and spring, low temperatures favoured the reduction of NO_3^- and volatilization of Cl^-, and $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$ were higher than 65%, even at low RH; $\varepsilon(NH_4^+)$ was lower than $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$. In spring, summer, and autumn, the average $\varepsilon(NH_4^+)$ was still lower than 0.3 even when the RH was >60%; this trend was associated with excess NH_3 in the NCP. In summary, higher RH and lower temperature are favourable conditions for the formation of secondary particles, which are typical meteorological characteristics of haze events in the NCP (Figure 1); hence, gaseous precursor emission control is crucially important.

Table 3.

5. Summary and Conclusions

Long-term high-temporal resolution $PM_{2.5}$ pH and size-resolved aerosol pH in Beijing were calculated with ISORROPIA-II ~~agreed pretty well when RH was higher than 30%. It~~. The model validation results indicated that it is not reasonable to assume ~~aerosol~~aerosols are in a liquid state (metastable) ~~and the aerosol pH could not be accurately predicted by a thermodynamic model where the RH is relatively low. Thus, we only discussed the $PM_{2.5}$ pH for data with RH higher than 30% in this work.~~

~~In~~ when the RH is lower than 30%. In 2016-2017 in Beijing, the mean $PM_{2.5}$ pH (RH>30%) over four seasons ~~(RH≥30%)~~ was ~~4.0±1.0 (spring),~~ 4.5±0.7 (winter~~), 3.8±1.2(summer),~~) > 4.4±1.2 (spring) > 4.3±0.8 (autumn~~), respectively,~~) > 3.8±1.2 (summer), showing ~~the~~ moderate acidity. In this work, both H_{air}^+ and ALWC had significant diurnal ~~variation, and the $PM_{2.5}$ acidity variation agreed well with sulfate~~variations, indicating ~~the~~that aerosol acidity in the NCP was ~~both~~ driven by both aerosol composition and ~~particle water.~~meteorological conditions. The ~~averaged~~average $PM_{2.5}$ nighttime pH ~~is~~ was 0.3~0.~~3~0.~~4 ~~unit~~units higher than that ~~on~~in the daytime. The $PM_{2.5}$ pH in ~~the~~ northerly ~~direction~~wind was generally higher than that in wind from the southwest ~~direction.~~

~~A sensitivity~~. Size-resolved aerosol pH analysis ~~was performed in this work to investigate how SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, RH, and T affect ALWC, H_{air}^+, and $PM_{2.5}$ acidity. The RH affects ALWC most, then followed by SO_4^{2-} or NO_3^-. The SO_4^{2-}, RH, NO_3^-, and NH_4^+, especially SO_4^{2-}, were all important influential factors for H_{air}^+. As for $PM_{2.5}$ pH, SO_4^{2-}, T, NH_4^+, and RH (only in summer) were crucial factors.~~ showed that the coarse-mode aerosol pH was approximately equal to or even higher than 7 for all three seasons, which was considerably higher than the pH of fine particles. The presence of Ca^{2+} and Mg^{2+} had a crucial effect on coarse-mode aerosol pH. Under heavily polluted conditions, the mass fractions of Ca^{2+} and Mg^{2+} in coarse particles decreased significantly, resulting in an evident increase in the acidity of the coarse particles. The $PM_{2.5}$ pH sensitivity tests also showed that when evaluating aerosol acidity, the role of crustal ions cannot be ignored in areas or seasons (such as spring) where mineral dust is an important particle source. In

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northern China, dust can effectively buffer acidity in aerosols or precipitation.

~~In winter, $PM_{2.5}$ pH decreased slightly with the increasing RH, whereas the $PM_{2.5}$ pH increased with the increasing RH in summer. The dilution effect of ALWC on H_{air}^+ was obvious only in summer. In spring and autumn, the RH had little impact on $PM_{2.5}$ pH due to the comparable variations of H_{air}^+ and ALWC. The measured $c(NH_4^+)$, $c(NO_3^-)$, and $c(Cl^-)$ increased with the elevated RH in all four seasons. In addition, the higher ambient temperature tended to lower $PM_{2.5}$ pH due to the volatilization of NH_4^+, NO_3^-, Cl^- and the decrease of ALWC.~~

~~SO_4^{2-} had a key role for aerosol acidity, especially in winter and spring. In spring and winter, the ALWC was relatively low, the variation of SO_4^{2-} concentration could generate dramatic changes in H_{air}^+. The impact of NO_3^- on $PM_{2.5}$ pH was different in four seasons. In winter, the $PM_{2.5}$ pH decreased with increasing NO_3^- concentration due to the low NH_4^T mass concentration. In summer, the excessive NH_3 could provide continuous buffering to the increasing NO_3^T and lead to little change in $PM_{2.5}$ pH.~~

~~The relationship between pH and NH_4^T was nonlinear, the impact of NH_4^T on $PM_{2.5}$ pH gradually weakened as NH_4^T increased. Elevated NH_4^T consumed H_{air}^+ swiftly and shifted more NO_3^T and Cl^T into particle phase. In NCP, NH_3 was much rich in spring, summer, and autumn, while less rich in winter. Although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral, which mainly attributed to the limited ALWC.~~

~~Cl^T and Ca^{2+} had little impact on the $PM_{2.5}$ pH due to the low mass concentration. Elevated Ca^{2+} concentration could increase the $PM_{2.5}$ pH because of the buffering capacity of Ca^{2+} to the acid species and the weak water solubility of $CaSO_4$.~~

~~The sensitivity analysis of the relationship between NO_3^T and $c(NH_4^+)$ imply~~The sensitivity tests in this work showed that the common important driving factors affecting $PM_{2.5}$ pH are SO_4^{2-}, TNH_3, and T, while unique influencing factors were Ca^{2+} in spring and RH in summer. In recent years, NO_3^- has generally dominated the inorganic ions in the NCP. However, owing to the significantly rich ammonia content in the atmosphere in spring and summer, the $PM_{2.5}$ pH in only winter and autumn decreased obviously with elevated TNO_3. Excess NH_3 in the atmosphere and a high NO_3^- mass fraction in $PM_{2.5}$ may be the reason why aerosol acidity in China is lower than that in Europe and the United States. Notably, TNH_3 had a great influence on aerosol acidity at lower concentrations but had a limited influence on $PM_{2.5}$ pH when present in excess. The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicated that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was still acidic, which might be attributed to the limited ALWC and the hydrolysis of

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ammonium salts.

In addition to the particle chemical compositions, meteorological conditions also had important impacts on aerosol acidity. When the mass concentration of water-soluble matter was higher, such as during severe haze events in winter, the higher RH clearly increased aerosol acidity. An opposite tendency was observed when the mass concentration of water-soluble matter was low, such as in summer: the dilution effect of ALWC on H_{air}^{+} was more obvious. At higher ambient temperatures, more ammonium nitrate and ammonium chloride volatilized, while ALWC decreased, which could further reduce the $PM_{2.5}$ pH.

In recent years, nitrates have dominated $PM_{2.5}$ in the NCP, especially on heavily polluted days. Sensitivity tests showed that decreasing TNO_3 could lower $\varepsilon(NH_4^+)$ and that decreasing ~~NO_3~~ TNH_3 could also lower $\varepsilon(NO_3^-)$, helping to reduce ~~the $\varepsilon(NH_4^+)$ effectively, which helped keep NH_3 in the gas phase. In contrast, the nitrate~~ nitrate production. However, the $\varepsilon(NO_3^-)$ response to ~~NH_4~~ TNH_3 control was highly nonlinear~~, the~~. Given that ammonia was excessive in most cases, a decrease ~~of~~in nitrate would ~~happen~~occur only ~~when the NH_4 was~~ if TNH_3 were greatly reduced.

~~The size-resolved results showed that the pH of coarse particles was approximately near or even higher~~ Therefore, in terms of controlling the generation of nitrate, a reduction in NO_x emissions is more feasible than ~~7 for all three seasons, which was quite higher than that of fine particles. The difference of aerosol pH between size bins in fine mode was not significant. The aerosol pH in coarse mode decreased significantly, becoming weak acid from neutral, when under heavily polluted condition. For summer and autumn, the pH in the nighttime was higher than that in the daytime. Whereas in winter, the pH was higher in the daytime~~a reduction in NH_3 emissions.

Data availability. All data in this work are available by contacting the corresponding author P. S. Zhao (pszhao@ium.cn).

Author contributions. P Z designed and led this study. J D and P Z interpreted the data and discussed the results. J S and X D ~~analyzed~~analysed the chemical compositions ~~from~~of size-resolved aerosol samples. J D and P Z wrote the manuscript.

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

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Table captions

Table 1. Average mass concentrations of NO_3^-, SO_4^{2-}, NH_4^+ and $PM_{2.5}$, as well as ~~RH,~~ ALWC, H_{air}^+, and $PM_{2.5}$ pH, under clean, polluted, and heavily polluted conditions over four seasons.

Table 2. ~~Average $c(NH_4^+)$, $c(NO_3^-)$, $c(Cl^-)$, and ambient temperature at different ambient RH levels in four seasons.~~

~~**Table 3.**~~ Sensitivity of ~~ALWC, H_{air}^+, and~~ $PM_{2.5}$ pH to SO_4^{2-}, ~~NH_4^+, NO_3^-, Cl^-~~ TNH_3, TNO_3, Ca^{2+}, $_{7}^{+}$, RH, and T. ~~The~~A larger magnitude of the relative standard deviation (RSD) represents ~~the~~a larger impact derived from ~~the variation of~~ variations in variables.

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Table 3. Average measured $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ based on the real-time MARGA dataset and ambient temperature at different ambient RH levels in four seasons.

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Table 1

Spring	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	μg m^{-3}	
Average	62±3657±42	12.6±14.9±14.62	9.8.4±7±.79	6.7.9±7.32	23±3521±33	6.8E3.7E-06±2.8E1.5E-05	4.04±1.02
Clean	44±1739±19	7.9±6.6±6.5	6.25.4±3.78	4.83.6±3.2	14±2613±23	3.2E-06±5.1E-061.9E-05	4.6±1±1.1.4
Polluted	100101±21	30.87±14.3	16.4±5.92±6.2	15.4±5.83±6.0	33±36	53.1E-06±4.3E2.9E-06	3.94.1±0.54
Heavily polluted	169±12199±62	45.3±36.4±19.8.5	3629.3±4.914.0	29.4±23.2±12.3	78±60	2.0E1.6E-05±6.5E5.4E-06	3.67±0.3
Winter	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Average	60±69	13.7±21.0	7.3±8.7	7.3±10.0	35±46	2.2E-05±2.3E-04	4.5±0.7
Clean	22±20	3.6±3.9	2.8±1.8	2.2±2.0	10±16	3.2E-07±4.8E-07	4.5±0.6
Polluted	107±21	18.9±8.6	11.0±5.7	11.0±4.7	41±45	1.9E-05±9.1E-05	4.8±1.0
Heavily polluted	209±39	59.7±21.8	26.2±6.3	29.1±8.7	80±52	7.0E-05±4.7E-04	4.4±0.7
Summer	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Average	39±24	9.5±9.5	8.6±7.5	7.2±5.6	50±68	1.6E-05±1.8E-05	3.8±1.2
Clean	33±18	7.3±6.8	7.0±6.0	5.9±4.0	42±61	1.4E-05±1.6E-05	3.8±1.2
Polluted	87±13	26.5±10.5	20.7±7.0	17.6±4.8	100±88	3.1E-05±2.0E-05	3.5±0.4
Autumn	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*

Average	59±48	18.5±19.5	6.5±5.9	8.2±8.2	109±160	8.1E-06±1.1E-05	4.3±0.8
Clean	33±21	7.6±7.4	4.4±4.1	3.8±3.5	49±83	3.8E-06±6.6E-06	4.5±1.0
Polluted	105±21	33.8±11.6	14.3±6.3	16.0±4.6	225±189	1.7E-05±1.2E-05	4.1±0.3
Heavily polluted	174±18	63.4±15.4	25.0±15.9	29.0±5.1	317±236	2.2E-05±1.0E-05	4.1±0.2

* For data with RH>30%.

Table 2

Impact Factor	RH	SO_4^{2-}	T, ℃	TN O_3	$\varepsilon(NH_4^+)$	TN H_3	$\varepsilon(NO_3^-)$	Ca^{2+}	$\varepsilon(Cl^-)$	RH	T
Spring-RSD	≤ 30	12.4%	5.2%		24.8 ± 3.79%		7.5%	0.17±0.14	1.3%	0.84±0.12	7.0%
	30–60 %		20.6 ± 3.8		0.25±0.14		0.91±0.06		0.82±0.16		
Winter-RSD	>60	28.1%	15.8 ± 2.7%		27.0%	0.28±0.12	1.0%	0.96±0.03	0.96±0.06	4.1%	6.7%
	≤ 30 %		5.4 ± 5.3		0.31±0.13		0.78±0.12		0.89±0.14		
Winter	30–60 %		1.0 ± 3.6		0.50±0.21		0.89±0.10		0.97±0.03		
	>60 %		1.9 ± 2.1		0.60±0.20		0.96±0.03		0.99±0.01		

Summer-RSD	≤ 30	353.6± 7.9%	0.06±0.028.1 0.4%	0.35±0.201.9 %	0.39±0.178.6 %	5.8 %	
	30–60 %	29.6 ± 4.2	0.17±0.11	0.65±0.23	0.43±0.16		
	>60 %	25.2 ± 3.8	0.26±0.12	0.90±0.12	0.71±0.15		
Autumn - RSD	≤ 30	3.3 %	16.1 %	0.8 %	2.4 %	21.7± 7.5%	0.07±0.0 6
	30–60 %	20.8± 6.3	0.21±0.14	0.82±0.19	0.67±0.21		
	>60 %	14.9 ± 5.7	0.30±0.19	0.92±0.10	0.86±0.13		

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Table 3

			N H C N O ε ε T N N . ° H O C 4 3- +))	RH	T
Impact Factor	SO4 2- RH		T N N . ° H O C 4 3- +))	Ca2+	ε(Cl-)
		50.5%	0 0 2 . . 4 1 8 . 7 4 8 ± ± ± 0 0 3 . . . 1 1 7 4 2 : 2 1 5 1. 2 % 2 2 % %		
	RSD ALW C ≦ 30%			13.1%	0.67±0.24
Spring		223%	2 1 4 6 2. 9. 2 4 8 0 % %		49.5%
	RSD Hair 30~ 60%		. 0 0 6 . . ± 2 9 3 5 1 , ± ± 8 0 0 % . .	115%	0 .82±0. 16

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		12.4%	5.2%	3.9%	15%.08±2.86±0.40%7	0%.96±0.06
		RSD				
		pH>6				
		0%				
Winter	R2S3D-A%L W C	1.9%	103%	5.4±5.3%	0.89±0.14	
	≤ 30.7%					
		431%	431%	187.4%	0.97±0.03	74.1%
	RSD					
	Hair 3					
	0~60					
	%					

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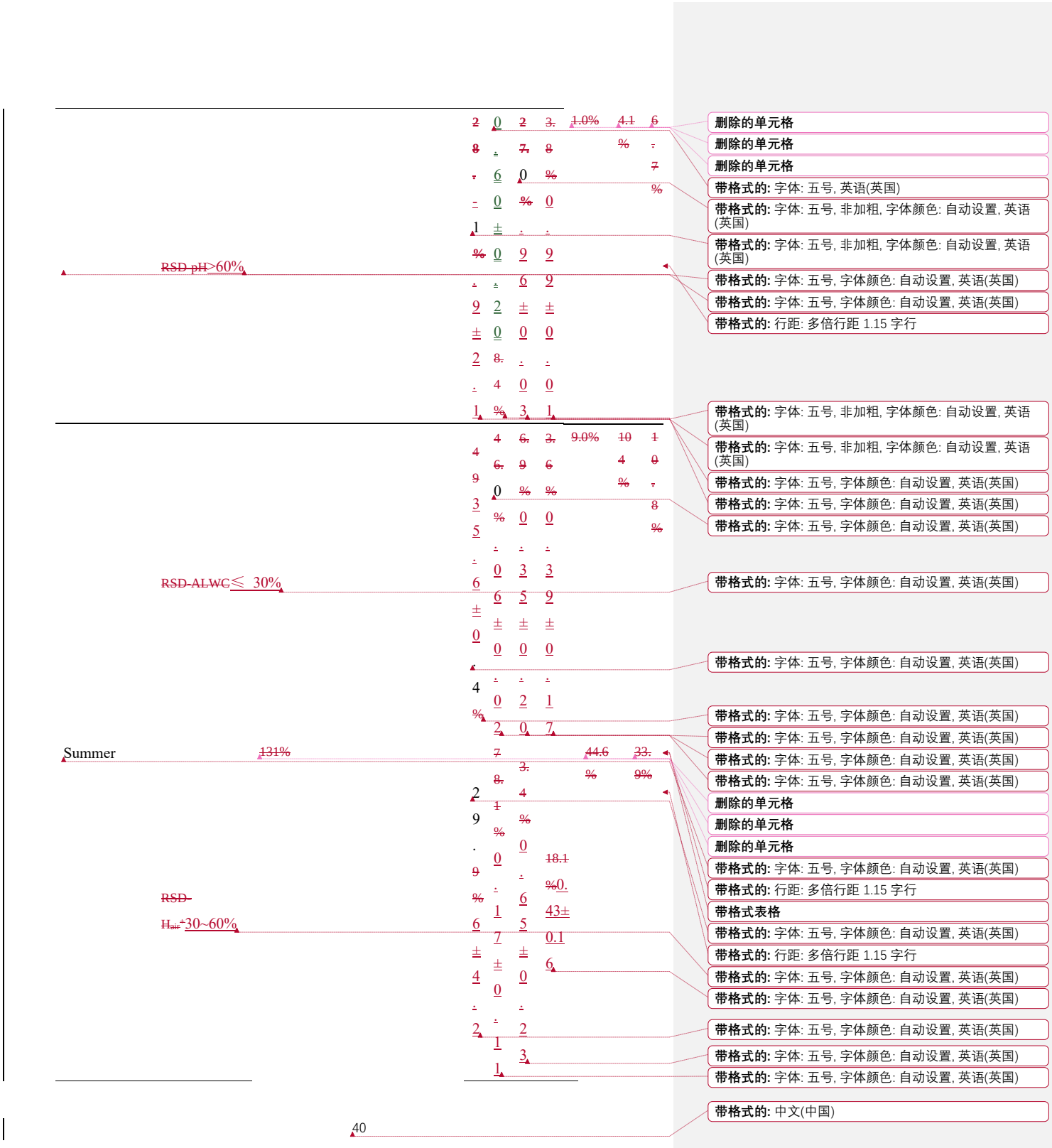
RSD_pH>60%
RSD-ALWC≤ 30%
Summer
131%
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H+30~60%
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RSD pH>60%		7.9%					25.2±3.6%8	8.1%0.26±0.12	0.8%90±0.12	1.9%0.71±0.15	8.6% 5.8%
RSD-ALWC≤30%	32.8%	58.1%	9.9%	6.9%	3.3%	7.6%	21.7±7.5.5%	0.07±0.06	0.49±0.25	0.45±0.21	
Autumn RSD-Hair 30~60%	171%	126.7%	333.1%	2.0%			920.8±63%	10.6%0.21±0.14	59.6%0.82±0.19	0.67±0.21	

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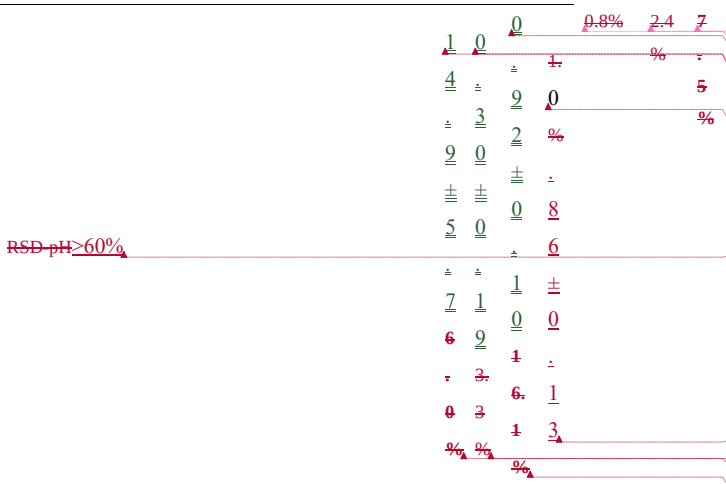

RSD pH>60%

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Figure captions

Figure 1. Time series of relative humidity (RH~~),~~) and temperature (T) (a, e, i, m); $PM_{2.5}$, PM_{10}, and NH_3 (b, f, g, n); dominant water-soluble ~~ion species~~ions; NO_3^-, SO_4^{2-}, and NH_4^+ (c, g, k, o); and $PM_{2.5}$ pH ~~colored~~coloured by $PM_{2.5}$ concentration (d, h, l, p) over four seasons.~~.~~

Figure 2. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ ~~colored~~coloured by RH. In this ~~Figure~~figure, the data ~~of~~from all four seasons were ~~put together, and the~~combined; comparisons ~~for each season were~~of individual seasons are shown in Figure S1-S4.

Figure 3. Comparisons of predicted and iterative NH_3, HNO_3, and HCl, as well as ~~the~~ predicted and measured NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ ~~colored~~coloured by particle size. In this ~~Figure~~figure, all MOUDI data were ~~put together~~combined.

Figure 4. Time series of mass ~~fraction~~fractions of NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, ~~and crustal ions (~~Mg^{2+}, and Ca^{2+}~~) in~~ $^{2+}$ with respect to the total ~~ion~~sion content, as well as $PM_{2.5}$ pH in all four seasons~~.~~ ($PM_{2.5}$ pH values at RH≤30% were excluded).

Figure 5. Wind~~-~~dependence map of $PM_{2.5}$ pH over four seasons. In each picture, the shaded contour indicates the ~~average~~mean value of ~~variables~~$PM_{2.5}$ pH for varying wind speeds (radial direction) and wind directions (transverse direction~~).~~) (data at RH≤30% were excluded).

Figure 6. Diurnal patterns of mass concentrations of NO_3^- and SO_4^{2-} in $PM_{2.5}$, predicted aerosol liquid water content (ALWC), H_{air}^+, and $PM_{2.5}$ pH over four seasons. Mean and median values are shown, together with 25% and 75~~-~~% quantiles. Data ~~with~~at RH ⩽ 30% were excluded, and the ~~shadow~~shaded area represents the time period when ~~the~~most RH values were lower than 30~~% mostly occurred.~~%.

Figure 7. ~~Sensitivities~~Sensitivity tests of ~~H_{air}^+~~$PM_{2.5}$ pH to ~~SO_4^{2-}, NO_3^-, NH_4^+,~~SO_4^{2-}, TNO_3, TNH_3, Ca^{2+}, and ~~Cl^-, as well as~~ meteorological parameters (RH~~,~~ and T) in summer (S) and winter~~. (W)~~.

Figure 8. ~~Sensitivities of ALWC to SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-, as well as meteorological parameters (RH, T) in summer and winter.~~

Figure 9. ~~Sensitivities of $PM_{2.5}$ pH to SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-, as well as meteorological parameters (RH, T) in summer and winter.~~

Figure 10. ~~Sensitivities~~Sensitivity tests of $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$~~, and $\varepsilon(Cl^-)$~~ to ~~NO_3~~TNO_3, TNH_3, RH and T~~, NH_4^+, and Cl^- colored~~ coloured by $PM_{2.5}$ pH in summer (S) and winter~~, (W)~~.

Figure 11. ~~Sensitivities of $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ to RH and T colored by $PM_{2.5}$ pH in summer and winter.~~

Figure 12. ~~The size~~**Figure 9.** Size distributions of aerosol pH and all ~~analyzed~~analysed chemical components under clean (a, d, g), polluted (b, e, h), and heavily polluted conditions (c, f, i) in summer, autumn, and winter.

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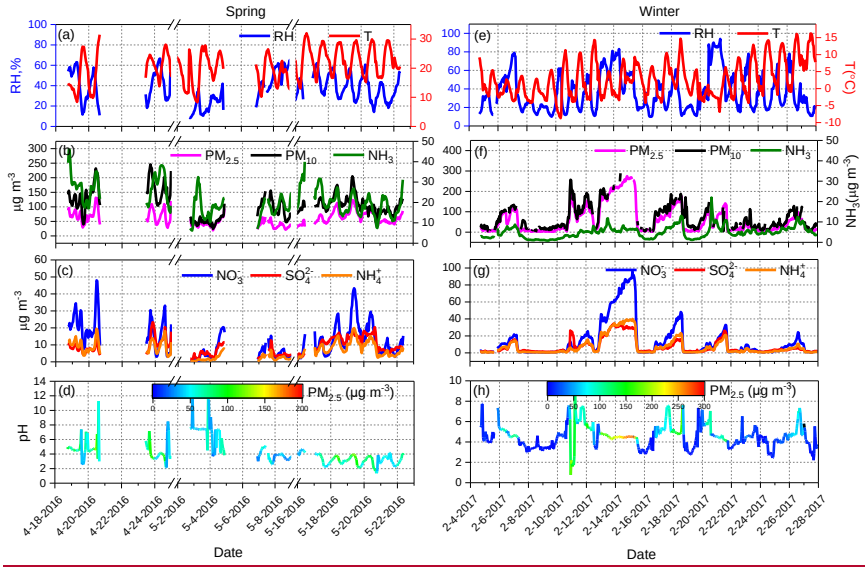

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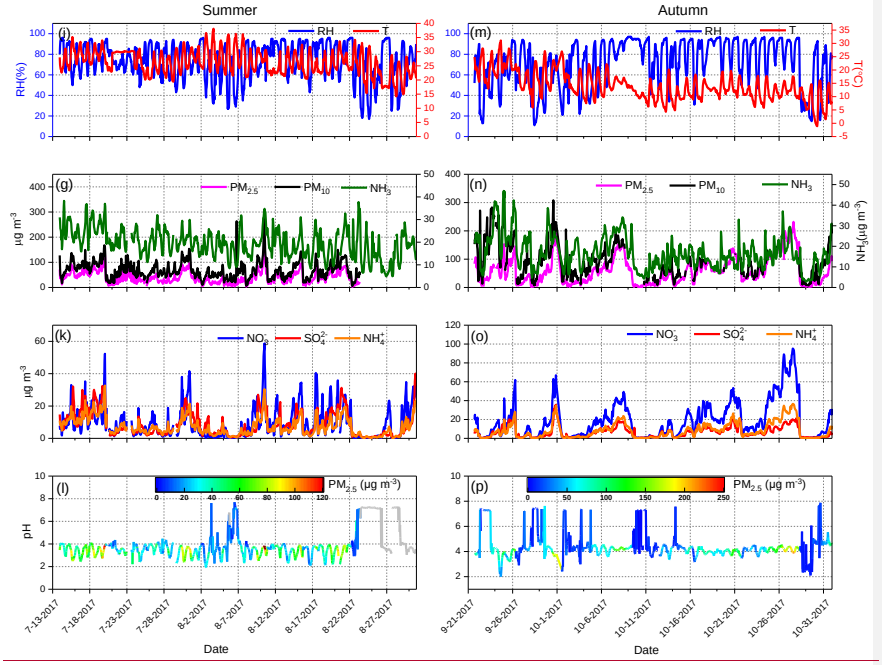

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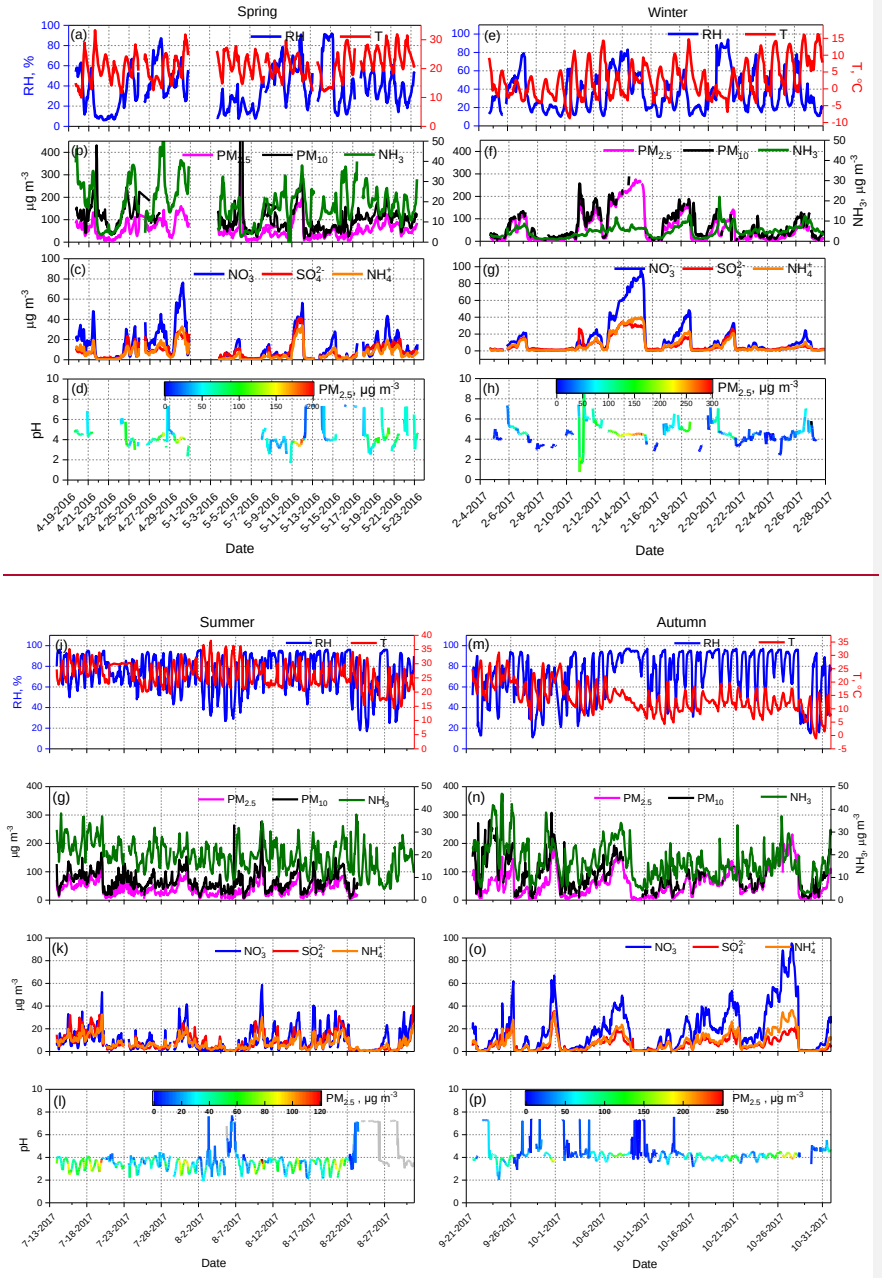

Figure 1.

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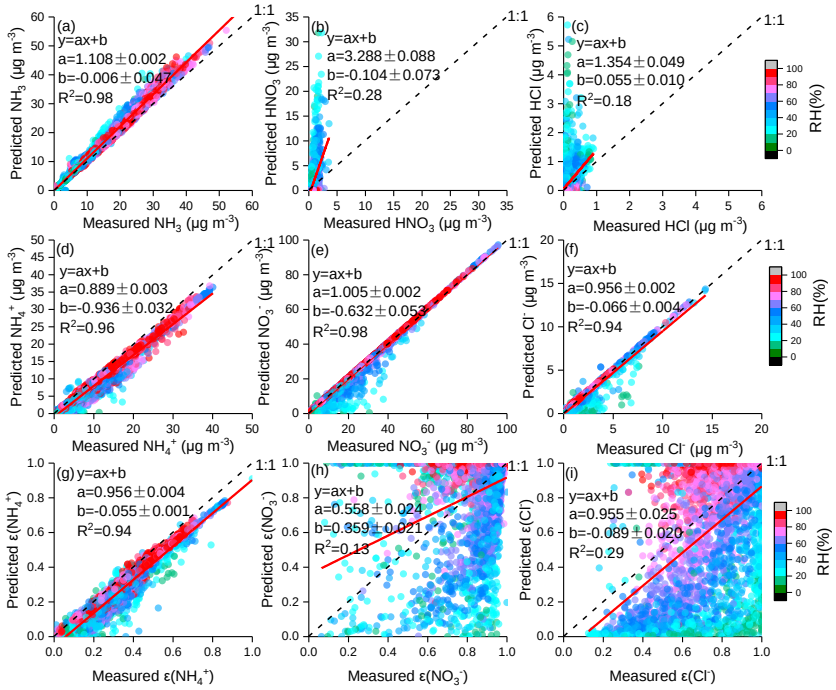
(a)
y=ax+b
a=1.108±0.002
b=-0.006±0.047
R²=0.98
Predicted NH3 (μg m-3)
Measured NH3 (μg m-3)
1:1
(b)
y=ax+b
a=3.288±0.088
b=-0.104±0.073
R²=0.28
Predicted HNO3 (μg m-3)
Measured HNO3 (μg m-3)
1:1
(c)
y=ax+b
a=1.354±0.049
b=0.055±0.010
R²=0.18
Predicted HCl (μg m-3)
Measured HCl (μg m-3)
1:1
RH(%)
(d)
y=ax+b
a=0.889±0.003
b=-0.936±0.032
R²=0.96
Predicted NH4+ (μg m-3)
Measured NH4+ (μg m-3)
1:1
(e)
y=ax+b
a=1.005±0.002
b=-0.632±0.053
R²=0.98
Predicted NO3- (μg m-3)
Measured NO3- (μg m-3)
1:1
(f)
y=ax+b
a=0.956±0.002
b=-0.066±0.004
R²=0.94
Predicted Cl- (μg m-3)
Measured Cl- (μg m-3)
1:1
RH(%)
(g)
y=ax+b
a=0.956±0.004
b=-0.055±0.001
R²=0.94
Predicted ε(NH4+)
Measured ε(NH4+)
1:1
(h)
y=ax+b
a=0.558±0.024
b=0.359±0.021
R²=0.13
Predicted ε(NO3-)
Measured ε(NO3-)
1:1
(i)
y=ax+b
a=0.955±0.025
b=-0.089±0.020
R²=0.29
Predicted ε(Cl-)
Measured ε(Cl-)
1:1
RH(%)

带格式的: 中文(中国)

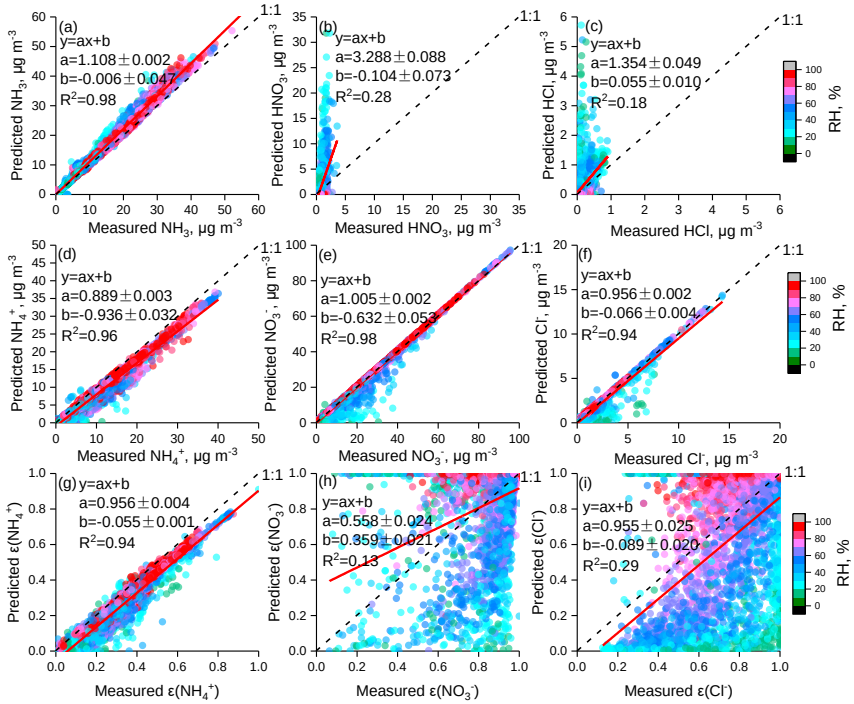

Figure 2.–

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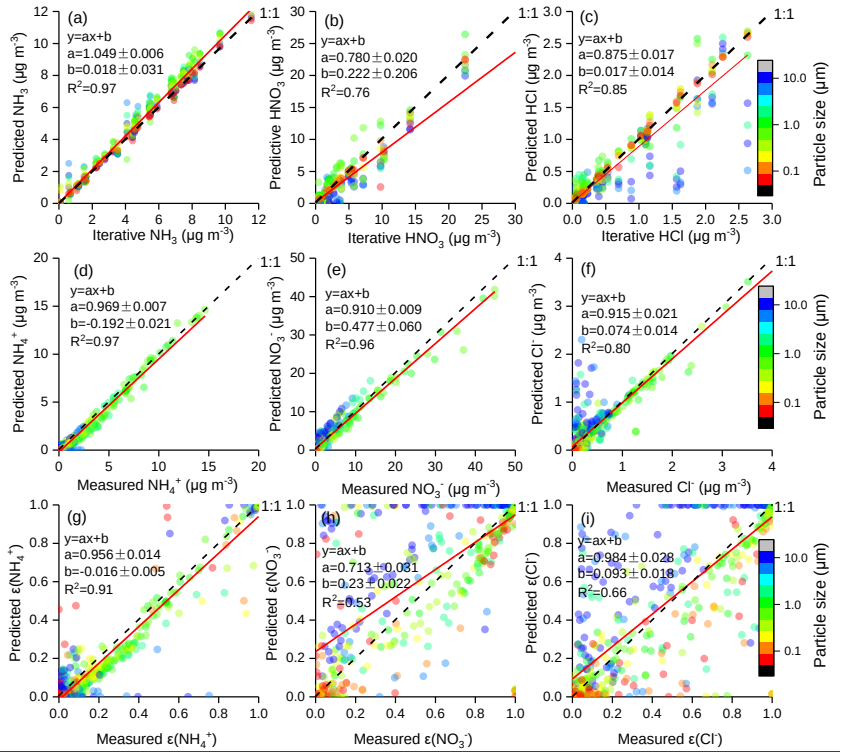

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1146

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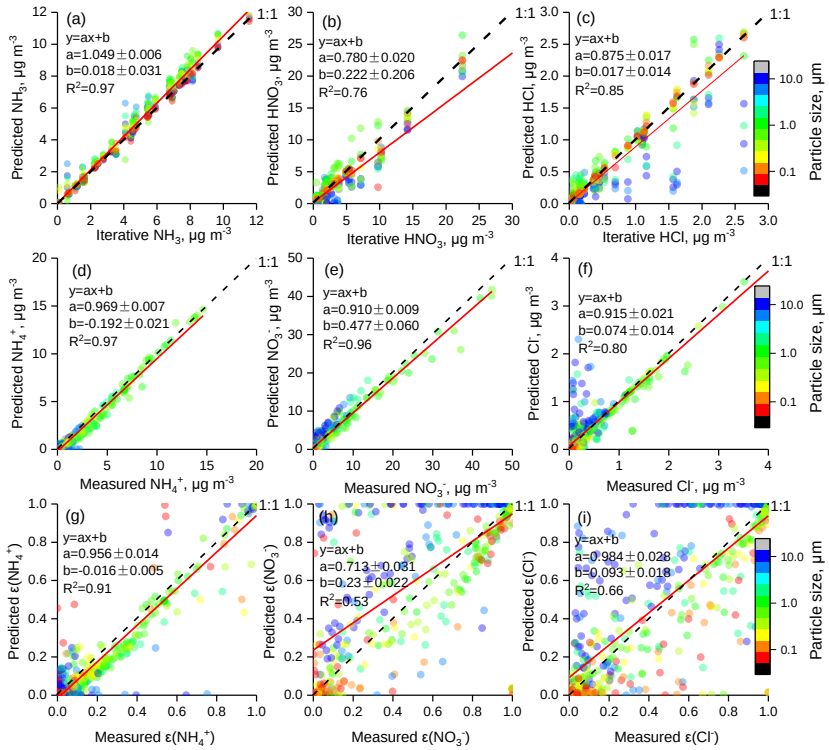

Figure 3.

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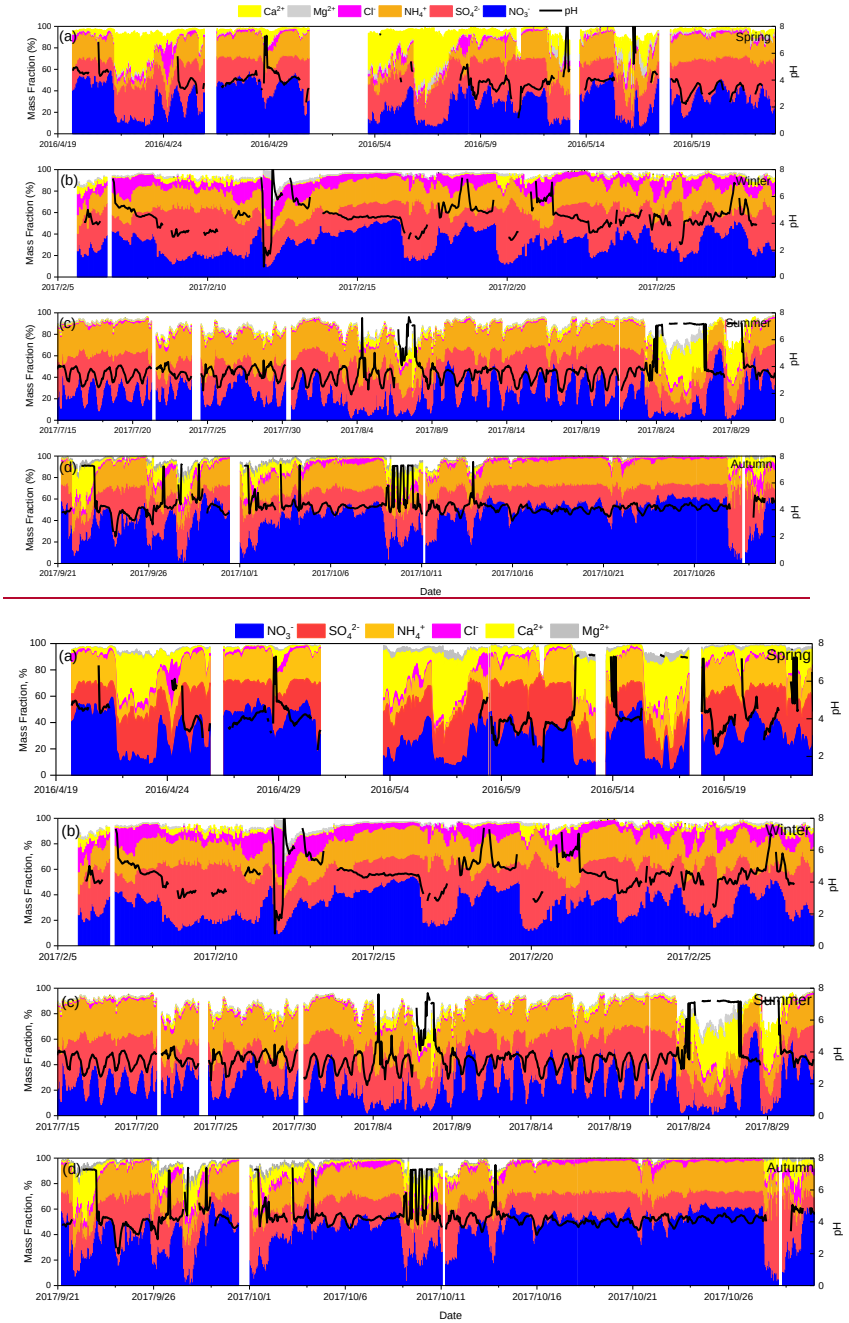

Figure 4.

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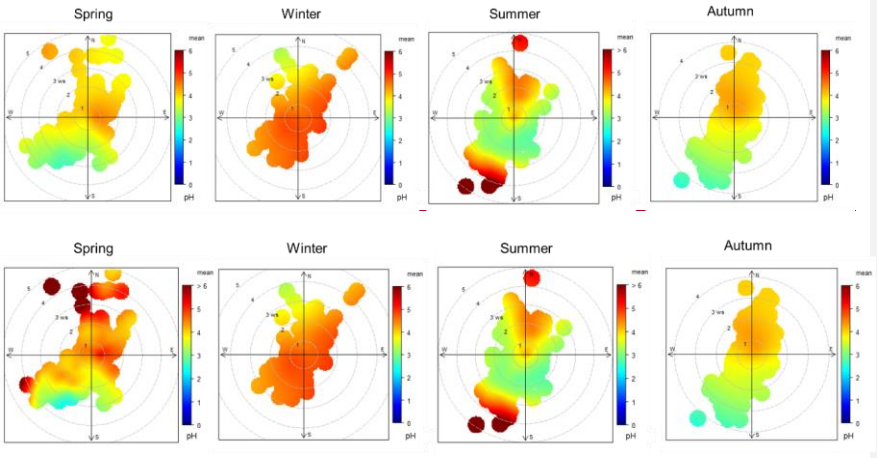

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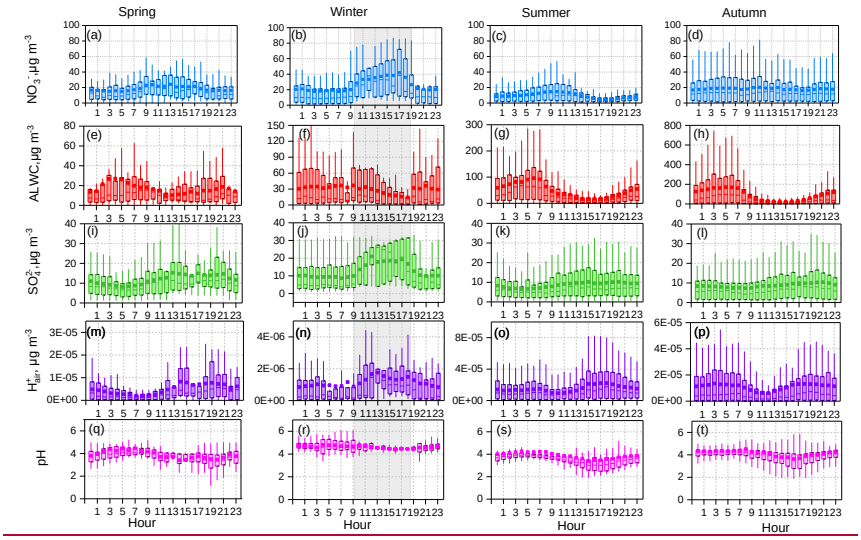

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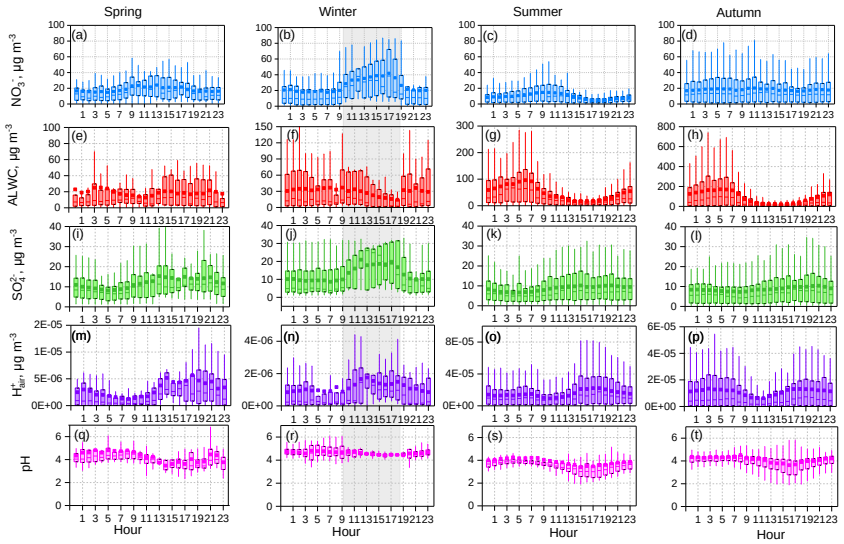

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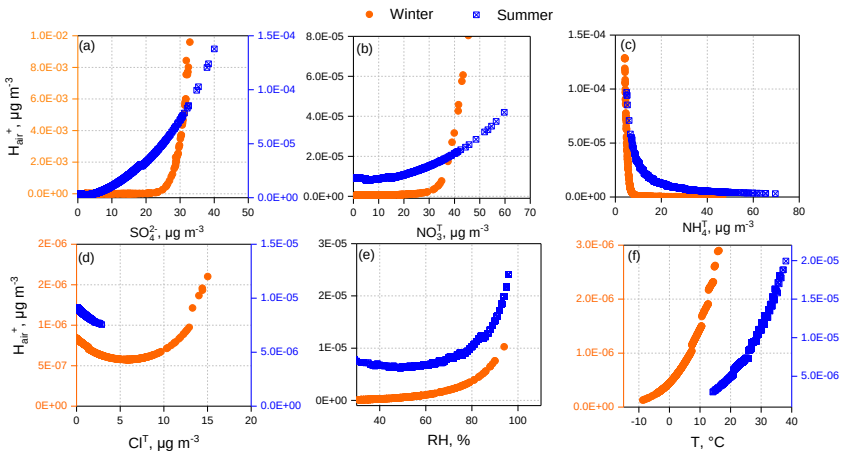

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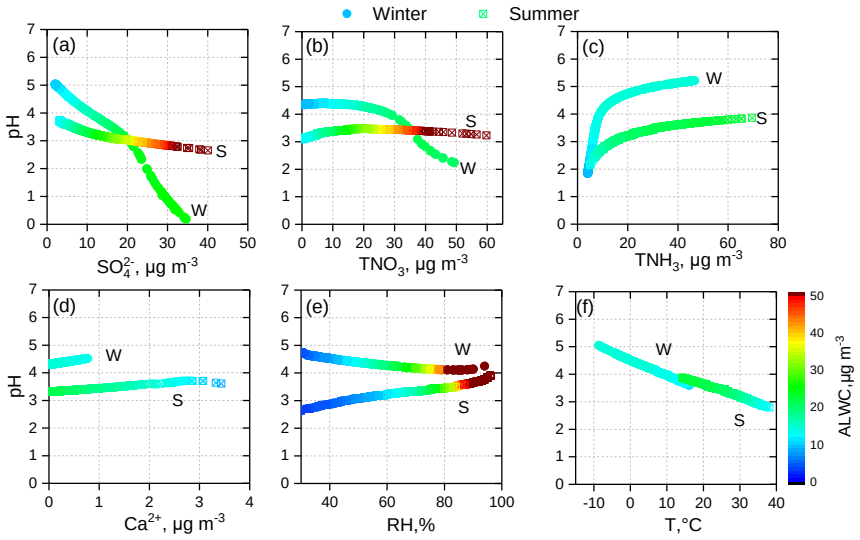

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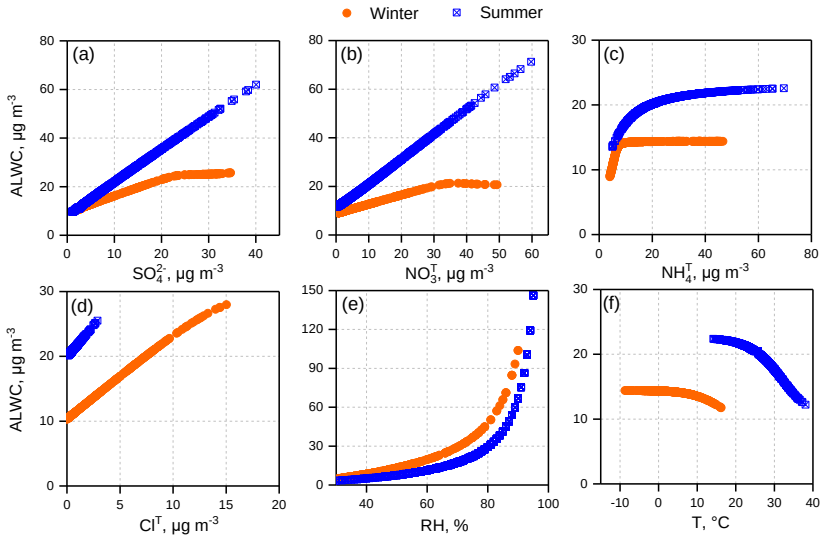

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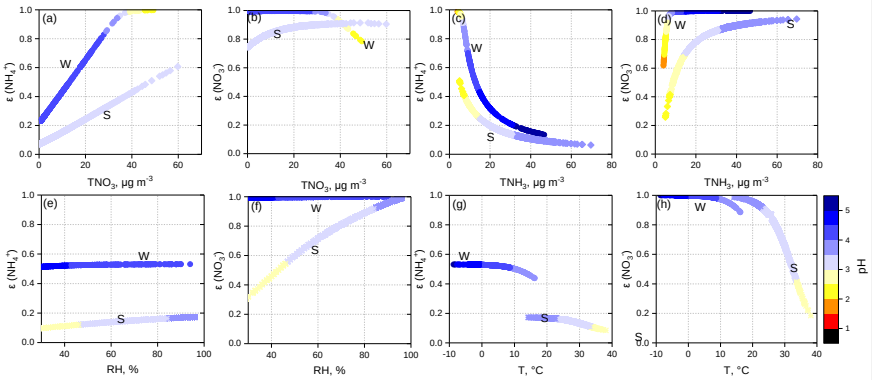

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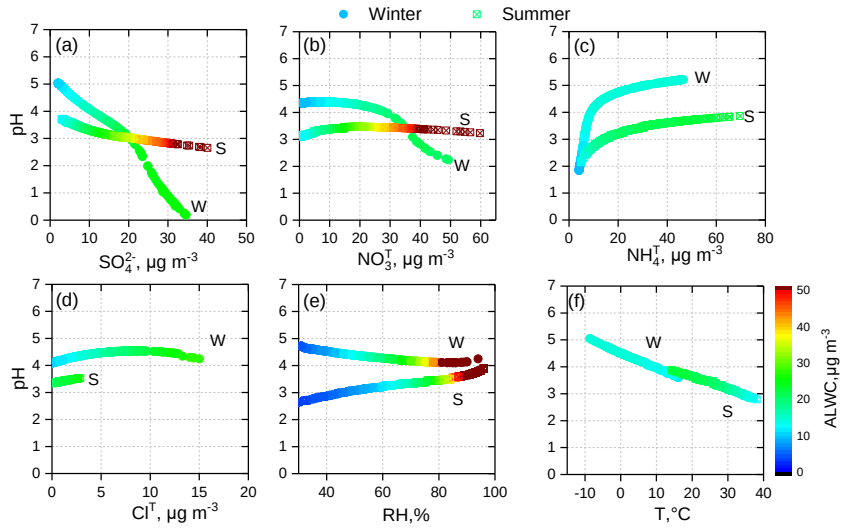

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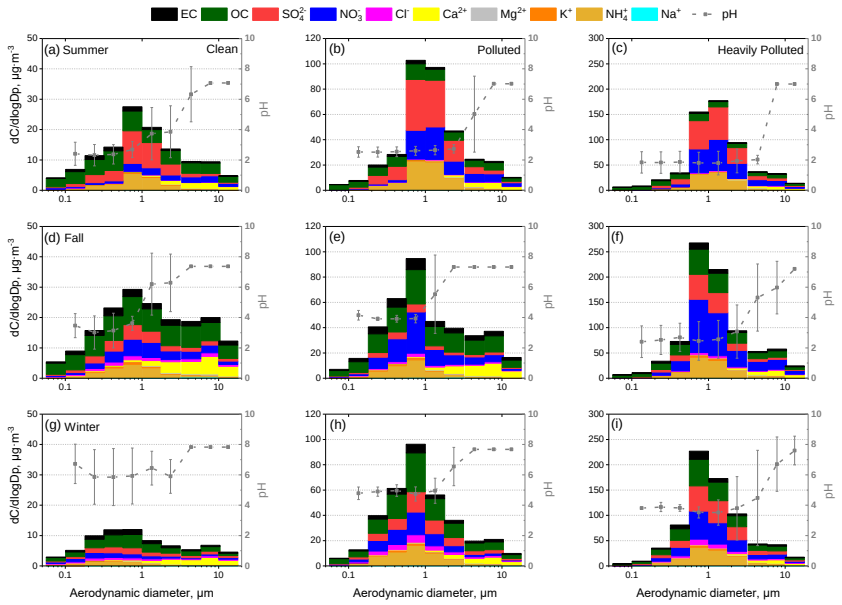

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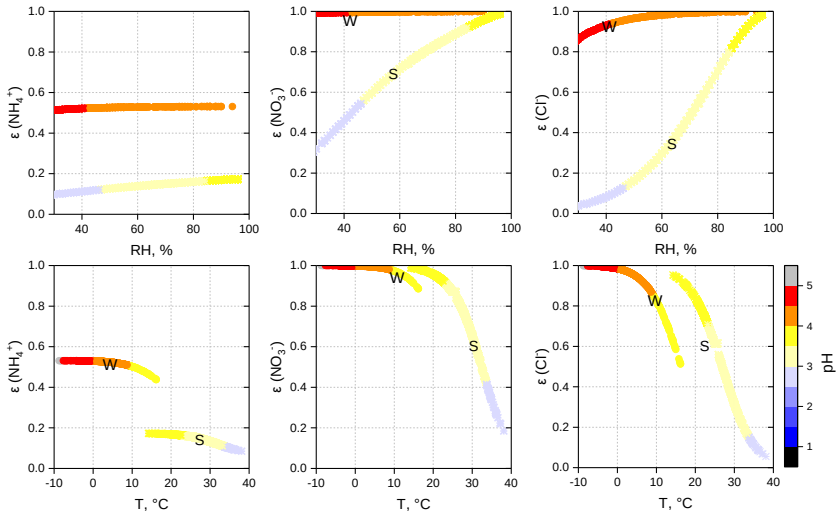

~~**Figure 10.**~~

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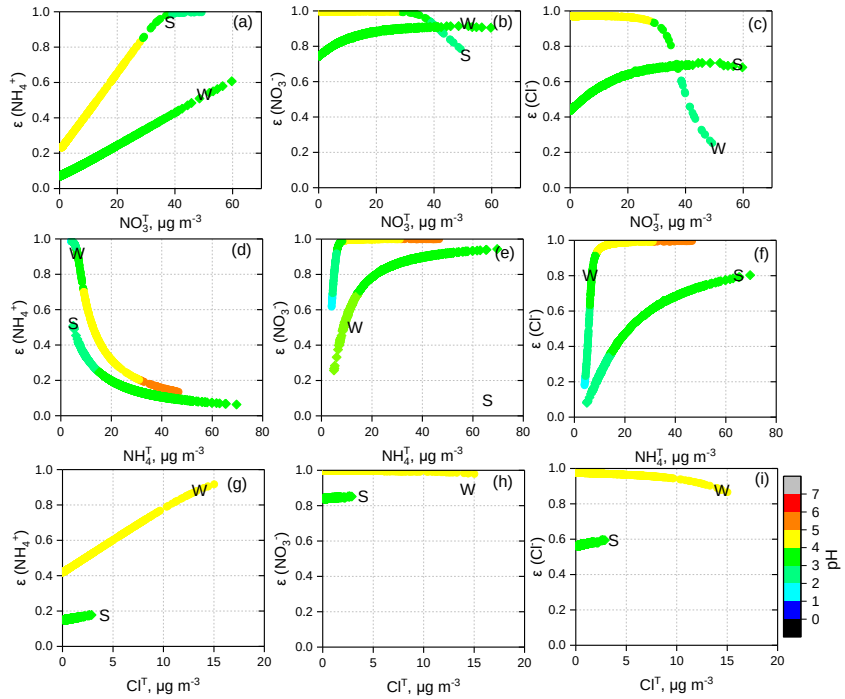

~~Figure 11.~~

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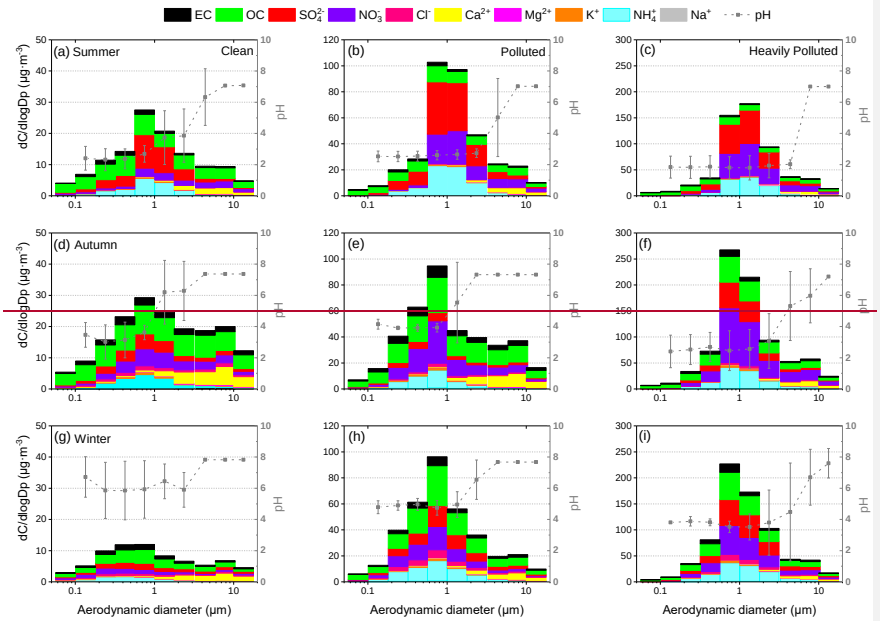

Figure 12.

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