Dear Editor:

We are truly grateful for your and other reviewers' comments on our manuscript. Based on these valuable comments, we have carefully addressed the concerns with this work. Please see our point-by-point responses to the comments and the revised manuscript for details.

Thank you very much for your concerning.

Best regards.

Sincerely yours,

Pusheng Zhao & Jing Ding

Anonymous Referee #1

This paper utilizes unique data sets to predict aerosol pH in the more polluted regions of China. Overall, the paper is a significant contribution since little is known about aerosol pH in these regions and even less on size resolved pH. However, in my view, the analysis is somewhat limited. The authors have an interesting data set that could be more fully utilized to assess the pH predictions, partitioning of inorganic species and understand aerosol pH from a more fundamental standpoint.

Response: Thank you for your valuable comments. Your comments have greatly improved our paper and made this work more rigorous. Please see our point-by-point responses to the comments and the revised manuscript for details. The order of the Figures or Tables in Response is the same as the corresponding Figure or Table appears in the main text and supplemental materials. Moreover, we carefully examined the grammar and expression in the text.

A suite of important inorganic gases was measured with the MARGA, but they are not significantly discussed in the paper. This is a major oversight. For example, in the comparison of the model to measurements the particle data are shown, but no gas data. For the MOUDI, no gas data is available so the pH is estimated by an iteration method, why not use the MARGA data, which includes gases, to test the sensitivity of pH to this approach?

Response: In the revised manuscript, comparisons and corresponding discussions of 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 ε(Cl^-) (Cl^-/(HCl+Cl^-), mol/mol) based on MARGA measurement were supplemented, and the detailed information was also showed there.

The data set of MOUDI was obtained during 2013 and 2014, which was not synchronous with the online ion data (obtained in 2016 and 2017), hence an iteration method used in Fang et al. (2017) and Guo et al. (2016) was applied in this work. The MOUDI samples were mainly used to investigate the size distribution of aerosol pH.

pH is calculated under the assumption of a completely deliquesced particle with no phase separation, all the way down to very low RH, ie, to 30%. These assumptions at low RH need to be justified. Eg, the predicted and measured partitioning of NH3/NH4+, HNO3/NO3-, HCl/Cl- etc (ie include analysis of the gases) could be assessed as a function of pH and see if changes occur at lower RH. Discussion of phase separation in the literature under various conditions (RH, T, O/C) etc should be discussed.

Response: In this work, particles were assumed in metastable, which means the aerosol is in the only liquid state. However, when the particles are exposed to the quite low RH or the ambient RH reached efflorescent RH, the state of particles may change. Figure 2 and Figure S1-S4 exhibit the comparisons between predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, ε(NH_4^+) (NH_4^+/(NH_3+NH_4^+), mol/mol), ε(NO_3^-) (NO_3^-/(HNO_3+NO_3^-), mol/mol)), ε(Cl^-) (Cl^-/(HCl+Cl^-), mol/mol) based on real-time ion chromatography data, which are all colored by the corresponding RH. It can be seen that agreement between predicted and measured NH_3, NH_4^+, NO_3^-, Cl^- were pretty well. However, measured and predicted partitioning of HNO_3 and HCl showed significant discrepancies (R^2 of 0.28 and 0.18), which may be attributed to the much lower gas concentrations compared with the particle concentrations, as well as the gas denuder measurement uncertainties from particle collection artifacts (Guo et al., 2018). Obviously, more scatter points deviate from the 1:1 line when ISORROPIA-II runs at RH≤30%, which is much evident in winter and spring. For data with RH ≤ 30%, the predictions were significantly improved when assuming aerosol in stable mode (solid + liquid) (Figure S5-S6). However, the aerosol liquid water was almost zero and cannot be used to predict aerosol pH. It reveals that it is not reasonable to predict the aerosol pH using the thermodynamic model when the RH is relatively low. Consequently, in the revised manuscript, the results were only discussed for data with RH higher than 30%. (**Page 8 and 9, line 195-217, in the**

revised manuscript)

A new section (Section 3.3 Gas-particle separation) was added in the revised manuscript. Table 2 exhibited the measured $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ at different RH levels. The measured $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ 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 winter and spring, NO_3^T and Cl^T were dominated by particle phases. Whereas in summer and autumn, more than half of the NO_3^T and Cl^T were partitioned into the gaseous phase. When the RH reaches 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 $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$, the $\varepsilon(NH_4^+)$ was pretty lower, which may attribute to the higher NH_3 mass concentration in the atmosphere. In winter, the average $\varepsilon(NH_4^+)$ were much higher than that in other seasons with the relatively lower NH_3 mass concentration. (**Page 14, line 357-371, in the revised manuscript**)

Greater utilization of the gas data could also help the authors understand fundamentally what is driving pH and the sensitivities to various parameters. This could include the use of S curves, as done extensively by Guo et al, to go beyond just simple variation of one variable at a time. Eg, why in the sensitivity analysis do changes in HNO3 not affect pH, but changes in NH3 do? These, and possibly other, more detailed analysis would reduce the sense that the authors simply run the thermodynamic model and plotted results.

Response: In the real ambient air, the thermodynamic process of the aerosol is complicated, it is not easy to tell the effect of one factor on aerosol pH. The ISORROPIA-II can well predict the effect of an input variable on output data. Thus, in this paper, we focus on the sensitivity analysis of single-factor variation, which can reflect the variation tendency of aerosol pH caused by the change of each variable. When running the ISO-II model, the total nitrate (NO_3^T, gas+aerosol), total ammonium (NH_4^T, gas+aerosol), and total chloride (Cl^T, gas+aerosol) are input, and the gas and aerosol phase of these three components would be reapportioned and output. In view of this, it is more reasonable to analyze the impact of NO_3^T, NH_4^T, and Cl^T on aerosol pH, rather than the impact of a single gas or aerosol phase of NO_3^T, NH_4^T, and Cl^T on aerosol pH. In the revised manuscript, the data analysis for the sensitivities of aerosol pH to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, RH, and T were fully reorganized and reinspected. More discussions about gas-particle partitioning were added to this section. The impacts of NO_3^T, NH_4^T, and Cl^T on $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ were also discussed.

More detailed information was shown in the revised manuscript.

The SO_4^{2-} and T are two crucial factors affecting aerosol pH variation. Aerosol pH is also sensitive to NH_4^T when NH_4^T in a lower range and sensitive to RH only in summer. Figure 7-9 and S12-S17 show how these factors affecting the ALWC, H_{air}^+, and aerosol acidity over four seasons. (**Page 15, line 380-391, in the revised manuscript**)

RH: RH has a different impact on aerosol pH in different seasons. In winter, aerosol pH decreased with the increasing RH, whereas the aerosol pH increased with the increasing RH in summer. In spring and autumn, the RH between 30~83% had little impact on aerosol pH. The explanation for this is that the increased RH actually dilutes the solution and promotes 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 variation in ALWC. The different impact of RH on aerosol pH indicated that the dilution effect of ALWC on H_{air}^+ is obvious only in summer, the high RH during the severe haze in winter could increase the aerosol acidity. (**Page 15, line 397-406, in the revised manuscript**)

T: At high ambient temperature, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ all showed a decreased tendency (Figure 10 and S19). And NH_4^+, NO_3^-, and Cl^- were volatilized partially, the procedure of $NH_4^+ \rightarrow NH_3$ released one H^+ to particle phase, whereas the procedure of $NO_3^- \rightarrow HNO_3$ and $Cl^- \rightarrow HCl$ needs 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, molality-based equilibrium constants (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 decrease the aerosol pH. The wide range of ambient temperature in autumn made a significant impact on aerosol pH in the sensitivity analysis. (**Page 15 and 16, line 407-416, in the revised manuscript**)

SO_4^{2-}: SO_4^{2-} has a key role in aerosol acidity, especially in winter and spring (Figure 9, S14, S17). More H^+ are released into particle phase during the formation of SO_4^{2-}, forming one SO_4^{2-} can release two H^+. In the sensitivity test, the aerosol pH decreases 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 goes up from 0 to 40 μg m^{-3} in spring, winter, summer, and autumn, respectively. In spring and winter, the ALWC is low, the variation of SO_4^{2-} mass concentration could generate dramatic changes in H_{air}^+. In section 3.1, the aerosol pH 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%. (**Page 16, line 418-425, in the revised manuscript**)

NO_3^T: The impact of NO_3^- on aerosol pH was also different, which is related to the averages of input NH_4^T in different seasons. In winter, the aerosol pH decreased with increasing NO_3^T concentration, whereas little impact was found in summer (Figure 9). In spring and autumn, the aerosol pH increases first and then drops with the increasing NO_3^T concentration (Figure S14, S17). In winter, the NH_4^T mass concentration was low. As NO_3^T increases, all NH_3 was converted into NH_4^+ ($\varepsilon(NH_4^+)$ ≈1). However, HNO_3 continues to dissolve and releases H_{air}^+, resulting in the decrease of aerosol 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}^+, leads to the little changes in aerosol pH. In spring and autumn, the increasing aerosol 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 higher NO_3^T concentrations, whereas the ALWC increase linearly with elevated NO_3^T concentration (Figure S12-S17), hence ALWC plays a dominant role when the NO_3^T concentration is low. With the further increase of NO_3^T, the variation in H_{air}^+ caused by NO_3^T addition is larger than variation in ALWC, leading to the decrease of aerosol 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 helps NH_3 maintain in the gas phase. (**Page 16 and 17, line 426-443, in the revised manuscript**)

NH_4^T: The relationship between aerosol pH and NH_4^T was nonlinear. NH_4^T in lower range had a significant impact on aerosol 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 increases, H_{air}^+ are consumed swiftly during the dissolution of NH_3 and the further reaction with SO_4^{2-}, NO_3^-, and Cl^-. And 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 alters the gas-particle partition and shifts more NO_3^T and Cl^T into particle phase, leading to the deliquescence of additional nitrate and chloride and 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 is highly nonlinear, which means the decrease of nitrate is effective only when the NH_4^T is greatly reduced. The same result was obtained from Guo et al (2018) using the S curve method. (**Page 17, line 445-457, in the revised manuscript**)

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] is much higher than 1 and belongs to rich-ammonia (Figure. S21). Although NH_3 in the NCP is abundant, the aerosol pH is far from neutral, which may attribute to the limited ALWC. Compared to the liquid water content in clouds and precipitation, ALWC is much lower, hence the dilution of aerosol liquid water to H_{air}^+ is weak. (**Page 17, line 458-465, in the revised manuscript**)

Cl^T: Cl^T has a relatively larger impact on aerosol pH in winter and spring compared to summer and autumn. Except for winter, the Cl^T mass concentration was generally lower than 10 μg m^{-3}, which accounted for the little impact on aerosol pH. On account of the low level of Cl^T, the dilution of ALWC on H_{air}^+ plays a dominant role, generating the aerosol pH increase with elevated Cl^T. However, similar to NO_3^T, higher Cl^T could decrease the aerosol pH. (**Page 17 and 18, line 466-470, in the revised manuscript**)

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 aerosol pH by decreasing H_{air}^+ and ALWC (Figure. S18), the decreased H_{air}^+ results from the buffering capacity of Ca^{2+} to the acid species, while the decreased ALWC result from the weak water solubility of $CaSO_4$. As discussed in Section 3.1, on clean conditions, the aerosol pH could reach

6~7 when the mass fraction of Ca^{2+} was high, hence the role of mineral ions on aerosol 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. (**Page 18, line 471-479, in the revised manuscript**)

Table 2. The averaged ambient temperature and $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ at different ambient RH levels in four seasons.

	RH	T, ℃	$\varepsilon(NH_4^+)$	$\varepsilon(NO_3^-)$	$\varepsilon(Cl^-)$
Spring	⩽ 30 %	24.8 ± 3.7	0.17±0.14	0.84±0.12	0.67±0.24
	30~60 %	20.6 ± 3.8	0.25±0.14	0.91±0.06	0.82±0.16
	>60 %	15.8 ± 2.7	0.28±0.12	0.96±0.03	0.96±0.06
Winter	⩽ 30 %	5.4 ± 5.3	0.31±0.13	0.78±0.12	0.89±0.14
	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	⩽ 30 %	35.6± 0.4	0.06±0.02	0.35±0.20	0.39±0.17
	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	⩽ 30 %	21.7± 7.5	0.07±0.06	0.49±0.25	0.45±0.21
	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

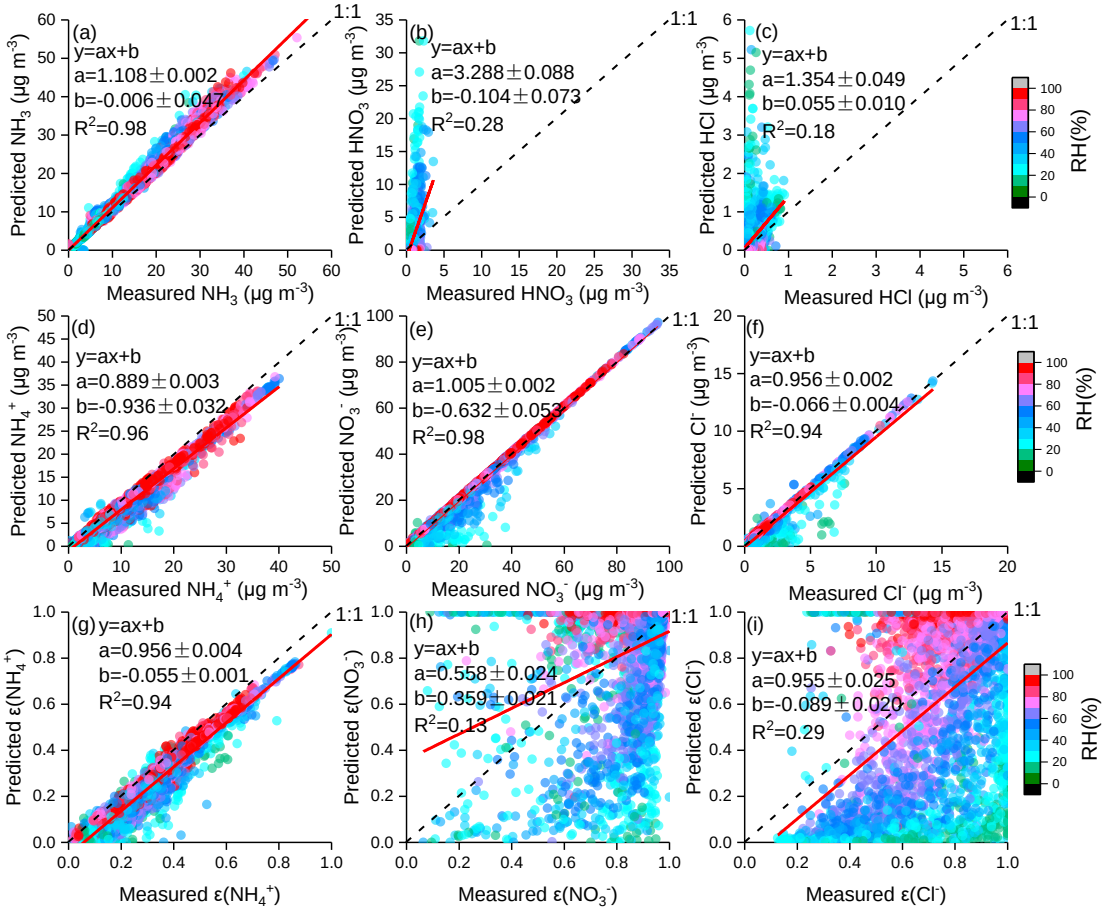

Figure 2. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by RH. In this Figure, the real-time data in four seasons were put together, and the comparisons for each season were shown in Figure S1-S4.

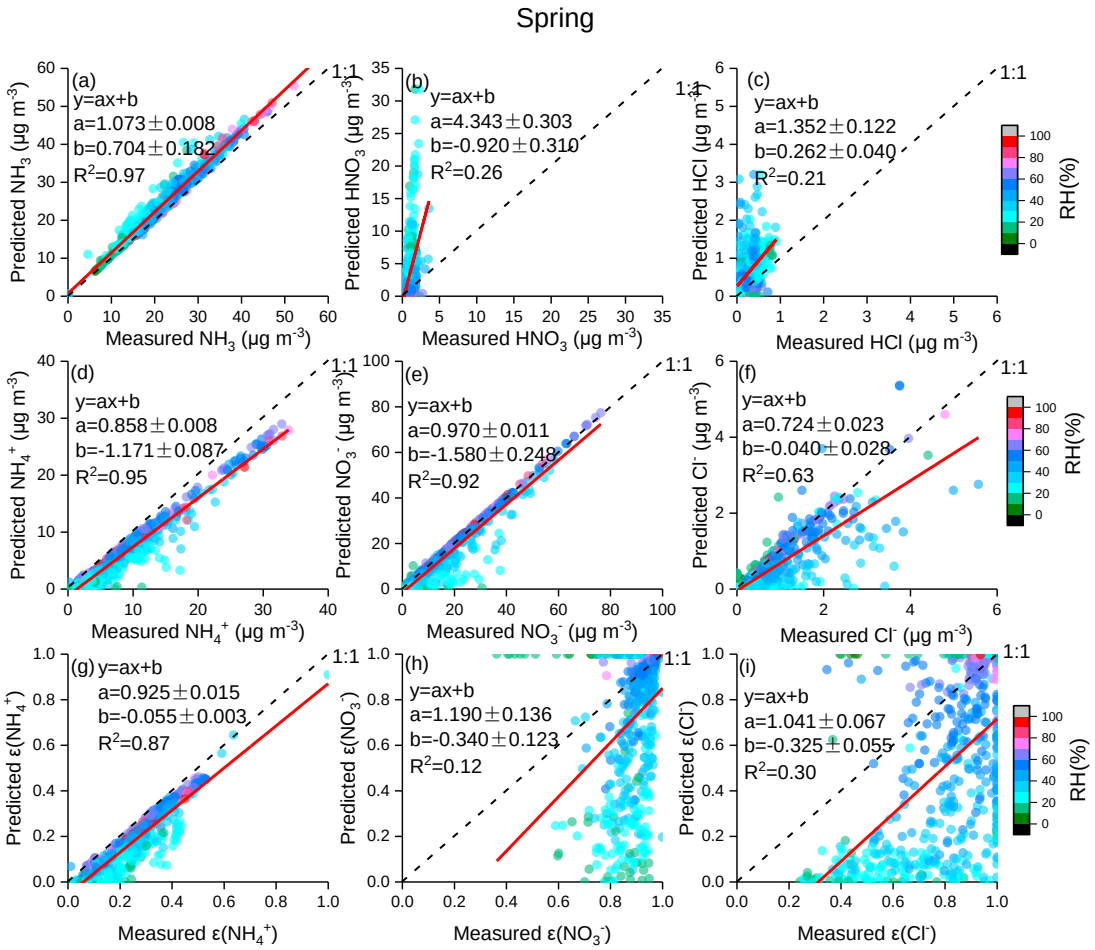

Figure S1. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by RH in spring.

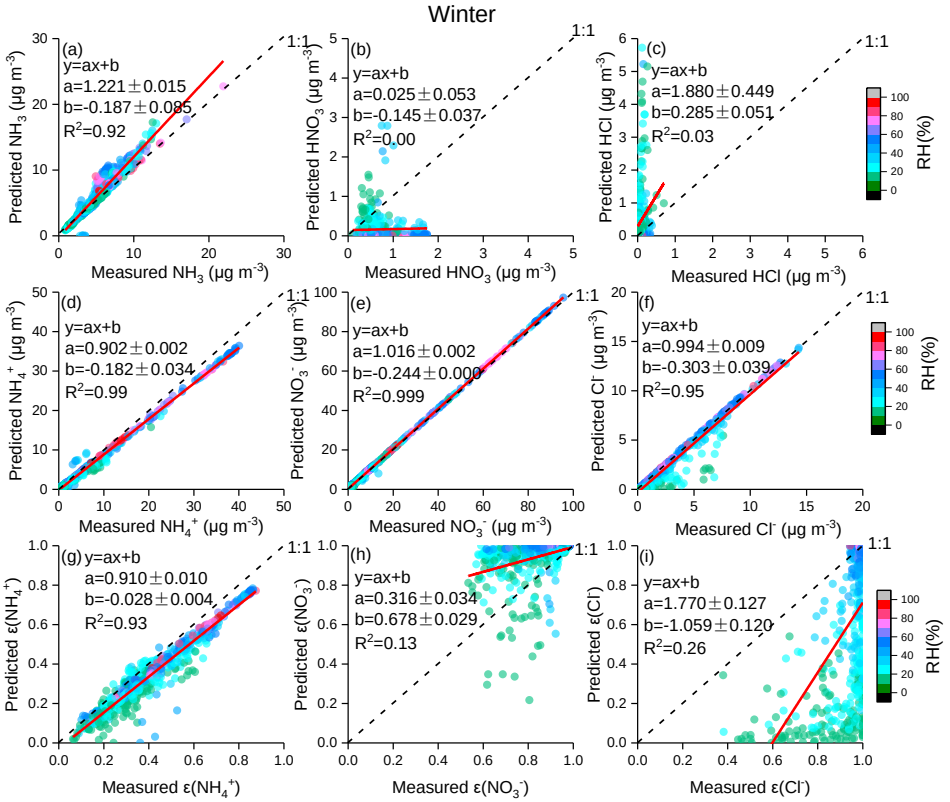

Figure S2. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by RH in winter.

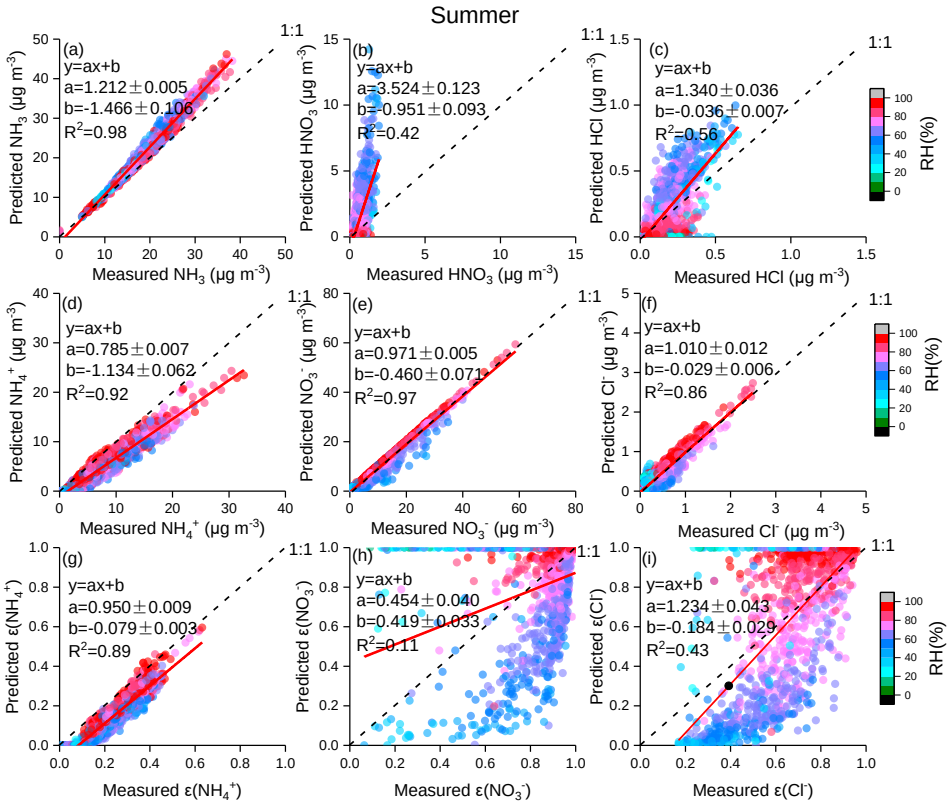

Figure S3. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by RH in summer.

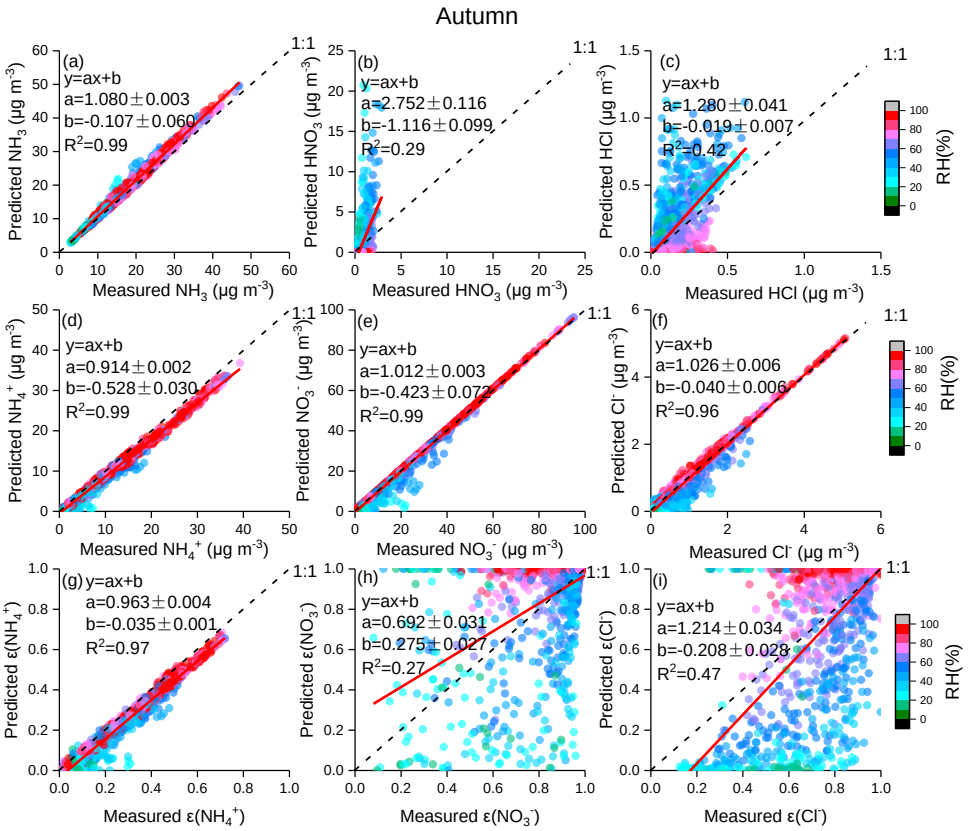

Figure S4. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by RH in autumn.

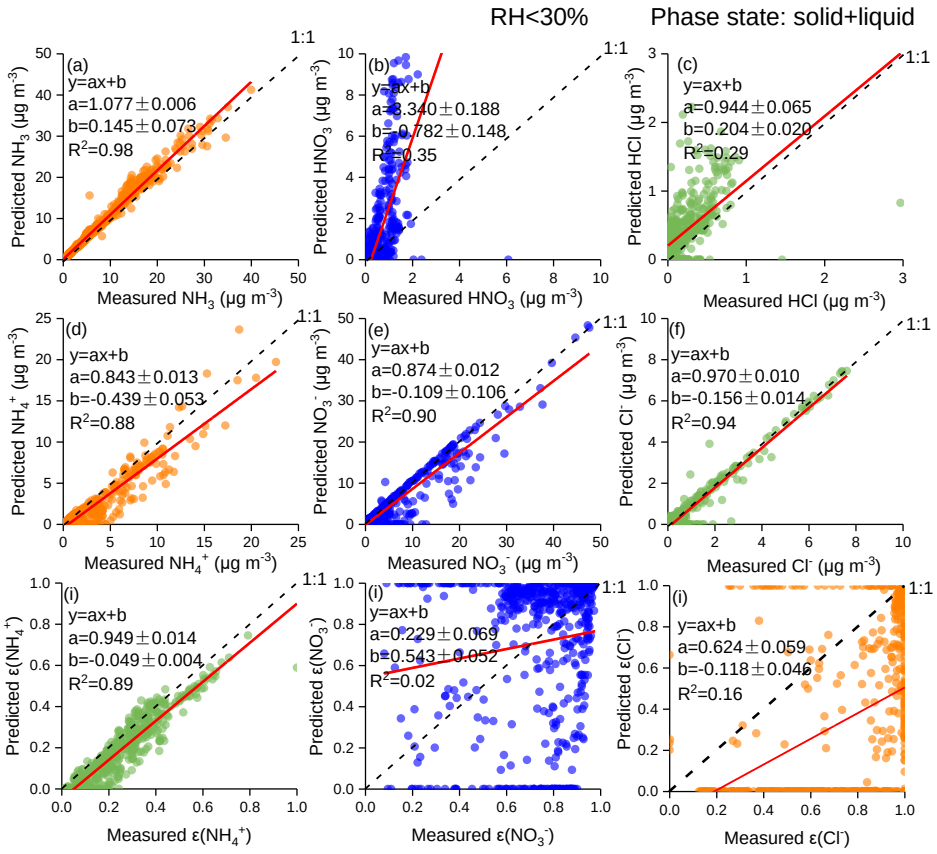

Figure S5. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ at the RH≤30%, the ISORROPIA-II runs in stable mode (solid + liquid).

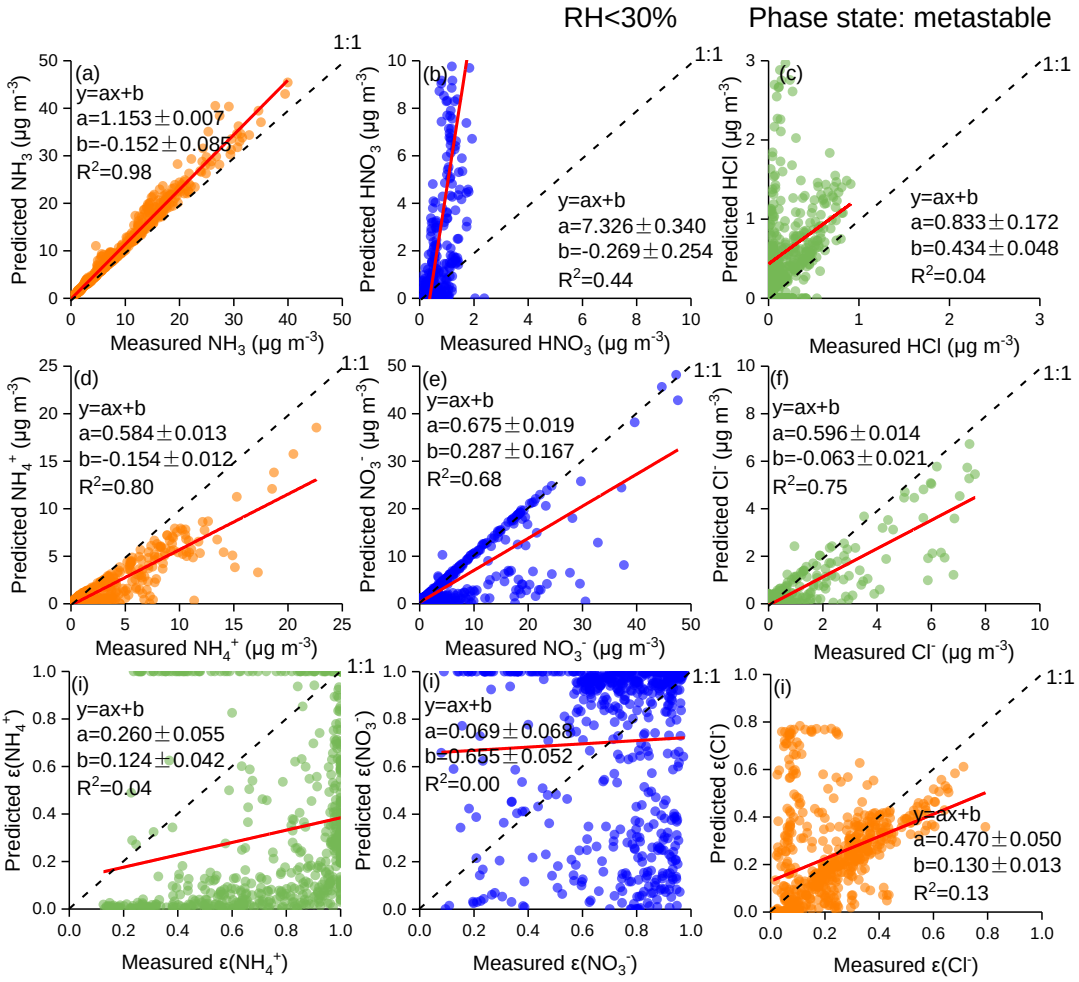

Figure S6. Comparisons of predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ at the RH≤30%, the ISORROPIA-II runs in metastable mode.

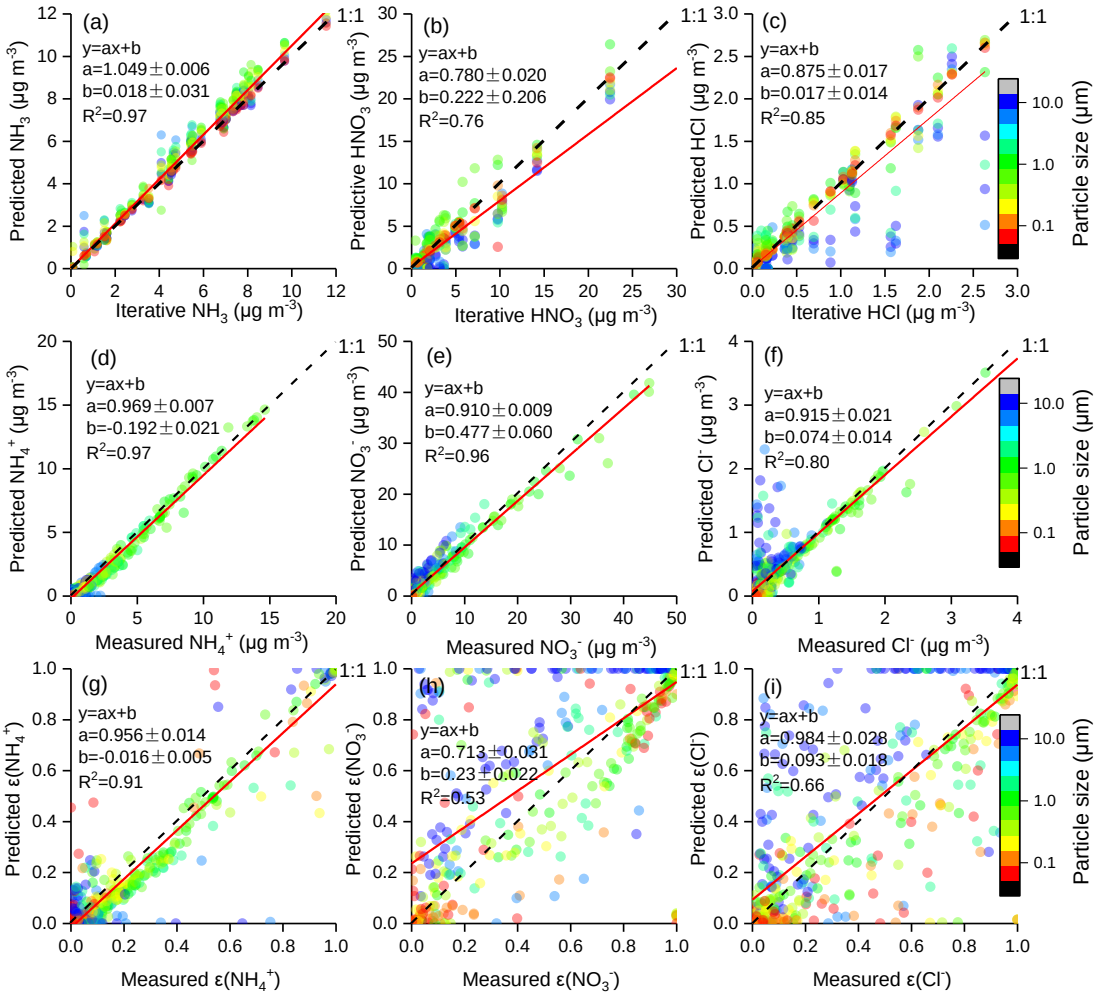

Figure 3. Comparisons of predicted and iterative NH_3, HNO_3, HCl, as well as the predicted and measured NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ colored by particle size. In this Figure, all MOUDI data were put together.

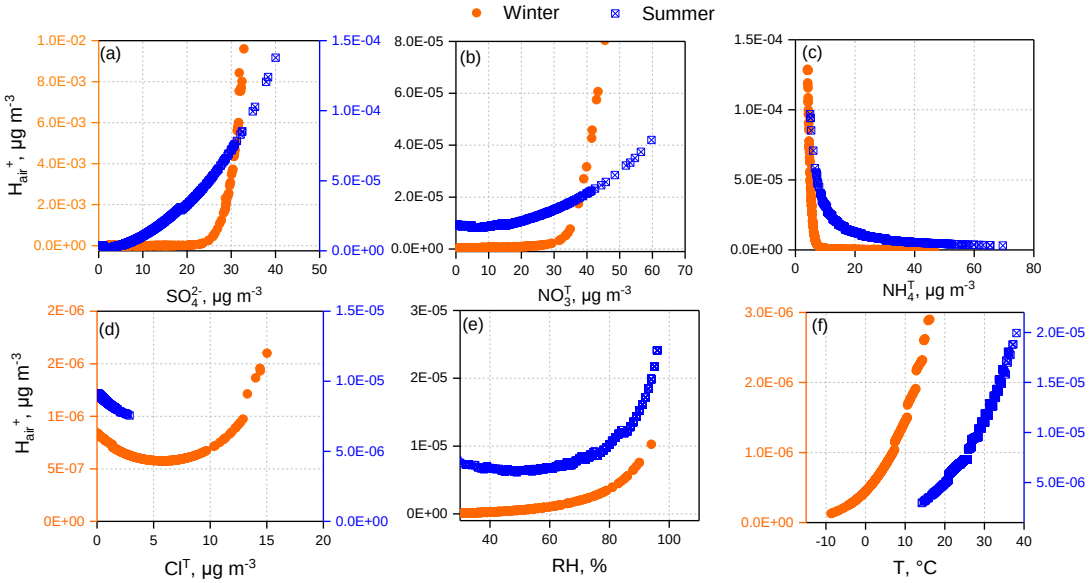

Figure 7. Sensitivities of H_{air}^+ to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, as well as meteorological parameters (RH, T) in summer and winter.

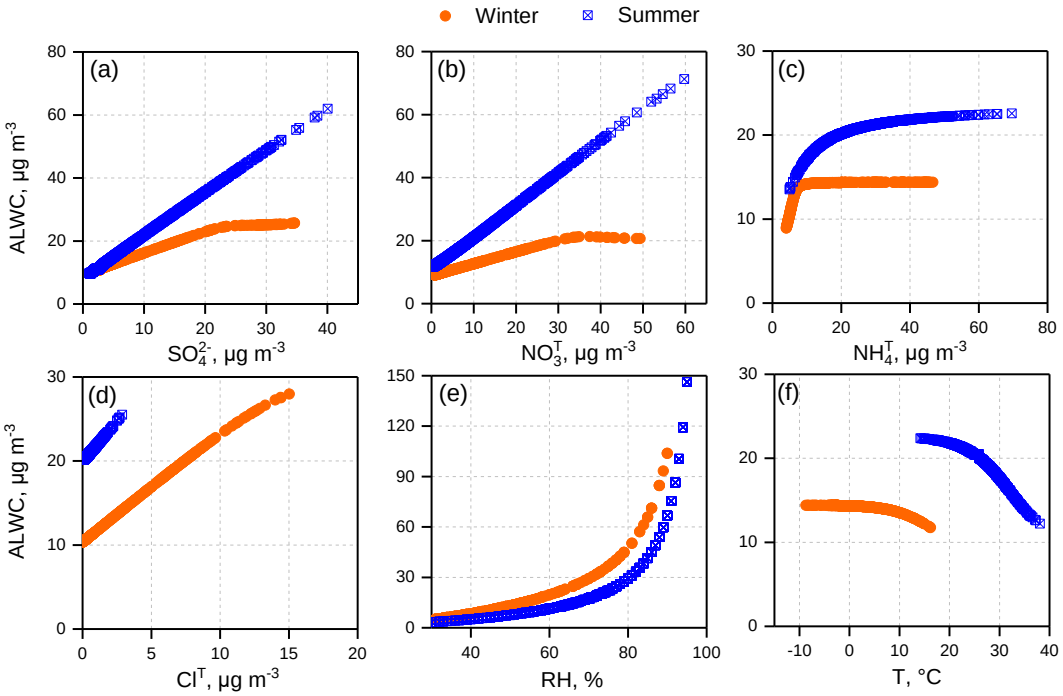

Figure 8. Sensitivities of ALWC to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, as well as meteorological parameters (RH, T) in summer and winter.

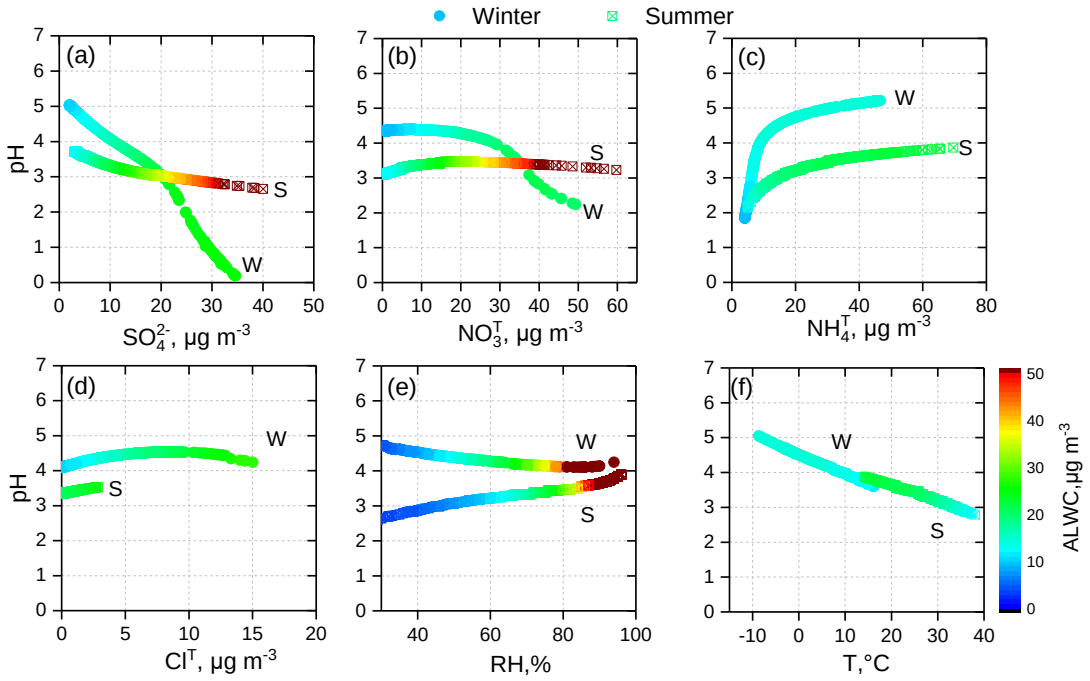

Figure 9. Sensitivities of aerosol pH to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, as well as meteorological parameters (RH, T) in summer and winter.

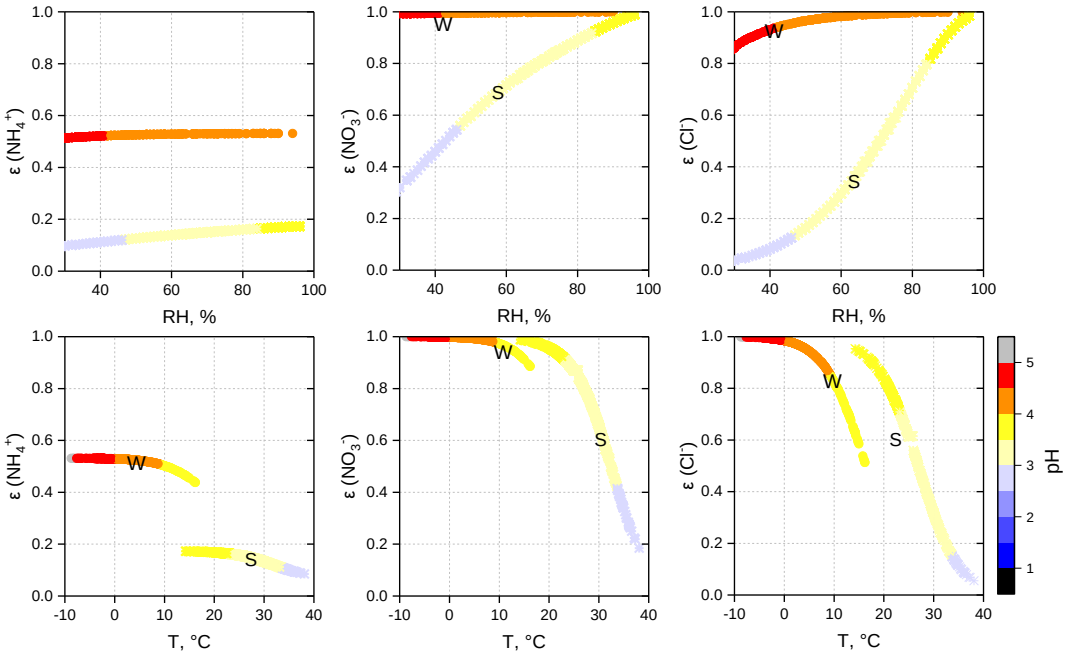

Figure 10. Sensitivities of ε(NH_4^+), ε(NO_3^-), ε(Cl^-) to RH and T colored by aerosol pH in summer and winter.

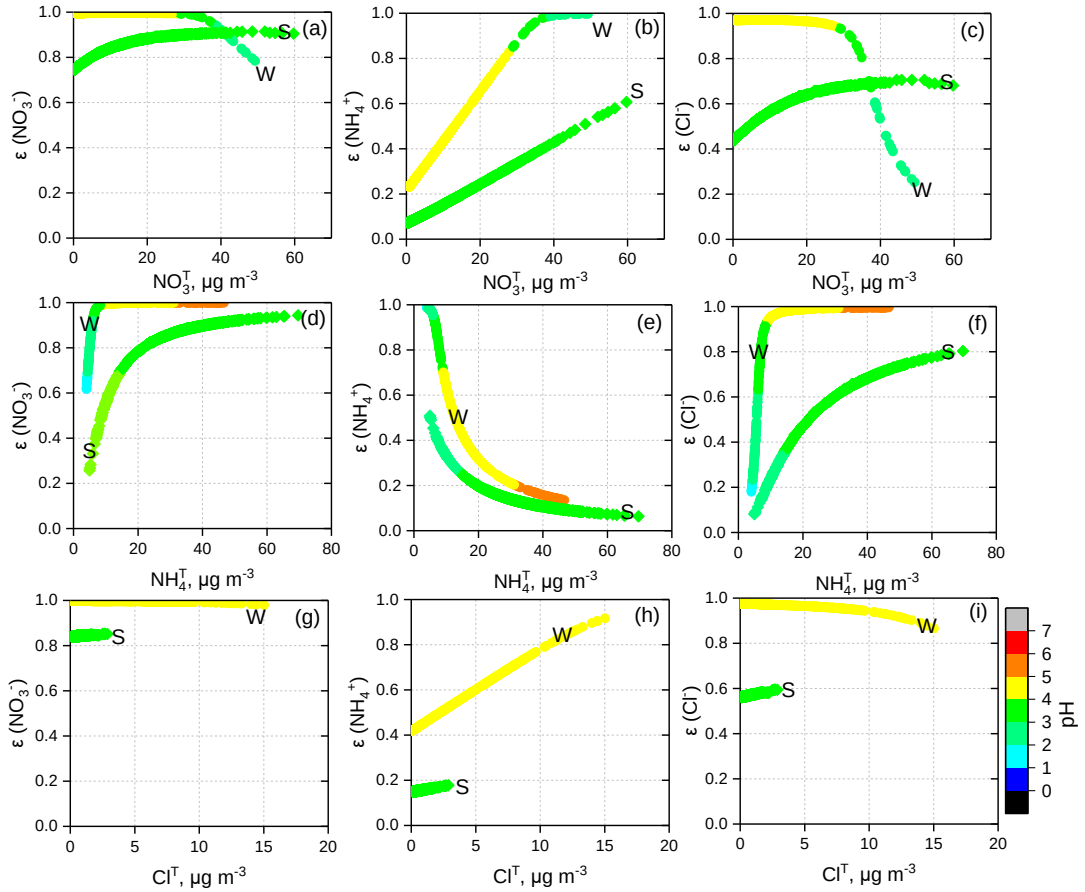

Figure 11. Sensitivities of $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ to NO_3^T, NH_4^T, Cl^T colored by aerosol pH in summer and winter.

Specific Comments:

1. Line 37 change specials to species

Response: In the revised manuscript, the word "specials" has been changed to "species" (**Page 3, line 38, in the revised manuscript**)

2. Line 202 and following, it is not just lack of NH3 data that can affect predicted pH, what about HNO3, HCl, etc?

Response: Thank you for your important advice, the gaseous precursor NH_3, HNO_3, HCl were all important for predicting pH with the forward mode. Actually, the NH_3, HNO_3, HCl obtained from the iteration method were all used in predicting the size-resolved aerosol pH. Here we missed other gases' names, in the revised manuscript, it has been corrected. (**Page 9, line 221-224, in the revised manuscript**)

3. Line 205, how much did the pH change when the iteration approach is used? Or, were the predicted gas species concentrations reasonable relative to what was measured during the MARGA study period.

Response: (1) As explained above, the MOUDI sampling was not synchronous with MARGA observation in time, hence the gas species concentrations were not available for MOUDI samples.

(2) The fine mode aerosol pH determined through the iteration procedure was higher than that with no gaseous species. In summer and autumn, the difference of fine mode aerosol pH was 0.1~1 between the predictions with and without gaseous species, while it was 0.1~2.9 in winter. The overall low RH in winter resulted in the low ALWC, hence in the gas-particle portioning procedure more NH_4^+ was portioned into the gas phase and led to the low aerosol pH for fine mode particles.

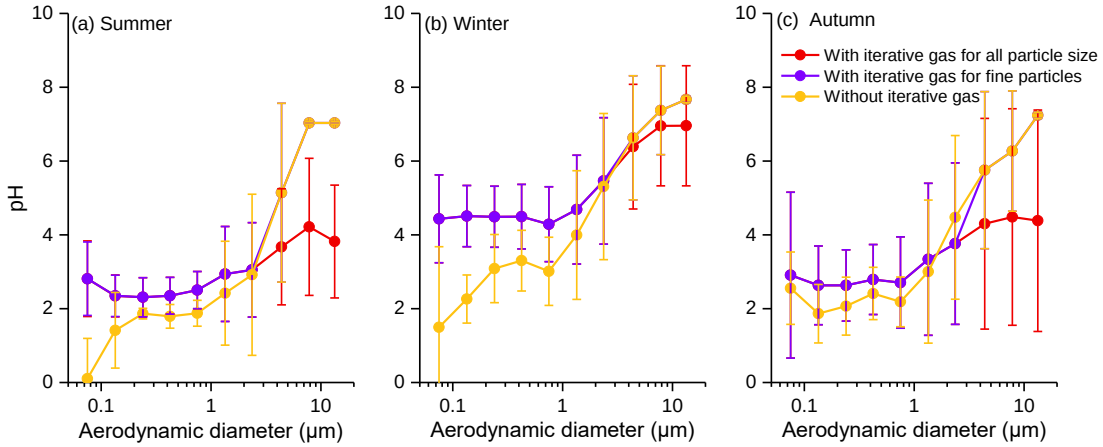

Figure R1 The averaged size-resolved aerosol pH in three seasons predicted with three assumptions: (1) predicted with no iterative gases, (2) predicted assuming lack of equilibrium with gas phase for coarse mode particles, (3) predicted assuming all particles in equilibrium with the gas phase.

4. Line 229 is superfluous, it is well known that low pH means high acidity.

Response: The sentence "implying the higher aerosol acidity" has been deleted in the revised manuscript.

5. Line 235 to 238: this paragraph seems out of place.

Response: Thank you for your advice, this paragraph has been deleted from the revised manuscript.

6. Fig 3 caption, what does transverse direction mean on a polar plot?

Response: In the polar plot, the shaded contour indicates the average of variables for varying wind

speeds (radial direction) and wind directions (transverse direction). And this was explicated in Figure 5.

7. Line 246 change souther to southern.

Response: "souther" has been changed to "southwest" and "southeast" in the revised manuscript. (**Page 12, line 312 and 313, in the revised manuscript**)

8. Line 276-286. From Fig 4 it does not appear that pH and sulfate diurnal trends are always the same (actually inverse), as stated. Looks like a stronger inverse trend with liquid water. The more quantitative analysis is needed to support the statements made in this section.

Response: Thanks for your suggestion. In fact, we want to express that the diurnal variation of aerosol acidity (not aerosol pH) is consistent with the diurnal variation of SO_4^{2-} over four seasons.

In the revised manuscript, the diurnal variation of NO_3^- was added in Figure 6. The diurnal variation of NO_3^- in winter and spring agreed well with the aerosol acidity. But in summer and autumn, the agreement was not well. Figure S11 shows the relationship between mass concentrations of SO_4^{2-} and NO_3^- and aerosol pH at different ALWC levels for all four seasons. At the relatively low ALWC, the increasing SO_4^{2-} could decrease the aerosol pH obviously; at the relatively high ALWC, the negative correlation still existed between SO_4^{2-} mass concentration and aerosol pH. On the contrary, a weak positive correlation was found between NO_3^- and aerosol pH at the relatively low ALWC and the aerosol 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 on aerosol pH. But 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. (**Page 13, line 337- 346, in the revised manuscript**)

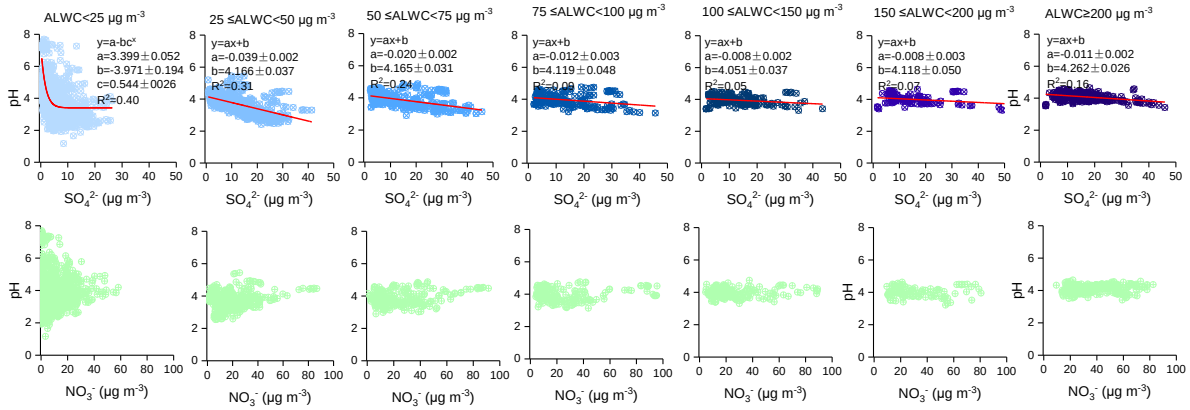

Figure S10. The relationship between SO_4^{2-} and NO_3^- mass concentration and aerosol pH at different ALWC levels.

9. Line 327, provide a physical explanation for the U shape dependency of H+ on NO3-

Response: As mentioned above, we discussed the dependency of H^+_{air} on NO_3^T instead of the NO_3^-. In addition, we find that the shape of the curve for the dependency of H_{air}^+ on total nitrate was also affected by the input average RH. In the revised manuscript, the data of RH lower than 30% were excluded. Similar with other seasons, the elevated NO_3^T could increase the H_{air}^+ exponentially.

10. Line 330-331: Is it really true that there is a straightforward relationship between NH3 and H+ over broad NH3 concentration ranges? Ie, will increases in NH3 always lead to higher dissolved NH3? Technically it may be true, but the relationship may be highly nonlinear under certain conditions. This statement seems too broad.

Response: Thanks for your advice, the statement here is not rigorous. The relationship between the reduction of H_{air}^+ and the increase of NH_3 was indeed nonlinear, and the increasing NH_3 could only promote NH_3 dissolution to a certain extent. The purpose of the statement of Line 330-331 was to explain the decrease of aerosol pH resulting from the elevated NH_4^T. As you commented, the gas-particle partition ($\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$) could help us understand fundamentally what is driving pH. We explain the decrease of aerosol pH resulting from the elevated NH_4^T in detail in your 13th comment.

11. Line 335, this is an obvious statement based on Eq (1). In fact much of the discussion throughout relating pH, H+ and LWC are obvious from Eq (1).

Response: The corresponding sentences in line 335 has been deleted in the revised manuscript.

12. Line 358 and on regarding changes in pH with NO3-. The authors discuss the trends they observe in the sensitivity analysis and NO3-/SO4=, but never provide an explanation. By just reporting of results, the value of this work is greatly limited, despite the what could be done with this unique data set.

Response: During the thermodynamic process of aerosol, all the SO_4^{2-} would dissolve in the aerosol liquid water, the amount of sulfate can be considered stable and it would not be affected by the NO_3^-. From the point of the model, the concentrations of NO_3^- and SO_4^{2-} are both the output of ISO-II. Thus, the ratio of NO_3^- / SO_4^{2-} can only reflect the objective state of particles, it is not the cause or the indicator of aerosol pH. After careful consideration, we decide to remove this part of the discussion.

13. Lines 380 and on regarding TA and TS. Most of these statements are technically incorrect (although, from a broad perspective they may have a grain of truth to them). The authors data show that the pH is far from neutral despite it being NH3 rich. This analysis largely continues misconceptions of how aerosol composition depends on interactions between SO4=, NH3, NH4+, HNO3, NO3- and LWC. Eg, is HNO3 only taken up once sulfate is so-called neutralized; maybe this can be tested with the data (there should be no NO3- and then a sudden jump in NO3- when [TA]/2[TS] is greater than 1. Another example, why does pH vary, even for this data set, if NH3 is is always in great excess? It is suggested that the authors look at S curves (partitioning of say NH3 and/or HNO3 vs pH) instead of the analysis currently being used.

Response: Firstly, we think you are right, our statements here have some problems. Figure S21 showed that the elevated [TA]/2[TS] didn't increase the NO_3^- mass concentration, high NO_3^- mass concentration occurred when [TA]/2[TS] varies over a wide range (2~15). But in the NCP, the excess of ammonia in the atmosphere is indeed true, the ratio of [TA]/2[TS] is much higher than 1. The poor-ammonia cases were not observed in this work.

The relationship between aerosol pH and NH_4^T was nonlinear. NH_4^T in lower range had a significant impact on aerosol 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 increases, H_{air}^+ are consumed swiftly during the dissolution of NH_3 and the further reaction with SO_4^{2-}, NO_3^-, and Cl^-. And 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 alters the gas-particle partition and shifts more NO_3^T and Cl^T into particle phase, leading to the deliquescence of additional nitrate and chloride and increase of ALWC. (**Page 17, line 445- 453, in the revised manuscript**)

Although NH_3 in the NCP is abundant, the aerosol pH is far from neutral, which may attribute to the limited ALWC. Compared to the liquid water content in clouds and precipitation, ALWC is much lower, hence the dilution of aerosol liquid water to H_{air}^+ is weak. (**Page 17, line 462- 465, in the revised manuscript**)

The relationship between $\varepsilon(NO_3^-)$, $\varepsilon(Cl^-)$ and aerosol pH was analyzed by S curves proposed by Guo et al (2016, 2017), which were calculated based on the average temperature, aerosol liquid water, and activity coefficients. Their result showed that for a given ALWC and T, about 4 pH units increase are needed when the $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$ varies from 0 to 100%. In our opinion, the ALWC, H_{air}^+, aerosol pH, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ are all the output of ISO-II. They reflect an objective state of particles. Accordingly, it is reasonable to discuss the impact of input variables on output parameters with the results of ISO-II. On the basis of overall moderate aerosol acidity, the variation of aerosol pH is related to aerosol composition and meteorological conditions (RH and T). In the sensitivity analysis of this work, the influence of single variables on aerosol acidity is explicit. In the ambient atmosphere, multiple variables interact with each other, and aerosol acidity largely depends on the dominant factor.

14. Line 419 to 421. The loss of buffering capacity of the coarse mode mineral dust during winter pollution events is very interesting and has direct implications for predictions of NO2 + SO2 oxidation pathways proposed by Wang et al 2016 and Cheng et al 2016. It is suggested that this finding be noted more prominently, maybe even included in the Abstract. However, this period does not seem to be shown in the plots?

Response: Wang et al (2016) and Cheng et al (2016) advocate that the aqueous oxidation of SO_2 by

NO_2 is key to efficient sulfate formation but is only feasible under two atmospheric conditions: on fine aerosols with high relative humidity and NH_3 neutralization (aerosol pH ~7) or under cloud conditions. Their results focused on the fine particles, hence whether the loss of buffering capacity of the coarse mode mineral dust during winter pollution has a direct implication on their results remains to be discussed. But for fine particles, excessive NH_3 does not raise aerosol pH sufficiently.

15. The use of the word synthetically throughout the paper is confusing, it is suggested that it not be used since its meaning is unclear.

Response: The word "synthetically" has been deleted in the revised manuscript.

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Ma, Q.X., Wu, Y.F., Zhang, D. Z., Wang, X.J., Xia, Y.J., Liu, X.Y., Tian, P., Han, Z.W., Xia, X.G., Wang, Y., Zhang, R.J.: Roles of regional transport and heterogeneous reactions in the $PM_{2.5}$ increase during winter haze episodes in Beijing, Sci. Total Environ., 599-600, 246-253, 2017.

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measurements of ambient aerosol in Beijing. J. Environ. Sci., 54, 298-313, 2017.

Anonymous Referee #2

This paper presents observations and analysis of the inorganic aerosol system in Beijing for 2017. The pH values are realistic; however, more analysis to verify the methods would make for a stronger paper.

Response:

Thanks for your important comments, which are very useful to make our paper more rigorous. Please see our point-by-point responses to the comments and the revised manuscript for details. The order of the Figures or Tables in Response is the same as the corresponding Figure or Table appears in the main text and supplemental materials.

Major comments:

1. Clarify the methodology in terms of how pH was calculated. How was the pH in different size ranges modeled and combined? Even if that appears in other work (as indicated in the text), a quick summary of the method would be useful. Line 209 indicates pH (for the coarse mode?) was determined by ignoring the gas phase and running ISORROPIA in a forward mode with zero gas. How was this assumption verified? Figure 2 shows a comparison of total species modeled vs predicted, but that doesn't give a sense of how the size-dependent predictions worked. Line 438 indicates that NH3, HNO3, and HCl were determined through iteration when MOUDI data was used. Was that just for the fine mode particles?

Response:

The data set of MOUDI was obtained during 2013 and 2015, which was not synchronous with the online ion data (obtained in 2016 and 2017). There was no observation of gas precursors during the periods of MOUDI sampling, hence an iteration method used in Fang et al. (2017) and Guo et al. (2016) was applied in this work. As a brief summary, the predicted NH_3, HNO_3, and HCl concentrations from the *i*-1 run were applied to the *i*th iteration, until the gas concentrations converged. Based on these iterative gas phase concentrations, each MOUDI stage's measured aerosol ion concentrations and estimated gas concentrations, as well as the averaged RH and T during each group sampling time, were input the ISORROPIA-II to determine pH for each stage. The particles at each size bin were assumed to be internally mixed. (**Page 9, line 221- 230, in the revised manuscript**)

The comparisons of iterative and predicted NH_3, HNO_3, and HCl as well as measured and predicted NO_3^-, NH_4^+, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ for data from MOUDI samples were showed in Figure 3. The previous study showed that coarse mode particles are very difficult to reach equilibrium with the gaseous precursors due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000). Assuming coarse mode particles in equilibrium with the gas phase could result in a large bias between measured and predicted NO_3^- and NH_4^+ in coarse mode particles (Fang et al, 2017). We also find that in this work, it can be clearly seen that assuming coarse mode particles in equilibrium with the gas phase could overpredict 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 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 coarse mode was determined by ignoring the gas phase. (**Page 9-10, line 231- 242, in the revised manuscript**)

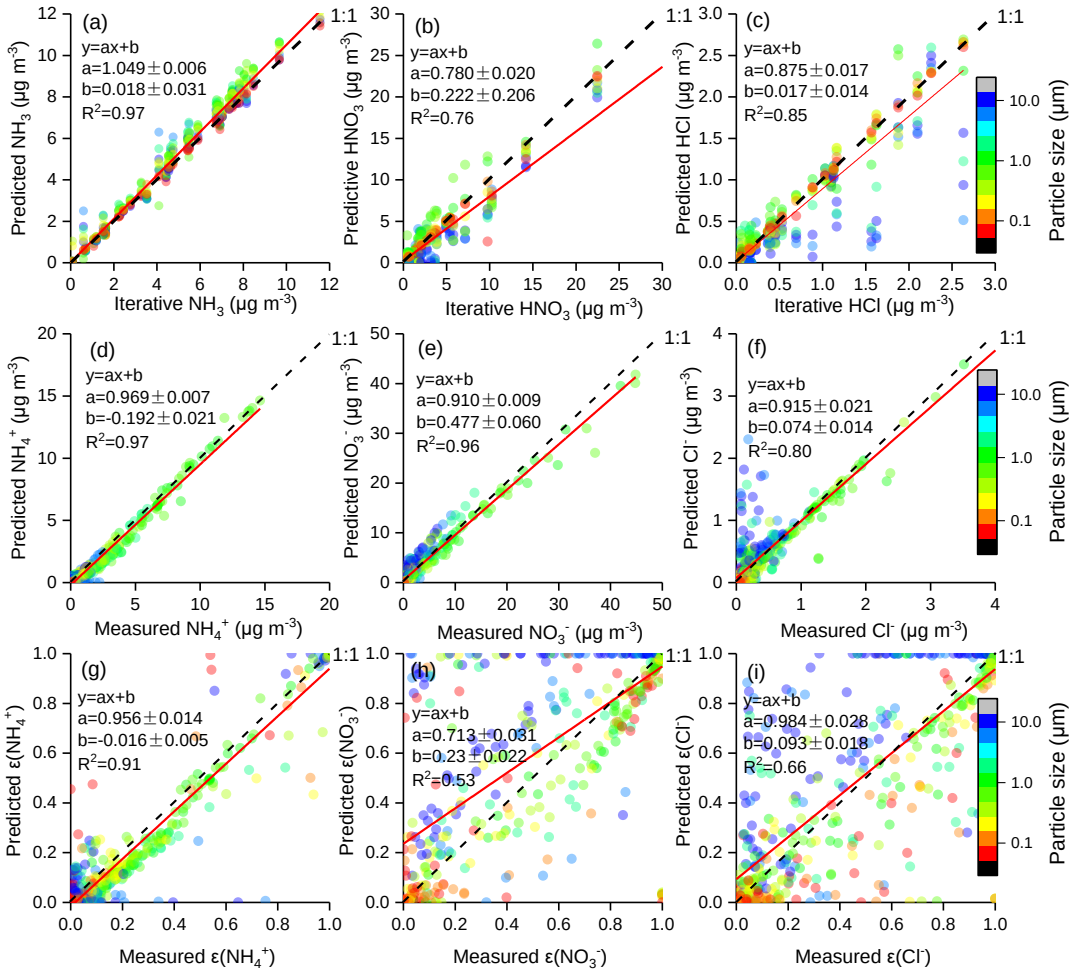

Figure 3. The comparisons of iterative and predicted NH_3, HNO_3, HCl as well as measured and predicted NO_3^-, NH_4^+, Cl^-, ε(NH_4^+) ε(NO3-) ε(Cl^-) for data from MOUDI samples, which all colored by particle size.

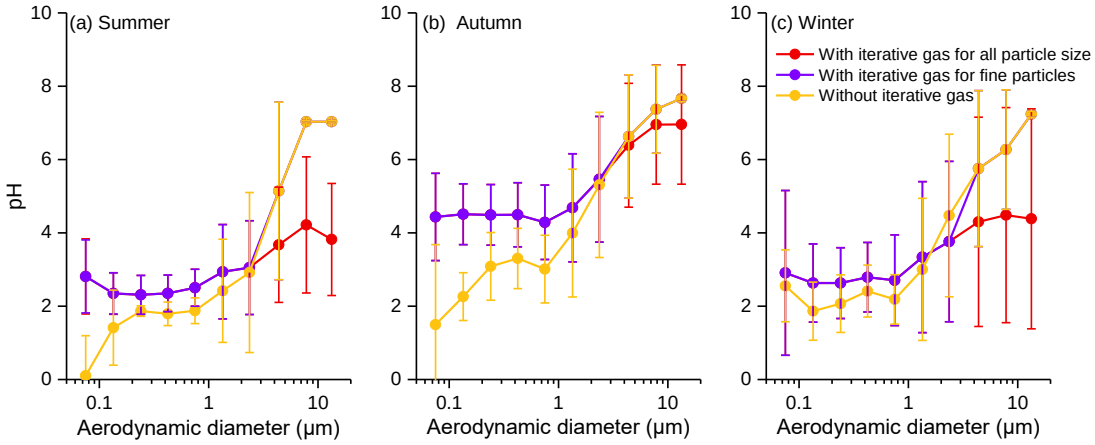

Figure R1 The averaged size-resolved aerosol pH in three seasons predicted with three assumptions: (1) predicted with no iterative gases, (2) predicted assuming lack of equilibrium with gas phase for

coarse mode particles, (3) predicted assuming all particles in equilibrium with the gas phase.

2. Driving factor analysis: The driving factors for pH were obtained by holding all composition, RH, and T parameters at average values and then varying one of the input values (line 291 and thereafter-consider putting some of this method in section 2). A larger change in ALWC, H+air, or pH due to varying one input was interpreted as that input having a major influence on pH. The authors do note that this method will not capture the effect of simultaneous changes in more than one factor.

Response:

Thanks for your important advice. The detailed introduction of the method about aerosol pH driving factor analysis has been put in section 2.5. In the real ambient air, the thermodynamic process of the aerosol is complicated, it is not easy to tell the effect of one certain factor on the aerosol pH. The ALWC, H_{air}^{+}, and aerosol pH are all the output of ISORROPIA-II. 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 sensitivity analysis of single-factor variation, which can reflect the variation tendency of aerosol pH caused by the change of each variable.

The detailed description of sensitivity analysis method was put in Section 2.5 **(Page 10-11, line 245- 270, in the revised manuscript)**

a. Did the authors consider restricting the output values used to calculate sensitivities (e.g. Table 2) to space actually probed in the ambient? For example, ALWC output from the simulation varying RH spans 0-140 ug/m3 while most other input parameters did not result in this range of ALWC values. Was 140 ug/m3 ALWC predicted for any of the actual atmospheric conditions? What space is actually probed in the ambient atmosphere in terms of ALWC, H+air, and pH compared to what is probed in the simulated data holding all but one parameter constant?

Response: All data used in the sensitivity analysis were based on the actual observation, not randomly generated simulation data, which helps us capture a more real impact. When the RH was considered as a variable, ALWC output spans 0-140 $\mu g/m^3$, this mainly attributed to the vital impact

of RH on ALWC, especially when the RH was higher than 80% owing to the exponential increase of ALWC with the RH. Whereas in other simulated cases, the averaged RH was generally within 50% ~ 75%, hence the output ALWC was relatively low. In summer and autumn, the actual ALWC was even more than 140 μg/m^3 when both aerosol components and RH were high.

b. How can the method be evaluated? Does using average inputs result in the same predicted pH that would be obtained by averaging all individual pH predictions from individual inputs? Could the average pH and input be indicated on each panel of Figure 5 to 7? How evenly distributed over the input range are the various inputs? Would it be more appropriate to focus on the interquartile range instead of a full range of inputs?

Response: The average value and variation range for each variable in all four seasons were listed in Table S1 and Figure S7. The aerosol pH1 is the value by averaging all individual pH predictions from each input variable, for example, the average aerosol pH was 3.74±0.47 when the SO_4^{2-} was regarded as an input variable while other input parameters were fixed with the average value. The aerosol pH2 is the value by using average inputs for all input parameters. In theory, pH1 and pH2 cannot be the same, otherwise, the effect of the variables on aerosol pH will not be reflected.

Table S1 The average value and range for each variable in all four seasons, as well as the two average aerosol pH types. The aerosol pH1 is the value by averaging all individual pH predictions from each continuous input variable, for example, the average aerosol pH was 3.74±0.47 when the SO_4^{2-} was regarded as a continuous input variable while other input parameters were fixed with the average value. The aerosol pH2 is the value by using average inputs for all input parameters. The unit of chemical components is μg m^{-3}.

Spring	SO_4^{2-}	NH_4^T	NO_3^T,	Cl^T	RH, %	T, °C	Ca	Na	K	Mg
Average input	8.4	25.7	13.5	1.1	52	20.9	1.29	0.20	0.34	0.3
Variable range	3.0~41.4	0.1~33.9	0.4~77.6	0.03~6.27	30~92	10.0~33.3	0.1~3.0			
pH1	3.74±0.47	3.69±0.19	3.65±0.53	3.81±0.09	3.79±0.05	3.81±0.27	3.73±0.16			
pH2					3.82					
Winter	SO_4^{2-}	NH_4^T	NO_3^T,	Cl^T	RH, %	T, °C	Ca	Na	K	Mg
Averaged	7.3	12.2	14.3	3.0	52	2.7	0.2	0.40	1.0	0.2
Ranges	2.0~34.6	1.3~46.7	0.8~49.3*	0.02~25.2	30~94	-8.7~16.2	0.01~0.7			
pH1	4.32±1.21	3.86±1.04	4.27±0.48	4.27±0.16	4.39±0.18	4.36±0.29	4.36±0.04			
pH2					4.36					
Summer	SO_4^{2-}	NH_4^T	NO_3^T,	Cl^T	RH, %	T, °C	Ca	Na	K	Mg

Averaged	8.6	26.8	10.2	0.6	74	26.1	0.5	0.60	0.2	0.1
Ranges	0.6~40.1	1.2~69.6	0.3~59.8	0.1~2.8	30~97	14.2~38.1	0.02~2.9			
pH1	3.43±0.27	3.31±0.32	3.31±0.12	4.38±0.03	3.40±0.27	3.37±0.20	3.38±0.06			
pH2					3.38					
Autumn	SO_4^{2-}	NH_4^T	NO_3^T,	Cl^T	RH, %	T, °C	Ca	Na	K	Mg
Averaged	9.3	27.8	20.3	1.0	72	16.4	0.4	0.3	0.2	0.1
Ranges	0.3~54.7	3.2~67.5	0.2~90.5	0.06~5.17	30~97	-1.1~33.3	0.02~2.3			
pH1	3.85±0.23	3.60±0.58	3.70±0.12	3.84±0.04	3.94±0.10	3.84±0.29	3.84±0.03			
pH2					3.84					

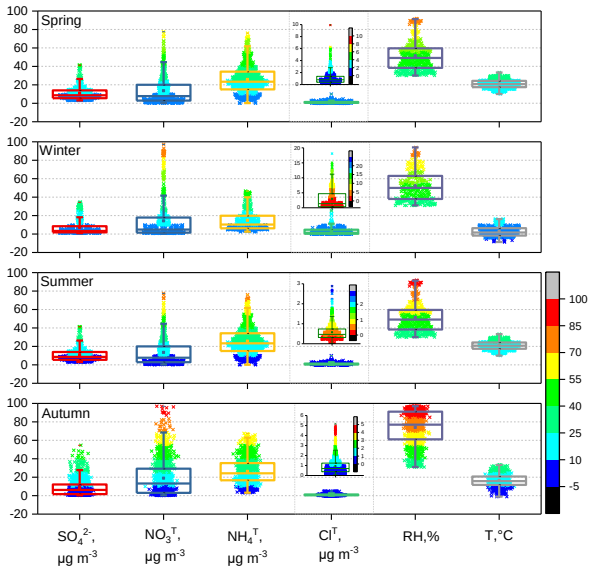

Figure S7. The distribution of each input variable for sensitivity analysis in four seasons

c. Are there units to the quantities in table 2?

Response: Units to the quantities in table 2 were missed in the manuscript, in the revised manuscript, we replace the deviation by relative standard deviation as the evaluation target, hence the unit is unified to %.

d. How would a multiple linear regression analysis differ from the technique of varying one quantity at a time?

Response: The relationships between input variables and aerosol pH are not simply linear. The method in this work based on the overall accurate relationship between variables rather than the permutation and combination in the mathematical sense, the latter may subversively change the

relationship between variables and does not conform to the actual physical laws. Moreover, the predicted aerosol pH in the sensitivity analysis was realistic, which confirms that the method we used was reasonable.

e. Could a Monte Carlo method or other technique be used to make sure atmospherically relevant combinations of inputs are being used?

Response: The Monte Carlo method is a good way to evaluate the uncertainty of the predicted aerosol pH and to determine if the input parameters are appropriate. However, as mentioned above, all input variables came from the actual observation to make sure the relationships between variables could conform to the actual physical laws. Moreover, the sensitivity analysis in this work focused on the variation tendency of aerosol pH rather the absolute aerosol pH value.

3. Instead of classifying PM2.5 into clean (0-75 ug/m3), polluted, and heavily polluted (>150 ug/m3), it may be illustrative to consider PM2.5 in a continuum. 0-75 ug/m3 on a daily average is not very clean as it includes concentrations that exceed air quality standards. In addition, by considering PM2.5 concentrations as continuous, you may be able to better determine the association of pH with PM2.5. Consider that the pH for the three classifications is reported with a range/uncertainty that indicates the differences in pH between clean, polluted, and heavily polluted conditions are not statistically significant (values on line 262 overlap). However, if considered as a continuous variable, a regression with confidence interval could be provided and might provide a more robust analysis of the association.

Response: Thanks for your suggestion. Firstly, three groups for $PM_{2.5}$ were classified by hourly $PM_{2.5}$ mass concentration, not daily average $PM_{2.5}$ mass concentration. Secondly, the differences in pH between clean, polluted, and heavily polluted conditions were indeed not significant, the conclusion in the manuscript was just taken from the average value of pH. More deep analysis has been added in the revised manuscript.

Table 1 showed that as the air quality deteriorates, all aerosol components, as well as ALWC and H_{air}^{+}, increased, but the differences in pH between clean, polluted, and heavily polluted conditions are not statistically significant. The relationship between $PM_{2.5}$ and aerosol pH was shown in Figure

S8, the aerosol pH under clean condition spanned 2~7 while the aerosol pH under polluted and heavily polluted conditions mostly concentrated in 3~5. 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, were showed in Figure 4. It can be seen that on clean days, high aerosol pH (>6) was generally companied by high mass fraction of crustal ions, while the relatively low aerosol pH (<3) was companied by high mass fraction of SO_4^{2-} and low mass fraction of crustal ion, which was most obvious in summer (large part of aerosol pH with RH≤30% were excluded in spring and winter). On polluted and heavily polluted days, the aerosol chemical composition was similar, mainly dominated by NO_3^-, hence the differences of aerosol pH on polluted and heavily polluted days were small. Compared with the mass concentration of $PM_{2.5}$, the different aerosol chemical compositions may be the essence that drives aerosol acidity. The impact of aerosol compositions on aerosol pH is discussed in Section 3.4. (**Page 11-12, line 291- 308, in the revised manuscript**)

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.

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}	
Averaged	62±36	14.9±14.6	9.7±7.9	7.9±7.3	23±35	6.8E-06±2.8E-05	4.0±1.0
Clean	44±17	7.9±6.6	6.2±3.7	4.8±3.2	14±26	3.2E-06±5.1E-06	4.1±1.1
Polluted	100±21	30.8±14.3	16.4±5.9	15.4±5.8	33±36	5.1E-06±4.3E-06	3.9±0.5
Heavily polluted	169±12	45.3±8.5	36.3±4.9	29.4±2.3	78±60	2.0E-05±6.5E-06	3.6±0.3
winter	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Averaged	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*
Averaged	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*
Averaged	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%.

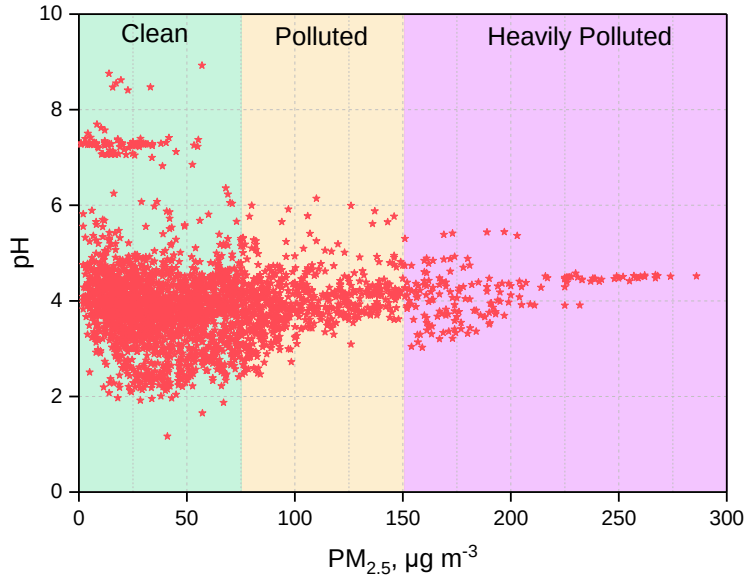

Figure S8. The relationship between $PM_{2.5}$ mass concentration and aerosol pH, the dots with RH≤30% were excluded.

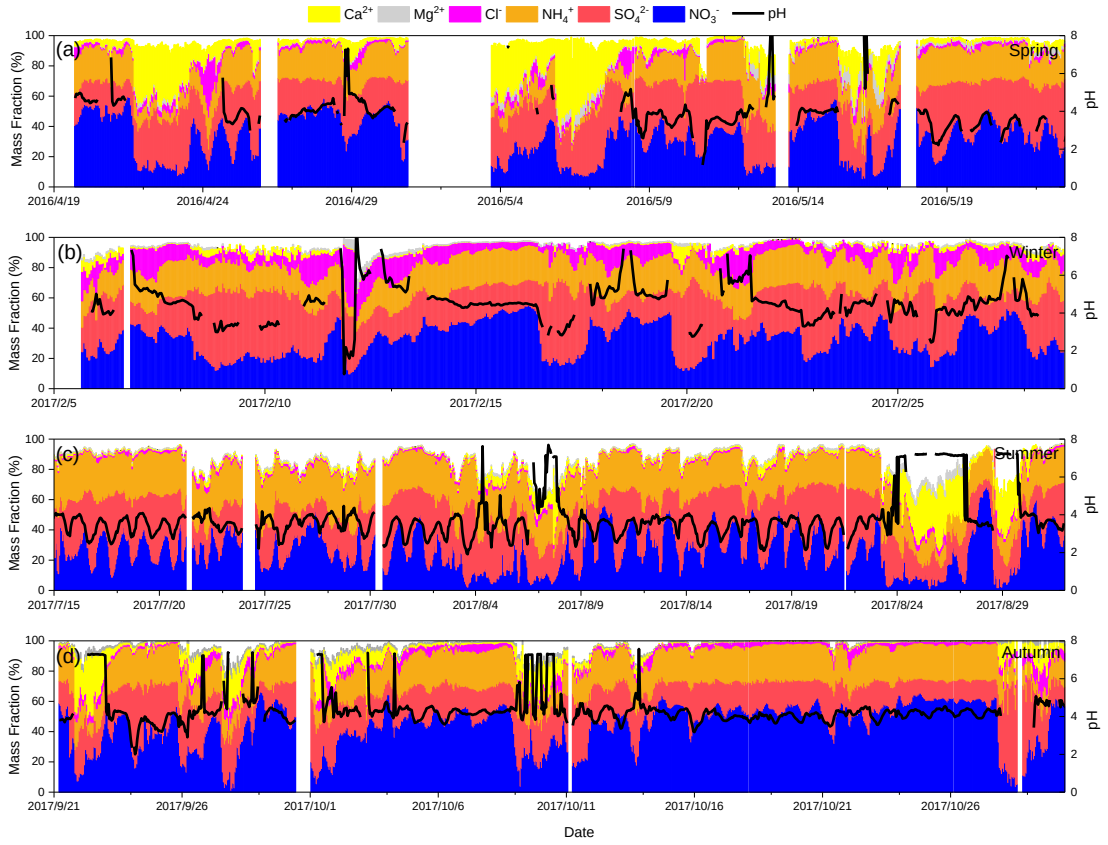

Figure 4. Time series of mass fraction of NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, crustal ions (Mg^{2+}, Ca^{2+}) in total ions as well as aerosol pH in all four seasons.

4. Better connect the size-resolved measurements with the rest of the text. To what degree did the presence of coarse material drive ambient pH? Do figures 5-7 and the analysis regarding drives of pH only consider fine mode pH?

Response: Thanks for your suggestion. The data set of MOUDI was obtained during 2013 and 2015, whereas the online ion data was obtained in 2016 and 2017. (1) The sensitivity analysis in this work aimed at the $PM_{2.5}$ (*ie* fine particles) since the $PM_{2.5}$ components in four seasons were available and has a high temporal resolution (1h). In addition, the data set has a wild range, covering different levels of haze events, making it suitable for sensitivity analysis. The MOUDI data were only utilized to determine the size-resolved aerosol pH. (2) In this work, the coarse mode aerosol acidity was generally neutral, which mainly attributed to the higher mass concentration of mineral materials in the coarse mode. The sensitivity analysis in this work showed that the aerosol pH increased approximately linearly with the elevated Ca^{2+} in $PM_{2.5}$ (Figure S18). However, the impact of Ca^{2+}

has a limited impact on fine mode aerosol pH due to its low mass concentration in $PM_{2.5}$. Our previous paper showed that the mineral materials such as Ca^{2+} and Mg^{2+} mainly concentrated in the coarse mode (Figure R2, same data set with this work, Zhao et al, 2017; Su et al., 2018). We did some supplementary simulations under extreme cases that Ca^{2+} and Mg^{2+} are removed from the input files. The results showed that the presence of Ca^{2+} and Mg^{2+} in coarse mode has a crucial effect on 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. The aerosol pH in coarse mode decreased by 4~6.5 unit when the Ca^{2+} and Mg^{2+} are removed. (**Page 19, line 508- 514, in the revised manuscript**)

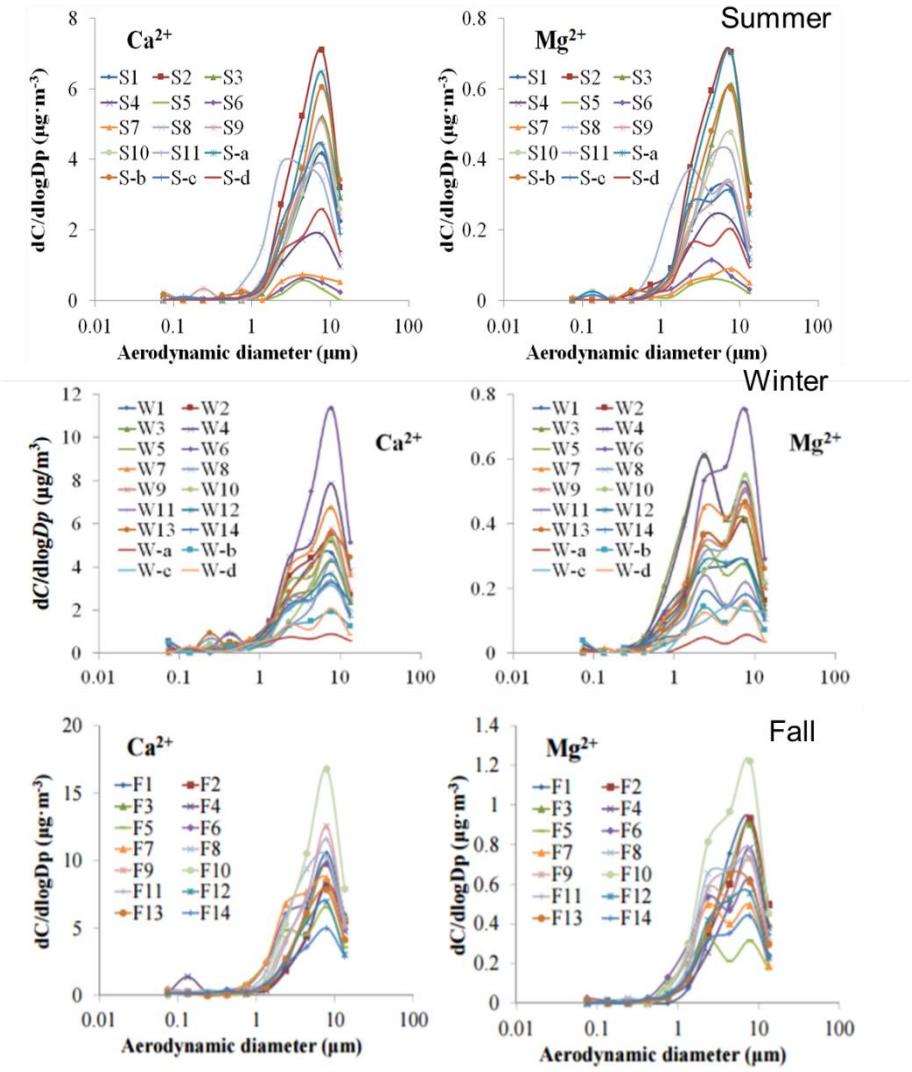

Figure R2. Size distributions of the mass concentration for Ca^{2+} and Mg^{2+} in summer, winter, and fall. (Zhao et al, 2017; Su et al., 2018)

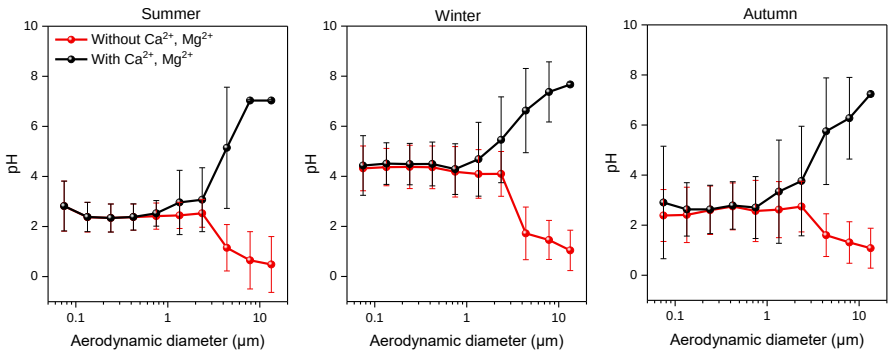

Figure S22. Size distributions of the aerosol pH with and without Ca^{2+} and Mg^{2+} in summer, winter, and autumn.

Minor comments:

1. Line 49. Instead of stating that aerosol acidity is "usually estimated" by the charge balance, I would indicate "sometimes" or "frequently," but not usually as many studies do use a thermodynamic model.

Response: Thank you for your good advice, "usually" has been changed to "frequently" in the revised manuscript. (**Page 3, line 50, in the revised manuscript**)

2. Line 52-55 wording indicates ion balance fails because acidity is estimated by aerosol water extract. This doesn't follow well as ion balance (e.g. difference between number of charge equivalent anions and cations) doesn't require extraction.

Response: Thank you for your correction, here we want to express that the simple ion balance cannot predict the hydronium ion concentration in the aerosol liquid water accurately. In the revised manuscript, this statement has been reworded. (**Page 3, line 53-55, in the revised manuscript**)

3. Line 95: may want to indicate models "often" assume internal mixtures (but that is not a requirement).

Response: The sentences about this assumption were deleted in the revised manuscript.

4. Line 98-99: For this statement indicating nitrate is mainly in the fine mode, does that need to be qualified by indicating a location or time of year? Does fine mode nitrate generally exceed coarse nitrate?

Response: Thank you for your question. This statement about nitrate is mainly aimed at the aerosol composition in China. Many studies in China showed that the fine mode nitrate generally exceeds

coarse nitrate except for the dust days. In Beijing, the fine mode (≤2.5 μm) nitrate concentration at different polluted level was 3~5 times higher than that in coarse mode (2.5~10 μm) (Meier et al., 2009; Tian et al., 2014; Sun et al., 2014), and the same size distribution was found in southern cities of China on non-dust days (Pan et al., 2009; Wang et al., 2015; Ding et al., 2017). However, in dust days, the PM_{10} concentration was much higher than that of $PM_{2.5}$, resulting in the elevated nitrates in coarse mode (Pan et al., 2009; Wang et al., 2015). In the revised manuscript, the statement was qualified. (**Page 5, line 91-92, in the revised manuscript**)

5. Near line 155 and Figure 1: Spring shows a fairly persistent difference in the concentration of PM10 vs PM2.5. Two dust episodes are mentioned. With the exception of these two episodes, do you have a sense of what is contributing to the PM10-PM2.5 material? Late September also indicates an episode in which PM10 is elevated compared to PM2.5.

Response: The $PM_{2.5\text{-}10}$ was generally was regarded as coarse particles. On clean days, the crustal materials could account for more than 30% of the total $PM_{2.5–10}$. During the dust events, crustal materials could account for more than 60% of the coarse particles (Xu, 2010). However, during the severe haze events, SO_4^{2-}, NO_3^-, NH_4^+, OM, and EC also substantially accumulated in the coarse mode (Pan et al., 2009; Tian et al., 2014).

6. Line 190 indicates water uptake onto hydrophilic organics can be ignored unless the fraction of particle water due to organics is near 1 (100%). Water due to uptake on organics is presumably important even when it is not the sole contributor to particulate water. The threshold of 1 should be removed and perhaps a statement about the potential error incurred by ignoring ALWCo should be added.

Response: Thank you for your good suggestion. Surely part of organic species in particles such as water-soluble secondary organic carbon is hygroscopic, especially in ultrafine particles. In the revised manuscript, the threshold of 1 has been removed and a statement about the potential error incurred by ignoring ALWCo has been added as below. (**Page 8, line 180-182, in the revised manuscript**)

7. Text on lines 235-238 seems misplaced or unnecessary.

Response: This paragraph has been deleted in the revised manuscript.

8. Line 277 highlights sulfate as a driving factor for pH. Sulfate peaked at night during the winter (Figure 4) when photochemical activity is lower. To what degree is the diurnal variation in sulfate driven by chemistry vs meteorology (e.g. planetary boundary layer depth)?

Response: The diurnal variation in sulfate was complex, especially during the severe haze episodes, where the rapid increase in mass concentration was mainly due to the accumulation induced by the unfavorable meteorological condition. Figure R2(a) and R2(b) showed that for most of the time, the mass fraction of SO_4^{2-} in total ions has little variation when SO_4^{2-} mass concentration increased largely, which could be regarded as the contribution of meteorology. However, at some moments in the nighttime (gray shadow in the figure), both mass concentration and mass fraction of SO_4^{2-} showed a significant increase, which mainly attributed to the secondary reaction of SO_2. Overall, the mean SO_4^{2-} fraction in total ions at night in winter was slightly higher than that in daytime (Figure R2(c)), but differences are not statistically significant. Hence the diurnal variation in sulfate was more driven by meteorology.

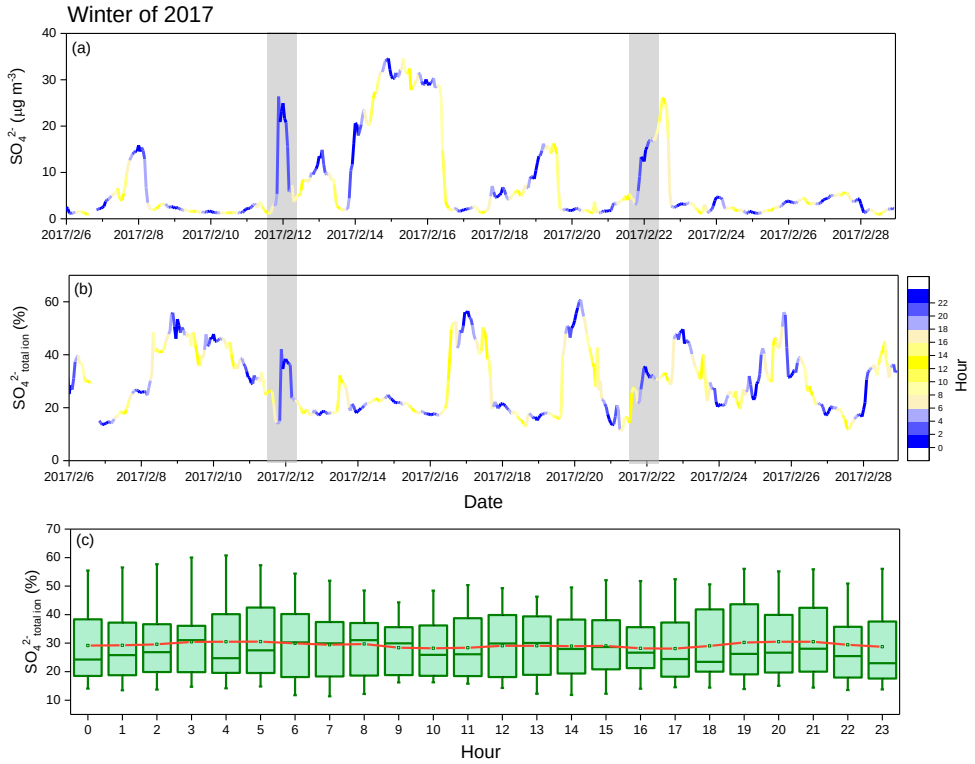

Figure R2. Time series of SO_4^{2-} mass concentration (a) and SO_4^{2-} mass fraction in total ions (b) as well as the diurnal variation of SO_4^{2-} mass fraction in total ions in winter.

9. Line 284: Is the key difference between the US and Beijing more driven by the higher concentrations or the greater variability in concentrations?

Response: Thank you for your question. According to the record of literature (Guo et al., 2015), H_{air}^+ diurnal variation was less significant while the ALWC diurnal variation was significant, hence the diurnal pattern in pH was mainly driven by particle water dilution. However, in this work, we find that both H_{air}^+ and ALWC had significant diurnal variation, and the aerosol acidity variation agreed with well with sulfate. In the North China Plain, the $PM_{2.5}$ mass concentration has a wide variation range and the average value was high. For example, in winter, the $PM_{2.5}$ mass concentration in Beijing was several to dozens times higher than that in the US, which means there are more seeds in the limited water vapor, hence the dilution of aerosol liquid water to H_{air}^+ doesn't work at all, the diurnal variation of aerosol components was more important. Therefore, we think both the higher concentrations and the greater variability in concentrations have important effects on the difference between the US and Beijing. (**Page 13-14, line 348-355, in the revised manuscript**)

10. Line 384:386 represents a simplified description of ammonia partitioning in which ammonia acts first to neutralize sulfate and then any leftover ammonia can react with nitrate to make ammonium nitrate. Perhaps the authors do not mean this so simply. Reword to reflect the semivolatile nature of ammonia and nitrate.

Response: The statements here indeed have some problems. In the revised manuscript, we try to give the impact of NH_4^T on aerosol pH with another explanation. Elevated NH_4^T could reduce H_{air}^+ exponentially and slightly increase ALWC when the other input parameters were held constant, leading to the decrease of aerosol pH. As the NH_4^T increases, H_{air}^+ are consumed swiftly during the dissolution of NH_3 as well as the further reaction with SO_4^{2-}, NO_3^-, and Cl^-. And the elevated NH_4^T increases the $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$ when NO_3^T and Cl^T were fixed (Figure 10), which means the elevated NH_4^T alter the gas-particle partition and shifts more NO_3^T and Cl^T into particle phase, and the deliquescence of additional nitrate and chloride increased ALWC slightly. (**Page 17, line 447-453, in the revised manuscript**)

11. Line 388: Do the authors mean that aerosol would be fully neutralized except for the fact that ammonia is taken up into clouds and precipitation? Reword to reflect the buffering nature of ammonia.

Response: We afraid that the reviewer misunderstood what we meant. Here we want to deliver that although the ammonia in the atmosphere is excessive, the other conditions are limited, the ALWC is one of them. Compared to the liquid water content in clouds and precipitation, ALWC is much lower, hence the dilution of aerosol liquid water to H_{air}^{+} is much weaker. In the revised manuscript, we reword Line 376-388 to more clearly express our point. (**Page 17, line 462-465, in the revised manuscript**)

12. Caption to table 2: This table appears to be the sensitivity of acidity, ALWC, and H+air to chemical components (not the other way around). Please clarify caption.

Response: Thanks for your careful check, the caption to Table 2 (Table 3 in the revised manuscript) has been clarified as below:

Table 3 Sensitivity of ALWC, H_{air}^{+}, and $PM_{2.5}$ pH to SO_4^{2-}, NH_4^T, NO_3^T, Cl^T, Ca^{2+}, RH, and T. The larger magnitude of the relative standard deviation (RSD) represents the larger impact derived from the variation of variables. (**Page 29, line 776-778, in the revised manuscript**)

13. Figure 3: use a common color scale for all panels.

Response: Color scale in figures has been unified.

14. Figure 5, 6, 7, caption. These figures appear to be the sensitivity of ALWC, H+air, and pH to chemical components. Reword caption.

Response: Thanks for your careful check, captions to Figure 5, 6, 7 (7-9 in the revised manuscript) have been clarified as below: (**Page 33, line 818-823, in the revised manuscript**)

Figure 7. Sensitivities of H_{air}^{+} to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, as well as meteorological parameters (RH, T) in summer and winter.

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

Figure 9. Sensitivities of aerosol pH to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, as well as meteorological parameters

(RH, T) in summer and winter.

15. Line 136: Have you looked at trends from 2013, 2015, and 2017 datasets you have collected?

Response: In this work, the water-soluble ions of $PM_{2.5}$ samples and MOUDI samples were not collected synchronously. Water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) of $PM_{2.5}$ and trace gases (HCl, HNO_3, HNO_2, SO_2, NH_3) in the ambient air were measured by an online analyzer (MARGA) at 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). While the 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. Compared to the real-time $PM_{2.5}$ sampling, MOUDI sampling time is short, which is not conducive to analyze the variation tendency of aerosol composition and acidity in time. MOUDI samples were mainly used to analyze the change of aerosol composition and acidity in different particle size.

16. Additional improvements in terms of editing would be useful.

Response: The English in the manuscript has been improved by an English native speaker.

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Aerosol pH and its influencing factors in Beijing

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Abstract

~~Acidity (pH) plays a key role in the physical and chemical behavior of aerosol and cannot be measured directly. In this work, aerosol liquid water content (ALWC) and size-resolved pH are predicted by thermodynamic model (ISORROPIA-II) in 2017 of Beijing. The mean aerosol pH over four seasons is 4.3±1.6 (spring), 4.5±1.1 (winter), 3.9±1.3 (summer), 4.1±1.0 (autumn), respectively, showing the moderate aerosol acidity. The aerosol pH in fine mode is in the range of 1.8 ~ 3.9, 2.4 ~ 6.3 and 3.5 ~ 6.5 for summer, autumn and winter, respectively. And coarse particles are generally neutral or alkaline. Diurnal variation of aerosol pH follows both aerosol components (especially the sulfate) and ALWC. For spring, summer and autumn, the averaged nighttime pH is 0.3~0.4 unit higher than that on daytime. Whereas in winter, the aerosol pH is relatively low at night and higher at sunset. SO_4^{2-} and RH are two crucial factors affecting aerosol pH. For spring, winter and autumn, the effect of SO_4^{2-} on aerosol pH is greater than RH, and it is comparable with RH in summer. The aerosol pH decreases with elevated SO_4^{2-} concentration. As the NO_3^- concentration increases, the aerosol pH firstly increases and then decreases. Sulfate-dominant aerosols are more acidic with pH lower than 4, whereas nitrate-dominated aerosols are weak in acidity with pH ranges 3~5. In recent years, the dominance of NO_3^- in inorganic ions may be another reason responsible for the moderately acidic aerosol. ALWC has a different effect on aerosol pH in different seasons. In winter, the increasing RH could reduce the aerosol pH whereas it shows a totally reverse tendency in summer, and the elevated RH has little effect on aerosol pH in spring and autumn when the RH is between 30% and 80%. The dilution effect of ALWC on H_{air}^+ is only obvious in summer. The elevated NH_3 and NH_4^+ could reduce aerosol acidity by decreasing H_{air}^+ concentration exponentially.~~

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.

Key words: Aerosol pH, ~~Size distribution, Influening~~ISORROPIA-II, Influencing factors, Beijing~~.~~

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 acidity has a significant effect on the aerosol secondary formation through the gas-aerosol partitioning of semi-volatile and volatile ~~specials~~species (Pathak et al., 2011a; Guo et al., 2016). Recent studies have shown that aerosol acidity could promote the generation of secondary organic aerosol by affecting the aerosol acid-catalyzed reactions (Rengarajan et al., 2011~~;).~~). Moreover, metals can become soluble by acid dissociation under lower aerosol pH ~~conditions~~ (Shi et al., 2011; Meskhidze et al., 2003) or by forming a ligand with~~–~~ organic species, such as oxalate at higher pH (Schwertmann et al., 1991). In addition, higher aerosol acidity ~~could~~can lower the acidification buffer capacity and ~~affect~~affects the formation of acid rain. The investigation ~~in~~of aerosol acidity is conducive to better understand 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 (Peng, 2001; Wang et al., 2017). The deliquescence relative humidity (DRH) for the mixed-salt is lower than that of any ~~one~~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 ~~usually~~frequently estimated by the charge balance of measurable cations and anions. A net negative balance correlated with an acidic aerosol and vice versa (Zhang et al., 2007; Pathak et al., 2011b; Zhao et al., 2017). Generally, a larger value of the ion balance implies a stronger acidity or stronger alkaline. Nevertheless, an ion balance or other similar proxies fail to represent the true aerosol pH because ~~the aerosol acidity estimated by this way is measured through the aerosol water extract, which poorly predicts the concentration of hydronium ion in the aerosol liquid water (Guo et al., they2015; Hennigan et al., 2015). Moreover, due to the large amounts of water is used for extraction, the results~~ cannot ~~reflect the characteristics of the in-situ aerosol acidity, and it cannot be applied to study the influence of aerosol acidity on gas-particle conversion. In-situ aerosol acidity, defined as the free~~predict H^+ concentration in the liquid phase accurately (Guo et al., 2015; Hennigan et al., 2015~~of a particle, is an important parameter that actually affects the chemical behavior of the particle,~~), which could be calculated by

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 (Guo et al., 2015; Bian et al. 2014; Engelhart et al. 2011). Under this assumption, ALWC could be calculated by the size-resolved 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. 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, ~~could~~can be measured by a H-TDMA (Hygroscopic Tandem Differential Mobility Analyzer) (Liu et al., 1978; Swietlicki et al., 2008; Liu et al., 2011). ~~And the~~The f(RH) ~~could~~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 ~~could~~can output both ALWC and ~~concentration of the hydronium ion in air (moles H^+ per volume of air, denoted hereafter as~~ 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 ~~most~~ 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 found among these methods, the H_{air}^+ could only be obtained by the thermodynamic models, which ~~have~~had been applied to predict aerosol acidity in many studies (Nowak et al., 2006; Fountoukis et al., 2009; Weber et al., 2016; Fang et al., 2017).

~~When calculating aerosol acidity with thermodynamic models, the aerosol is assumed internally mixed and the bulk properties of aerosol are used, without considering variability of chemical compositions with particle size. However, the size-resolved~~The characteristics of aerosol chemical components are ~~obviously~~ different~~.~~ among multiple size ranges. Among inorganic ions, SO_4^{2-}, NO_3^-, Cl^-, K^+, NH_4^+ ~~are~~ mainly ~~concentrated~~concentrate in fine mode~~,~~ except for the dust days (Meier 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). The aerosol acidity is affected by coupling among many variables. Therefore, it could be expected that the aerosol pH is ~~the result of the balance between the soluble acidic (SO_4^{2-}, NO_3^-, Cl^- and some soluble organic acids) and alkaline (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) component in the aerosol.~~ also diverse under different particle size. The gas precursor (NH_3, HNO_3, and HCl ~~for~~) 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 ~~PM~~particle matter concentration is very low, the pH diurnal variation was mainly driven by meteorological conditions (Guo et al., 2015, 2016; Bougiatioti et al., 2016). In China, however, the annual average $PM_{2.5}$ concentration in some ~~mega cities~~megacities was ~2 times higher than the national standard value (35 μg m^{-3}) and the inorganic ions ~~account~~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. Nevertheless, only a few studies have focused on aerosol pH ~~at~~in this region. ~~Cheng et al. (2016) estimated the averaged pH by ISORROPIA-II, and Wang et al. (2016) derived the particle pH by using a molar ratio approach in Beijing, their results show~~Some studies conducted in NCP showed that the aerosol acidity was close to neutral~~. However, Liu et al. (2017) and Shi et al. (2017) found that~~, while in

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some other studies the fine particles ~~in the North China Plain were~~showed moderately acidic ~~based on the hourly measured particulate water-soluble ions and precursor gases along with ISORROPIA-II, with an average pH of 4.2 in winter of Beijing and 4.9 in Tianjin.~~(Cheng et al., 2016; Wang et al., 2016; Liu et al., 2017; Shi et al., 2017). These results ~~are~~were all significantly higher than that in the United States or Europe, where aerosols ~~are~~were 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 North China Plain~~NCP mainly ~~result~~resulted from the different ~~calculated~~ methods (ion balance & thermodynamic equilibrium models~~). Several studies have shown that the ion balance and reverse-mode calculations of thermodynamic equilibrium models are~~) or different data sets. ~~not applicable to interpret the aerosol acidity (Hennigan et al., 2015; Liu et al. 2017; Song et al., 2018).~~ Moreover, the ~~change~~variation of ~~the~~$PM_{2.5}$ chemical composition ~~of $PM_{2.5}$~~ in ~~the North China Plain~~NCP in recent years also contributed to the differences in aerosol pH. The observations in previous studies exploring aerosol acidity in ~~the North China Plain~~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., 2017; Huang et al., 2017; Ma et al., 2017). Moreover, studies about seasonal variation of aerosol pH and size-resolved aerosol pH are rare in ~~the North China Plain~~NCP, and the key factors affecting aerosol acidity are still not well understood.

In this work, thermodynamic model ISORROPIA-II with the forward mode ~~is~~was utilized to predict ALWC and aerosol pH in Beijing. The hourly measured $PM_{2.5}$ inorganic ions and precursor gases in four seasons during 2016 to 2017 ~~are~~were used to analyze the seasonal and diurnal variation of aerosol acidity, and the sensitivity analysis ~~is~~was conducted to identify the key factors that affecting the aerosol pH. In our previous studies, the multi-stage cascade impactors (MOUDI-122) were used for size-resolved aerosol sampling ~~during~~from 2013 to 2015. The actual relative humidity inside the impactors was calculated, and the size ~~distribution~~distributions of water-soluble ions, organic carbon, and elemental carbon in three seasons were discussed (Zhao et al., 2017; Su et al., 2018). Based on these size-resolved results, the pH for aerosol in different size ranges could also be ~~modeled, which can help to evaluate whether it is appropriate to calculate the overall pH of $PM_{2.5}$ ignoring the differences in particle size~~predicted.

2. Data Collection and Methods

2.1 Site

The measurements were performed at the Institute of Urban Meteorology in Haidian district of Beijing (39°56'N, 116°17'E). The sampling site was located next to a high-density residential area, without significant air pollution emissions around the site. Therefore, the observation 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 $PM_{2.5}$ and trace gases (HCl, HNO_3, HNO_2, SO_2, and NH_3) in the ambient air were measured by an online analyzer (MARGA) at 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 details about MARGA can be found at ten Brink et al. (2007). The $PM_{2.5}$ and PM_{10} mass concentrations (TEOM 1405DF), the hourly ambient temperature and relative humidity were also synchronously attained.

Hourly concentrations of $PM_{2.5}$, PM_{10}, and water-soluble ions in $PM_{2.5}$, as well as meteorological parameters during the observation, are shown in Figure 1. In the spring, two dust events occurred (21-22, April and 5-6, May). During the first dust ~~event~~events, the wind came predominantly from the north with mean wind speed 3.5 m s^{-1}. ~~And the~~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 ~~was~~ resulted from the strong wind ~~come~~coming from the northwest direction. In the following pH analysis based on MARGA data, it ~~is~~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, these two dust events were excluded from this analysis.

Figure 1

2.3 size-resolved chemical compositions

A 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 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 for filter changing and nozzle plate washing with ethanol. The water-soluble ions were analyzed from the samples by using an ion chromatography (DIONEX ICS-1000). The 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).~~2018). It should be noted that there was no observation of gas precursors during the periods of MOUDI sampling.

2.4 Aerosol pH prediction

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

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

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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 H_{air}^+ (μg m^{-3}) divided by the concentration of ALWC associated with inorganic species, $ALWC_i$ (μg m^{-3}). Both inorganic and part of organic species in particles are hygroscopic. However, the pH prediction is not highly sensitive to the water uptake by organic species ($ALWC_o$~~), unless the $ALWC_o$ mass fraction to the total particle water is close to 1~~) (Guo et al., 2015, 2016). ~~And~~The similar result was also found in Beijing in Liu et al. (2017). Hence the aerosol pH could be fairly predicted by ISORROPIA-II with just measurements of inorganic species in most cases. However, it should be noted that the potential error could be incurred by ignoring $ALWC_o$ in regions where hygroscopic organic species has a relatively high contribution to fine particles.

In ISORROPIA-II, forward and reverse mode are provided to predict ALWC and H_{air}^+. In forward mode, ~~known quantities are~~ 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 mode calculates the equilibrium partitioning given the ~~concentration~~concentrations of only aerosol ~~composition~~compositions together with RH and T as input. In this work, the online ion chromatography MARGA was used to measure both inorganic ions of $PM_{2.5}$ and precursor gases. 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)~~, hence ISORROPIA-II was run in the "forward mode" for aerosols in metastable condition. Moreover, the forward mode was~~ The forward mode was also reported 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 in this study.

When using ISORROPIA-II to calculate the $PM_{2.5}$ acidity, all particles were assumed internally mixed and the bulk properties were used, without considering the variability of chemical compositions with particle size. In the ambient atmosphere, the aerosol chemical composition is complicated, hence the deliquescent relative humidity of aerosol 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 low RH, the state of particles may change. Figure 2 and Figure S1-S4 exhibit the comparisons between 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 are all colored by the corresponding RH. It can be seen that agreements between predicted and measured NH_3, NH_4^+, NO_3^-, and Cl^- are pretty well, the R^2 of linear regressions are all higher than 0.94, and the slopes are around 1. Moreover, the agreement between predicted and measured $\varepsilon(NH_4^+)$ is better when compared with $\varepsilon(NO_3^-)$ and $\varepsilon(Cl^-)$. The slope of linear regression between predicted and measured $\varepsilon(NH_4^+)$ was 0.93, 0.91, 0.95, and 0.96 and the R^2 is 0.87, 0.93, 0.89, and 0.97 in spring, winter, summer, and autumn, respectively. However, measured and predicted partitioning of HNO_3 and HCl show significant discrepancies (R^2 of 0.28 and 0.18), which may attribute to the much lower gas

concentrations compared with the particle concentrations, as well as the gas denuder measurement uncertainties from particle collection artifacts (Guo et al., 2018). Obviously, more scatter points deviate from the 1:1 line when ISORROPIA-II runs at RH≤30%, which is much evident in winter and spring. For data with RH ≤ 30%, the predictions are significantly improved when assuming aerosol in stable mode (solid + liquid) (Figure S5-S6). However, the aerosol liquid water was almost zero and cannot be used to predict aerosol pH. It 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 the $PM_{2.5}$ pH for data with RH higher than 30% in this work.

Figure 2

Running ISORROPIA-II in the forward mode with only aerosol 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 ~~$NH_{3(g)}$~~gas phase was available for the size-resolved pH prediction. We determined aerosol pH ~~in the fine mode~~ through an iteration procedure that used the measured particulate species and ISORROPIA-II to predict gas species, the detailed information could be found in Fang et al. (2017) and Guo et al. (~~2017~~2016). As ~~for coarse mode particles, equilibrium is not considered between the gas and particles~~ a brief summary, ~~due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000),~~ the ~~pH was determined by ignoring the gas phase and ISORROPIA-II was run in forward mode with zero gas~~predicted NH_3, HNO_3, and HCl concentrations. ~~—~~ from the *i*-1 run were applied to the *i*th iteration, until the gas concentrations converged. Based on these iterative gas phase concentrations, the ion concentrations from samples collected by the MOUDI as well as the averaged RH and T during each sampling period were used to determine aerosol pH for different size ranges. Just like calculating the pH of $PM_{2.5}$, it was also assumed that all the particles at each size bin were internally mixed and had the same pH.

The comparisons of iterative and predicted NH_3, HNO_3, and HCl as well as measured and predicted NO_3^-, NH_4^+, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ for data from MOUDI samples are showed in Figure 3. The previous study showed that coarse mode particles were very difficult to reach equilibrium with the gaseous precursors due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000~~The accuracy of the aerosol pH prediction is primarily assessed by the reproduction of~~

~~semivolatile components partitioning between gas and particle phases. A comparison between predicted NO_3^-, NH_4^+ and measured values colored by RH is shown in Figure 2. Overall, the model captures the measured NO_3^-, NH_4^+, and the predicted NO_3^-, NH_4^+ are on average within ±20% of the measurements, with R^2>0.9, and best agreement is observed at RH above 60%.~~

). Assuming coarse mode particles in equilibrium with the gas phase could result in a large bias between measured and predicted NO_3^- and NH_4^+ in coarse mode particles (Fang et al, 2017). We also find that in this work, it can be clearly seen that assuming coarse mode particles in equilibrium with the gas phase could overpredict 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 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 coarse mode was determined by ignoring the gas phase.

Figure ~~1~~ 3

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2.5 Sensitivities of aerosol pH to SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, 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 on the aerosol pH. The ALWC, H_{air}^+, aerosol pH, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ 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 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 (total nitrate (gas+aerosol) expressed as equivalent HNO_3), NH_4^T (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^T, and Cl^T on aerosol pH, rather than the impact of a single gas or

aerosol phase of NO_3^T, NH_4^T, and Cl^T 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^T, NH_4^T, Cl^T, Ca^{2+}, RH, and T. When assessing how a variable affects ALWC, H_{air}^+, and aerosol pH, the real-time measured values of this variable and the averaged values of other variables in each season were input ISORROPIA-II. The magnitude of the relative standard deviation (RSD) of calculated aerosol pH can reflect the impact of one variable on the aerosol acidity. The higher the RSD, the greater the impact, vice versa. The average value and variation range for each variable in all four seasons are listed in Table S1 and Figure S7.

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

3. Results and Discussion

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

The averaged $PM_{2.5}$ ~~concentration is~~concentrations were 62±36, 60±69, 39±24, and 59±48 μg m^{-3} ~~in~~for observation periods of spring, winter, summer, and autumn ~~observation~~, respectively. (Table 1). Among all ions measured, NO_3^-, SO_4^{2-}, and NH_4^+ ~~are~~were three dominant species, accounting for 83% ~ 87~~%.~~% of total ions. Compared with other seasons, the averaged concentration of primary inorganic ions (Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) was higher in spring. The aerosol in Beijing showed the moderate acidity with ~~aerosol~~$PM_{2.5}$ pH ~~was~~of 4.30±1.60, 4.5±0.7, 3.8±1.~~1, 3.9±1.3~~2, and 4.~~1±1.3~~±0~~in~~.8 for spring, winter, summer, and autumn observation, respectively. (data at RH ≤30% were excluded). The overall winter ~~aerosol~~$PM_{2.5}$ pH ~~is~~was comparable to the result found in Beijing ~~(~~, 4.2~~, winter)~~ from Liu et al. (2017) and 4.5 from Guo et al. (2017), but lower than that (4.9, winter and spring) in Tianjin (Shi et al., 2017), another mega city about 120 km away from Beijing. The summer ~~aerosol~~$PM_{2.5}$ pH was lowest among all four seasons~~, implying the higher aerosol acidity.~~. The seasonal variation of ~~aerosol~~$PM_{2.5}$ pH in this work was similar to the result from Tan et al. (2018) except for spring, which was 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 ~~2014~~

of Beijing in 2014, the distinction in the aerosol composition may becompositions was probably responsible for the lower aerosol$PM_{2.5}$ pH in their work.

The acid liquid surface has a catalytic effect on the gas-liquid reaction process, and the presence of the oxidant can significantly increase the reaction rate and promote the formation of secondary aerosols (Liu et al., 2012). How the moderate acidity of aerosol in the North China Plain affect the formation of secondary aerosols needs to be further investigated.

Figure 2

Wind dependence of $PM_{2.5}$, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+} concentration and the averaged pH are shown in Figure 3 and Fig. S1. In spring and summer, the high aerosol pH occurs with both NW and SW strong winds (wind speed >3 m s^{-1}) while the low aerosol pH occurs with calm winds (wind speed <2 m s^{-1}) and SW winds with wind speed lower than 3 m s^{-1}. For winter, we surprisingly found that the high aerosol pH is mainly concentrated in the SSW direction, while the aerosol pH in northerly winds is as low as 3~4. In autumn, the aerosol pH accompanied by NW winds is much higher than that accompanied by souther winds. Generally, the northerly winds usually occur with cold front systems and high wind speeds, which could sweep away air pollutants but raise dust in which the crustal species (Ca^{2+}, Mg^{2+}) content are higher.

Haze episodes usually occur with SW and SE winds and calm winds in Beijing, the air pollutants are transported to Beijing from other cities located in SW and SE directions, leading to the accumulation of pollutants. Beijing is surrounded by mountains on three sides, and south Beijing is plain. The industry is mainly concentrated in the south of Beijing, and there are plenty of emission sources in these two major transport pathways from southwest and southeast directions, leading to the higher $PM_{2.5}$ concentration. We find that the aerosol pH is negatively correlated with $PM_{2.5}$ concentration in spring, summer, and autumn whereas it shows the positive relationship in winter. **Table 1**

To further investigate the aerosol$PM_{2.5}$ pH performance under different pollution levellevels over four seasons, the $PM_{2.5}$ concentration isconcentrations 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 daysconditions, respectively. Overall, as the air quality deteriorates, ALWC and H_{air}^+ all increased, but the aerosol acidity performs differently. In spring, summer, and autumn, the pH on The

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relationship between $PM_{2.5}$ and its pH is shown in Figure S8. The $PM_{2.5}$ pH under clean ~~days is~~condition spanned 2~7 while the $PM_{2.5}$ pH under polluted and heavily polluted conditions mostly concentrated in 3~5. Table 1 shows that as the air quality deteriorated, aerosol components, as well as ALWC and H_{air}^+, all increased for 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 $PM_{2.5}$ pH under the clean condition was the highest (Table 1), then followed by polluted ~~days~~ and heavily polluted ~~days~~conditions in spring, summer, and autumn. In winter, however, the averaged pH ~~on~~under polluted ~~days (5.~~condition (4.8±1.0) ~~is~~was the highest, then followed by clean (4.5±0.6) and heavily polluted ~~days~~conditions (4.4±0.9) ~~and clean days (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.~~3±1.1).~~ It can be seen that on clean days, high $PM_{2.5}$ pH (>6) was generally companied by high mass fraction of crustal ions, while the relatively low $PM_{2.5}$ pH (<3) was companied by high mass fraction of SO_4^{2-} and low mass fraction of crustal ion, which was most obvious in summer (large part of $PM_{2.5}$ pH with RH≤30% were excluded in spring and winter). On polluted and heavily polluted days, 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 that drove aerosol acidity. The impact of aerosol compositions on $PM_{2.5}$ pH is discussed in Section 3.4.

Figure ~~3~~4

~~**Table 1**~~

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 spring, summer, and autumn, the $PM_{2.5}$ pH in northern direction were

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generally higher than that in the southwest direction, but the high pH in summer also occurred with southwest strong winds (wind speed >3 m s^{-1}). Generally, the northerly winds usually occur with cold front systems, which could sweep away air pollutants but raised dust in which the crustal ion species (Ca^{2+}, Mg^{2+}) were higher. In winter, the $PM_{2.5}$ pH distributed relatively evenly in each wind direction, but we surprisingly found that the pH in northerly winds is 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 winds.

Figure 5

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

The diurnal ~~variation for~~ variations of NO_3^-, SO_4^{2-}, ALWC ~~is similar over four seasons, but distinctions are found in,~~ H_{air}^+ and ~~pH~~ $PM_{2.5}$ pH are exhibited in Figure 6. The diurnal variations ~~(Figure 4).~~for ALWC, H_{air}^+, and pH was similar over four seasons. Generally, nighttime mean ALWC ~~is~~was higher than daytime and reached a peak at near 04:00 ~ 06:00 (local time). After sunrise, the increasing temperatures resulted in a rapid drop in RH, leading to the obvious loss of particle water, ALWC reached the lowest level in the afternoon. ~~For spring, summer, and autumn, the significant H_{air}^+ peak starting at roughly 12:00 and reaching a maximum between 16:00 and 18:00, the~~H_{air}^+ was highest in the afternoon and then followed by nighttime, and H_{air}^+ was relatively low in the forenoon. The low ALWC and high H_{air}^+ resulted in the minimum pH in the afternoon. The averaged nighttime pH is 0.3~0.4 unit higher than that on daytime ~~for spring, summer, and autumn, respectively. However, for winter, H_{air}^+ in the nighttime is slightly higher than that in the daytime, and the aerosol pH is relatively low at night and higher at sunset.~~ Noted that the diurnal ~~variation~~variations of ~~aerosol~~$PM_{2.5}$ pH ~~is all consistent~~here were for the cases with RH higher than 30%. If the data at RH≤30% were included, the diurnal ~~variation~~variations of H_{air}^+, pH, and SO_4^{2-} ~~over four seasons, it seems that the~~ in winter were changed (Figure S10). H_{air}^+ and SO_4^{2-} ~~is~~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 ~~key factor affecting aerosol~~lower pH at the night.

~~**Figure 4**~~

~~The distinguishing diurnal patterns of aerosol pH over four seasons indicate that aerosol~~

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~~composition is a key factor for the diurnal variation of aerosol pH, which is very different from what Guo et al. (2015) found in the southeastern United States: the pH diurnal variation is largely driven by meteorological conditions due to the dilution of ALWC to H_{air}^+, not aerosol composition. The biggest reason for the discrepancy is that the hygroscopic components in particles such as $(NH_4)_2SO_4$ and NH_4NO_3 in Beijing are much higher than that in the southeastern United States (lower than 5 μg m^{-3}) while the mean RH is lower. Thus the influence of aerosol composition on pH cannot be ignored in Beijing.~~

~~3.3~~ The diurnal variation of NO_3^- in winter and spring agreed well with the aerosol acidity. Nevertheless, in summer and autumn, the agreement was not well. 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 increasing SO_4^{2-} could decrease the pH obviously; at the relatively high ALWC, the 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 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, both H_{air}^+ and ALWC had significant diurnal variations, and the aerosol acidity variation agreed well with sulfate, indicating the aerosol acidity in NCP was both driven by aerosol composition and particle water. For example, in the winter of NCP, the $PM_{2.5}$ mass concentration in Beijing was several to dozens times higher than that in the US, which means there are more seeds in the limited particle water, and the RH was generally low, hence the dilution of 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 $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ at different RH levels. The measured

ε(NH_4^+), ε(NO_3^-), and ε(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 winter and spring, NO_3^T and Cl^T were dominated by particle phases, ε(NO_3^-) and ε(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 ε(NO_3^-) and ε(Cl^-), the ε(NH_4^+) was pretty lower. In spring, summer, and autumn, the average ε(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 ε(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.

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

As mentioned above, the aerosol chemical composition has a non-negligible effect on ~~aerosol~~$PM_{2.5}$ pH. In this work, the effects of ~~aerosol chemical components (NO_3^-, SO_4^{2-}, NH_4^+,~~SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, ~~Ca^{2+}) and precursor gases (NH_3, HNO_3), as well as meteorological parameters (RH, T)~~$^+$, RH, and T on ~~aerosol~~$PM_{2.5}$ pH ~~are~~were performed through a sensitivity analysis over four seasons. ~~When assessing how a factor affects aerosol acidity, ALWC, or H_{air}^+, the real-time measured values of an evaluated factor and the averaged values for other factors in~~

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. The SO_4^{2-}, RH, NO_3^T, and NH_4^T were all important influential factors for H_{air}^+, especially SO_4^{2-}. The SO_4^{2-} and T were two crucial factors affecting the $PM_{2.5}$ pH variation. The $PM_{2.5}$ pH was also sensitive to NH_4^T when it was in a lower range and sensitive to RH only in summer. The relationship between pH and NH_4^T was nonlinear, the impact of NH_4^T on pH weakened as NH_4^T increased. In spring, the crucial factor for the $PM_{2.5}$ pH variation was SO_4^{2-} while it was SO_4^{2-} and NH_4^T in winter. In summer, the most important factor affecting $PM_{2.5}$ pH was RH, then

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followed by NH_4^T and SO_4^{2-}. In autumn, the effect of NH_4^T on $PM_{2.5}$ pH was considerable, SO_4^{2-} and T were also important. Figure 7-9 and S12-S17 show how these factors affecting the ALWC, H_{air}^+, and aerosol acidity over four seasons. The 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^T in four seasons were different from each ~~season are input in ISORROPIA-II. For example, the magnitude of the deviation for calculated aerosol pH can reflect the effect of an evaluated factor on the aerosol acidity. The higher the deviation, the greater the effect, vice versa. Noted~~ 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

Figure 9

RH: RH had a different impact on $PM_{2.5}$ 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 ~~sensitivity analysis in this work only reflects the characteristics~~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 ~~observation period,~~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 procedure of $NO_3^- \rightarrow HNO_3$ or $Cl^- \rightarrow HCl$ 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,

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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 ~~work is needed to determine whether the sensitivity analysis is valid in other environments. And~~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 ~~in this paper only focused on single factor variations, however, in reality, changes in one factor could alter other factors and made it more complicated~~.

Figure 10

~~As show in Table 2, for ALWC, the largest deviation is observed when RH is taken as the evaluated factor, then followed by SO_4^{2-} and NO_3^- (NO_3^- and SO_4^{2-} in autumn), which means that the RH affect ALWC most and SO_4^{2-} and NO_3^- are major hygroscopic components in the aerosol. SO_4^{2-} is the most influential factor for H_{air}^+, and RH, NO_3^-, and NH_3 are also important factors affecting H_{air}^+. Synthetically, SO_4^{2-} and RH are two crucial factors affecting aerosol pH. For spring, winter and autumn, the effect of SO_4^{2-} on aerosol pH is greater than the RH, and it is comparable with RH in summer. Figure 4-6 and S2-S7 show how these factors affecting the aerosol acidity, ALWC and H_{air}^+ in detail over four seasons. The sensitivity analysis for ALWC and H_{air}^+ are similar over four seasons, while the sensitivity analysis of RH on aerosol pH in summer is different from the other three seasons. In this study, the sensitivity analysis in winter and summer are chosen for detailed description since winter is of a lot of concern due to the poor air quality while the photochemical reactions are strongest in summer.~~

~~Table 2~~

~~The positive linear relationships between SO_4^{2-}, NO_3^-, HNO_3 concentration and ALWC as well as negative linear relationship between Ca^{2+} concentration and ALWC are observed in the sensitive analysis. Exponential relationships between RH and ALWC are observed, and the ALWC increased rapidly with increasing RH, especially when the RH higher than 80%. Elevated NH_4^+ and NH_3 concentration could increase ALWC slightly. As for temperature, ALWC decreased with the increasing temperature nonlinearly. High temperature could affect gas-aerosol portioning, shifts the~~

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~~equilibrium from NO_3^- to HNO_3, underpredicted the NO_3^- and NH_4^+ concentration, thus decreasing the ALWC. In addition, the higher temperature could also decrease RH and results in low ALWC in the real atmosphere.~~

~~**Figure 5**~~

~~As mentioned above, SO_4^{2-} and RH are the most important factors on H_{air}^+. An exponential growth of H_{air}^+ with elevated SO_4^{2-}, RH, NO_3^-, and T are found, whereas an exponential decrease of H_{air}^+ with elevated NH_3 and NH_4^+ are found. Though H_{air}^+ concentration decreased linearly with the augment of Ca^{2+} concentration, Ca^{2+} concentration is generally lower than 3 μg m^{-3} and generates a little variation in H_{air}^+ compared to other factors. It should be noted that a "U" shape between NO_3^- and H_{air}^+ are found in spring (Fig.S2), H_{air}^+ drops with the increasing NO_3^- concentration within ~ 20 μg m^{-3} and then starts to grow with the increasing NO_3^- concentration. The addition of NH_3 or NH_4^+ has a much more obvious effect on H_{air}^+ than ALWC. The higher the NH_3 concentration in the atmosphere, the more NH_3 will dissolve in the aerosol liquid water and balance the H_{air}^+ partially. Increasing temperature or RH alone will increase H_{air}^+ when other influencing factors were fixed, which is consistent over four seasons.~~

~~**Figure 6**~~

~~The effects of all these factors on aerosol pH is actually a superposition of the effects on ALWC and H_{air}^+. Synthetically, the effect of chemical components (NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}) and precursor gases (NH_3, HNO_3), as well as meteorological parameters (RH, T) on aerosol pH is shown in Figure 7. The most important influencing factor on aerosol acidity is SO_4^{2-}. The aerosol pH decreases about 2.8 (5 to 2.2), 6.0 (6 to 0), 1.0 (3.8 to 2.8), and 1.1 (4 to 2.9) unit with SO_4^{2-} concentration goes~~**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 ~~is~~was low, the variation of SO_4^{2-} mass concentration could generate dramatic changes in ~~aerosol pH.~~H_{air}^+. In section 3.1, the ~~aerosol pH shows an obvious seasonal variation, the aerosol pH is generally low~~$PM_{2.5}$ pH was lowest in

summer whereas highest in winter, which ~~is~~was consistent with the SO_4^{2-} mass faction in total ions. The SO_4^{2-} mass faction in total ions in summer ~~is~~was highest among four seasons with 32.4%±11.1%, whereas it ~~is~~was lowest in winter with 20.9%±4.4%. ~~Similarly, the low aerosol pH on clean days in winter also relates to the leading position of SO_4^{2-} (Table 1).~~

NO_3^T: The ~~second important factor on aerosol acidity is RH. In the North China Plain, the severe haze episodes usually occur with very high RH at a stable whether condition, resulting in the considerable ALWC. In this work, except for summer, the increasing RH could reduce the aerosol pH significantly when RH lower than ~30%, and then the aerosol pH decreases slowly or keeps almost a constant at ~4 when the RH is between 30~80%, and the aerosol pH starts to increase with the further increasing RH. However, the aerosol pH increases continuously ~1.5 unit (2.5 to 4) when RH goes up from 20% to 96% in summer. The $PM_{2.5}$ concentration is lowest in summer, while the RH is relatively high, the high ALWC tends to dilute H_{air}^+ and increase aerosol pH. The sensitivity analysis suggests that ALWC has a different effect on aerosol pH~~ 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 ~~dilution effect of ALWC on H_{air}^+ is obvious only~~$PM_{2.5}$ pH decreased with increasing NO_3^T concentration, whereas little impact was found in summer~~.~~

(Figure ~~7~~

~~Different from SO_4^{2-}, the effect of NO_3^- on aerosol pH is not always same. In winter, summer~~9). In spring and autumn, the ~~aerosol~~$PM_{2.5}$ pH increases first and then ~~starts to decrease when NO_3^-~~dropped with the increasing NO_3^T concentration ~~is larger than ~30 μg m^{-3}. There seems to be a threshold for the effect of NO_3^- on aerosol acidity. From a mathematical point of view, the~~(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^+ ($\varepsilon(NH_4^+) \approx 1$). 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

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of ALWC to H_{air}^+. H_{air}^+ concentration increased exponentially with elevated ~~NO_3^-~~NO_3^T concentration, especially at higher ~~NO_3^-~~NO_3^T concentrations, whereas the ALWC ~~increase~~increased linearly with elevated ~~NO_3^-~~ concentration. When ~~NO_3^-~~NO_3^T concentration ~~is less than the threshold,~~(Figure S12-S17), hence ALWC ~~plays~~played a dominant role~~, while~~ when the ~~NO_3^-~~NO_3^T concentration ~~is greater than the threshold, the H_{air}^+ has a greater effect and the aerosol acidity begins to increase.~~

~~Moreover,~~was low. With the further increase of NO_3^T, the variation in ~~spring, the aerosol pH increases continuously with the~~H_{air}^+ caused by NO_3^T addition ~~of NO_3^-, which is not consistent with the previous thought that addition of anion could reduce the aerosol pH. Same results are found in Guo et al. (2017): at a constant ALWC, more NO_3^- is measured at higher pH. Based on the measured $NO_3^-/2SO_4^{2-}$ ratio (mole mole^{-1}) of this work, we find that aerosol pH is generally between 3~5 when the aerosol anionic composition is dominated by nitrate ($NO_3^-/2SO_4^{2-}>1$), whereas when $NO_3^-/2SO_4^{2-}<1$, about 86%~~was larger than the variation in ALWC, leading to the decrease of ~~aerosol pH is lower than 4 (Figure 8). In recent years, the average annual concentration of SO_4^{2-}~~$PM_{2.5}$ pH. Besides, the relationship between NO_3^T and $\varepsilon(NH_4^+)$ in ~~Beijing decreased significantly due to the strict emission control measures for industries and power plants, in most cases NO_3^- dominates inorganic ions (Zhao et al., 2017; Huang et al., 2017; Ma et al., 2017), which may be another reason responsible for the moderately acidic aerosol.~~

~~Elevated NH_3 and NH_4^+ could reduce aerosol acidity by~~ the sensitivity analysis showed that decreasing ~~H_{air}^+ concentration exponentially. In this work, NH_3 is rich in spring (21.5±8.7 μg m^{-3}), summer (19.6±6.4 μg m^{-3}) and autumn (16.8±8.0 μg m^{-3}), and poor in winter (4.9±2.8 μg m^{-3}). The ratio of [TA]/2[TS] provides~~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

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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] ~~is~~was much higher than 1 and ~~belongs~~belonged to rich-ammonia (~~Fig. S8). In the poor-ammonia case, there is insufficient~~Figure. S21). Although NH_3 ~~to neutralize the available sulfate, hence the aerosol will be acidic. Whereas~~ in the ~~rich-ammonia case there is excess ammonia, the remaining ammonia after reaction with sulfuric acid will be available to react with nitric acid to produce NH_4NO_3, so that the aerosol phase will be neutralized to a large extent. However, the moderate aerosol acidity suggests that though there is excess ammonia in the atmosphere, due~~NCP was abundant, the $PM_{2.5}$ pH was far from neutral, which might attribute to the limited ALWC ~~compared with~~. Compared to the ~~cloud~~ liquid water content in clouds and precipitation, ~~in most cases~~ALWC was much lower, hence the dilution of aerosol ~~will not be alkaline~~liquid water to H_{air}^+ was weak.

~~Furthermore, elevated Ca^{2+} concentration could increase the aerosol pH and the change of HNO_3 concentration has little effect on pH. Elevated temperature in favor of enhancement the aerosol acidity by reducing ALWC and increasing H_{air}^+.~~

~~**Figure 8**~~

~~**3.4**~~**Cl^T:** Cl^T had a relatively larger impact on the $PM_{2.5}$ pH in winter and spring compared to summer and autumn. Except for winter, the Cl^T 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^T, the

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dilution of ALWC on H_{air}^+ played a dominant role, generating the $PM_{2.5}$ pH increase with elevated Cl^T. However, similar to NO_3^T, higher Cl^T 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 ~~period~~periods, all the samples ~~are~~were also classified into three groups (clean, polluted, heavily polluted) with the same rule described in Section 3.~~2~~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 ~~9~~12 shows the averaged size distributions of PM components and pH on clean, polluted, and heavily polluted ~~days~~conditions in summer, autumn, and winter, respectively. The NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, K^+, OC, and EC ~~were~~ mainly concentrated in the size range with aerodynamic diameters between 0.32~3.1μm, while Mg^{2+} and Ca^{2+} ~~were~~ predominantly distributed in the coarse mode. As shown in Figure ~~9~~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 ~~make~~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 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 912

The aerosol pH for both ~~accumulation~~fine mode and coarse mode in summer ~~were~~was lowest among three seasons, then followed by autumn and winter. The seasonal variation of aerosol pH derived from MOUDI data was consistent with that derived from real-time $PM_{2.5}$ chemical components measurement. In summer, the predominance of sulfate in the fine mode and high ambient temperature resulted in a low pH, ranging between 1.8 and 3.9. ~~The sensitivity analysis of this work shows sulfate plays a key role in predicting pH, its high hygroscopicity leads to the formation of the aqueous drops and provides H_{aq}^+ (Fang et al., 2017).~~ Aerosol pH for fine particles in autumn and winter ~~are~~was in the range of 2.4 ~ 6.3 and 3.5 ~ 6.5, respectively. The difference of aerosol pH between size bins in fine mode was not significant, probably owing to the excessive NH_3 (Guo et al., 2017).

As for coarse particles, the predicted pH ~~is~~was approximately near or even higher than 7 for all of the three seasons in this work~~. It should be noted that assuming~~ , 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 ~~equilibrium with the gas phase generally overestimates acidity (pH<4) (Fang et al., 2017).~~

~~On~~coarse mode decreased significantly when under the heavily polluted ~~days, the aerosol pH in coarse mode showed a marked fall~~condition, especially in autumn and winter. For example, the pH in stage 3 (3.1-6.2 μm) declined from 7.8 ~~on~~under the clean ~~days~~condition to 4.5 ~~on~~under the heavily polluted ~~days~~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 ~~may~~might responsible for this. Moreover, the significant decrease of mass ratios of Ca^{2+} and Mg^{2+} ~~also~~

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~~weakened~~resulted in the ~~alkaline.~~loss of coarse mode buffering capacity.

The size ~~distribution~~distributions of aerosol pH and all analyzed chemical components in the daytime and nighttime are illustrated in Figure ~~10~~S23. For summer and autumn, the pH in the nighttime ~~is~~was higher than that in the daytime. ~~Whereas, in winter, the pH is higher in the daytime.~~ The diurnal variation for aerosol pH based on MOUDI data ~~is~~was consistent with the online data. ~~In the daytime of summer and autumn, the solar radiation is strong and photochemical reaction is active as well as the RH is lower, leading to a lower aerosol pH than nighttime.~~ Whereas in winter, the pH was higher in the daytime. In winter, the averaged RH during the sampling period ~~is 43%,~~was relatively low, leading to a low ALWC, but the SO_4^{2-} and NO_3^- in the nighttime ~~are~~were obviously higher due to the lower boundary layer height. Therefore, H_{air}^+ ~~is~~was more abundant in nighttime while the low ALWC had little effect on pH.

~~**Figure 10**~~

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5. Summary and conclusions

~~Aerosol acidity is important for~~ On the ~~formation~~basis of ~~secondary~~online measurements, the measured and predicted NH_3, NH_4^+, NO_3^-, Cl^-, and $\varepsilon(NH_4^+)$ by using ISORROPIA-II agreed pretty well when RH was higher than 30%. It is not reasonable to assume aerosol ~~and is of many challenges to be measured directly. In~~ 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~~, ISORROPIA-II with forward mode is applied to calculate the H_{air}^+ and ALWC based on the 1-h $PM_{2.5}$ inorganic ions, precursor gases (HCl, HNO_3, NH_3) and RH, T. Moreover, the size distribution of pH is predicted based on the MOUDI samples with the same way, the gas-phase NH_3, HNO_3 and HCl are determined through an iteration procedure. In~~ .

In Beijing, the mean ~~aerosol~~$PM_{2.5}$ pH over four seasons ~~is~~(RH≥30%) was 4.~~3~~0±1.~~6~~0 (spring), 4.5±~~1.1~~0.7(winter), 3.~~9~~8±1.~~3~~2(summer), 4.~~1±1.3±~~0.8 (autumn), respectively, 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, indicating the aerosol acidity~~. The seasonal variation of~~ in NCP was both driven by aerosol ~~pH is closely related to the SO_4^{2-}. Overall, the aerosol is more acidic on hazy days than clean days. The aerosol pH in fine mode is in the range of 1.8 ~ 3.9, 2.4 ~ 6.3 and~~

~~3.5 ~ 6.5 for summer, autumn~~composition and ~~winter, respectively. As for coarse particles, the predicted pH is approximately near or even higher than 7.~~

~~Due to the significantly high level of hygroscopic components in particulate matter in Beijing, pH has a diurnal trend that follows both aerosol components (especially the sulfate) and ALWC. For spring, summer and autumn, the~~particle water. The averaged nighttime pH is 0.3~0.4 unit higher than that on daytime. ~~However, in winter, H_{air}^+ in nighttime is slightly~~ The $PM_{2.5}$ pH in the northerly direction was higher than that in ~~daytime and the aerosol pH is relatively low at night and higher at sunset. This result is very different from that found in southeastern United States: the pH diurnal variation is largely driven by meteorological conditions~~the southwest direction.

A sensitivity analysis ~~is~~was performed in this work to investigate how ~~aerosol components, precursor gases~~SO_4^{2-}, NO_3^T, NH_4^T, Cl^T, Ca^{2+}, RH, and ~~meteorological conditions~~T affect ~~aerosol~~ ALWC, H_{air}^+, and $PM_{2.5}$ acidity. The RH affects ALWC most, then followed by SO_4^{2-} ~~and NO_3^-. For H_{air}^+, SO_4^{2-} is the most~~ or NO_3^-. The SO_4^{2-}, RH, NO_3^T, and NH_4^T, especially SO_4^{2-}, were all important influential ~~factor, and RH, NO_3^-, NH_3 are also important~~ factors ~~affecting~~for H_{air}^+. ~~Synthetically~~As for $PM_{2.5}$ pH, ~~SO_4^{2-}~~SO_4^{2-}, T, NH_4^T, and RH ~~are two~~(only in summer) were crucial factors ~~affecting aerosol pH. For spring,~~.

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 ~~effect of SO_4^{2-}~~RH had little impact on ~~aerosol~~$PM_{2.5}$ pH ~~is greater than RH, and it is~~due to the comparable ~~with RH in summer. The aerosol pH decreases with~~ variations of H_{air}^+ and ALWC. The measured $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ increased with the elevated ~~SO_4^{2-} concentration~~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 ~~aerosol pH in spring and winter. As the NO_3^- concentration increases, the aerosol pH firstly increases and then decrease at a inflection point with 30 μg m^{-3}. In this work, sulfate-dominant aerosols are more acidic with pH lower than 4, whereas nitrate-dominated aerosols are weak in acidity with pH ranges 3~5. In recent years, the SO_4^{2-} concentration of $PM_{2.5}$ in Beijing~~H_{air}^+. The impact of NO_3^- on

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$PM_{2.5}$ 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 $\varepsilon(NH_4^+)$ imply that decreasing NO_3^T could reduce the $\varepsilon(NH_4^+)$ effectively, which helped keep NH_3 in the gas phase. In contrast, the nitrate response to NH_4^T control was highly nonlinear, the decrease of nitrate would happen only when the NH_4^T was greatly reduced.

The size-resolved results showed that the pH of coarse particles was approximately near or even higher 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 ~~due to the strict emission control measures, in most cases NO_3^- dominates inorganic ions, which may be another reason responsible for the moderately acidic aerosol.~~ , 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.

~~ALWC has a different effect on aerosol pH in different seasons. In winter, the increasing RH could reduce the aerosol pH whereas it shows a totally reverse tendency in summer, and the elevated RH has little effect on aerosol pH in spring and autumn when the RH is between 30% and 80%. The sensitivity analysis of this work highlights the diverse influence of ALWC on aerosol pH, the dilution effect of ALWC on H_{air}^+ is only obvious in summer. The elevated NH_3 and NH_4^+ could reduce aerosol acidity by decreasing H_{air}^+ concentration exponentially. In the North China Plain, the~~

~~ammonia is rich, the remaining ammonia after reaction with sulfuric acid will be available to react with nitric acid to produce NH_4NO_3, so that the aerosol phase will be neutralized to a large extent. However, the moderate aerosol acidity suggests that though there are excess ammonia in the atmosphere, in most cases the aerosol will not be alkaline due to the limited ALWC.~~

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 the chemical compositions from 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. ~~The averaged $PM_{2.5}$ and~~ Average mass concentrations of NO_3^-, SO_4^{2-}, NH_4^+ ~~mass concentration~~ and $PM_{2.5}$ as well as RH, ALWC, H_{air}^+, and $PM_{2.5}$ pH ~~on~~under clean, polluted, and heavily polluted ~~days~~conditions over four seasons.

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

Table 3. Sensitivity of ~~aerosol chemical components (NO_3^-,~~ ALWC, H_{air}^+, and $PM_{2.5}$ pH to SO_4^{2-}, ~~NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3) and meteorological parameters (RH,~~ NH_4^T, NO_3^T, Cl^T, Ca^{2+}, RH, and T~~) to aerosol acidity, ALWC and H_{air}^+~~. The larger magnitude of the relative standard deviation (RSD) represents the larger impact derived from the variation of variables.

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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}	
AveragedAverage	62±36	14.9±14.6	9.7±7.9	7.9±7.3	17±3023±35	4.7E6.8E-06±9.5E-062.8E-05	4.30±1.60
Clean	44±17	7.9±6.6	6.2±3.7	4.8±3.2	10±2114±26	3.5E2E-06±8.4E5.1E-06	4.5±1.9±1.1
Polluted	100±21	30.8±14.3	16.4±5.9	15.4±5.8	28±3433±36	5.6E1E-06±7.4E4.3E-06	3.9±0.75
Heavily polluted	169±12	45.3±8.5	36.3±4.9	29.4±2.3	7778±60	1.9E2.0E-05±6.1E5E-06	3.6±0.3
winterWinter	PM2.5	NO3−	SO4²−	NH4+	ALWC*	Hair+*	pH*
AveragedAverage	60±69	13.7±21.0	7.3±8.7	7.3±10.0	17±3735±46	9.0E-06±12.2E-05±2.3E-04	4.5±1.10.7
Clean	22±20	3.6±3.9	2.8±1.8	2.2±2.0	4±1110±16	2.6E-07±43.2E-07±4.8E-07	4.3±1.15±0.6
Polluted	107±21	18.9±8.6	11.0±5.7	11.0±4.7	31±4241±45	1.2E-05±6.9E-05±9.1E-05	5.34.8±1.20
Heavily polluted	209±39	59.7±21.8	26.2±6.3	29.1±8.7	77±5180±52	5.2E7.0E-05±3.4E4.7E-04	4.54±0.7
Summer	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+}*	pH*
AveragedAverage	39±24	9.5±9.5	8.6±7.5	7.2±5.6	5150±68	1.6E-05±1.6E8E-05	3.98±1.32
Clean	33±18	7.3±6.8	7.0±6.0	5.9±4.0	4142±61	1.3E4E-05±1.6E-05	3.98±1.32
Polluted	87±13	26.5±10.5	20.7±7.0	17.6±4.8	102±85100±88	3.1E-05±1.7E-062.0E-05	3.5±0.4
Autumn	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+}*	pH*
AveragedAverage	59±48	18.5±19.5	6.5±5.9	8.2±8.2	91±145109±160	8.1E-06±1.1E-05±1.5E-05	4.1±1.3±0.8

Clean	33±21	7.6±7.4	4.4±4.1	3.8±3.5	37±7249±83	5.1E3.8E-06±9.4E6.6E-06	4.25±1.20
Polluted	105±21	33.8±11.6	14.3±6.3	16.0±4.6	182±172225±189	1.8E7E-05±1.3E2E-05	3.94.1±0.43
Heavily polluted	174±18	63.4±15.4	25.0±15.9	29.0±5.1	315±212317±236	3.6E2.2E-05±2.6E1.0E-05	3.94.1±0.32

* For data with RH>30%.

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Table 2

	RH	T, ℃	ε(NH_4^+)	ε(NO_3^-)	ε(Cl^-)
Spring	≤ 30 %	24.8 ± 3.7	0.17±0.14	0.84±0.12	0.67±0.24
	30~60 %	20.6 ± 3.8	0.25±0.14	0.91±0.06	0.82±0.16
	>60 %	15.8 ± 2.7	0.28±0.12	0.96±0.03	0.96±0.06
Winter	≤ 30 %	5.4 ± 5.3	0.31±0.13	0.78±0.12	0.89±0.14
	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	≤ 30 %	35.6± 0.4	0.06±0.02	0.35±0.20	0.39±0.17
	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	≤ 30 %	21.7± 7.5	0.07±0.06	0.49±0.25	0.45±0.21
	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

Impact Factor		SO_4^{2-}	NO_3^T	NH_4^T	Cl^T	Ca^{2+}	RH	T
Spring	RSD-ALWC	50.5%	53.4%	2.9%	7.5%	21.2%	122%	13.1%
	RSD-H_{air}^+	223%	34.4%	26.8%	12.4%	49.8%	115%	49.5%
	RSD-pH	**12.4%**	5.2%	3.9%	2.4%	5.5%	1.3%	7.0%
Winter	RSD-ALWC	33.8%	28.7%	14.2%	30.7%	1.9%	103%	3.5%
	RSD-H_{air}^+	431%	431%	187.4%	52.3%	11.3%	136%	74.1%
	RSD-pH	**28.1%**	8.4%	**27.0%**	3.8%	1.0%	4.1%	6.7%
Summer	RSD-ALWC	49.4%	46.0%	6.9%	3.6%	9.0%	104%	10.8%
	RSD-H_{air}^+	131%	29.9%	78.1%	3.4%	18.1%	44.6%	33.9%
	RSD-pH	**7.9%**	3.6%	**8.1%**	0.8%	1.9%	**8.6%**	5.8%
Autumn	RSD-ALWC	32.8%	58.1%	9.9%	6.9%	3.3%	77.6%	5.5%
	RSD-H_{air}^+	171%	126.7%	333.1%	2.0%	9.3%	106%	59.6%
	RSD-pH	**6.0%**	3.3%	**16.1%**	1.0%	0.8%	2.4%	**7.5%**

Figure captions

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

Figure 2. Comparisons of predicted ~~NO_3^-, NH_4^+ to~~ and measured ~~values based on (a, b) online ion chromatography~~NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ colored by RH. In this Figure, the data ~~and (c, d)~~of four seasons were put together, and the comparisons for each season were 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 by particle size. In this Figure, all MOUDI data~~.~~ were put together.

~~**Figure 3.**~~ **Figure 4.** Time series of mass fraction of NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, and crustal ions (Mg^{2+}, Ca^{2+}) in total ions as well as $PM_{2.5}$ pH in all four seasons.

Figure 5. Wind dependence map of ~~aerosol~~$PM_{2.5}$ pH over four seasons. In each picture, the shaded contour indicates the average of variables for varying wind speeds (radial direction) and wind directions (transverse direction).

Figure ~~4~~6. Diurnal patterns of mass concentrations of NO_3^- and SO_4^{2-} in $PM_{2.5}$, predicted aerosol liquid water content (ALWC~~) (a-d);~~), H_{air}^+ ~~predicted by ISORROPIAII (i-l); predicted aerosol~~$^+$, and $PM_{2.5}$ pH ~~(m-p)~~ over four seasons. Mean and median values are shown, together with 25% and 75 % quantiles. Data with RH≤30% were excluded, the shadow represents the time period when the RH lower than 30% mostly occurred.

Figure ~~5~~7. Sensitivities of ~~chemical components (NO_3^-, H_{air}^+ to~~ SO_4^{2-}, NO_3^T, ~~NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3)~~$_4^T$, and Cl^T, as well as meteorological parameters (RH, T) ~~to ALWC~~ in summer and winter.

Figure ~~6~~8. Sensitivities of ~~chemical components (NO_3^-,~~ ALWC to SO_4^{2-}, NO_3^T, ~~NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3)~~$_4^T$, and Cl^T, as well as meteorological parameters (RH, T) ~~to H_{air}^+~~ in summer and winter.

Figure ~~7~~9. Sensitivities of ~~chemical components (NO_3^-,~~$PM_{2.5}$ pH to SO_4^{2-}, NO_3^T, ~~NH_4^+, Ca^{2+}), precursor gases (NH_3, HNO_3)~~$_4^T$, and Cl^T, as well as meteorological parameters (RH, T) ~~to pH~~ in

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summer and winter.

~~**Figure 8.** Measured $NO_3^-/2SO_4^{2-}$ ratio (mole $mole^{-1}$) versus predicted pH colored by ambient RH. NO_3^-, SO_4^{2-} dominant zone denotes $NO_3^-/2SO_4^{2-}$ > 1 or < 1.~~

~~**Figure 9.**~~ **Figure 10.** Sensitivities of $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ to NO_3^T, NH_4^T, and Cl^T colored by $PM_{2.5}$ pH in summer and winter.

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 ~~distribution~~distributions of aerosol pH and all analyzed chemical components ~~on~~under clean (a, d, g), polluted (b, e, h~~)~~), and heavily polluted ~~days~~conditions (c, f, i) in summer, autumn, and winter.

~~**Figure 10.** The size distribution of pH and all analyzed chemical components in the daytime (a, c, e) and (b, d, f) nighttime in summer, autumn and winter.~~

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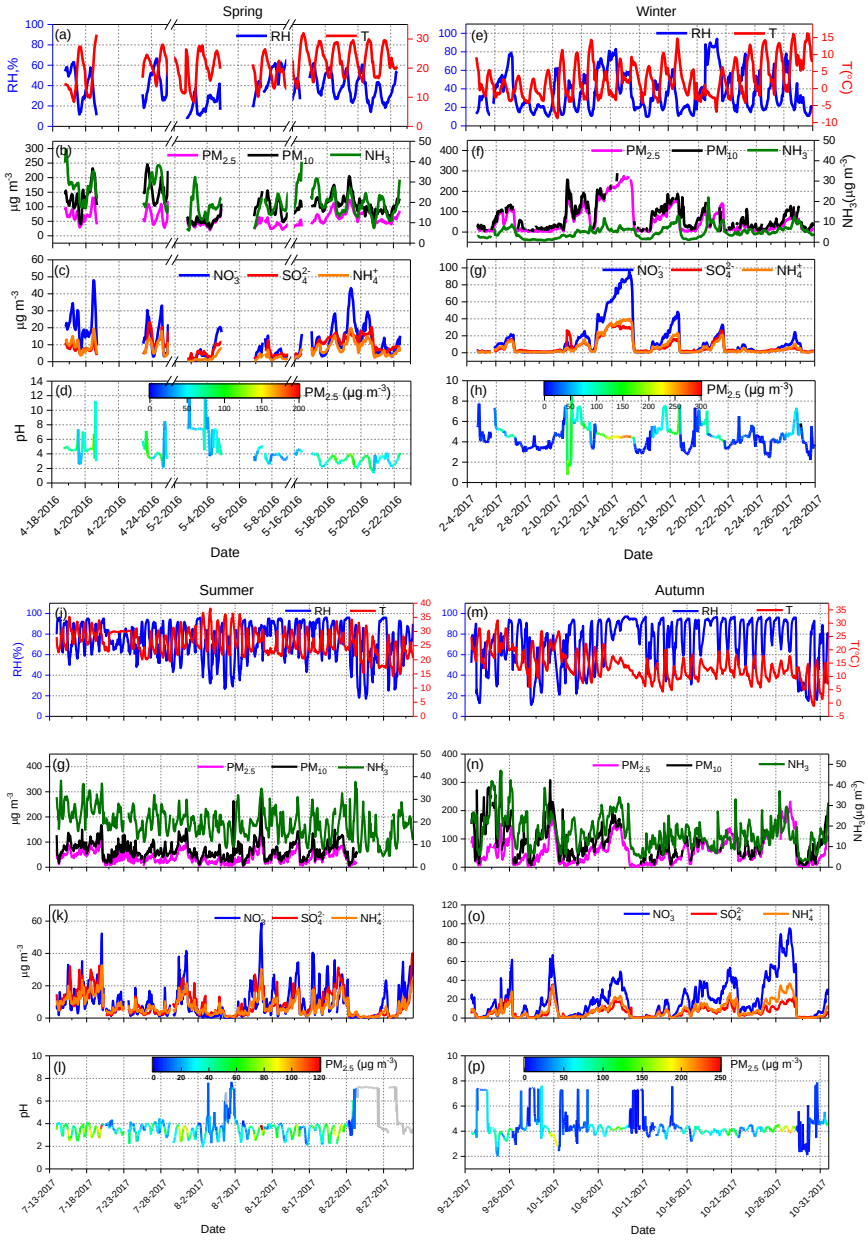

Figure 1.

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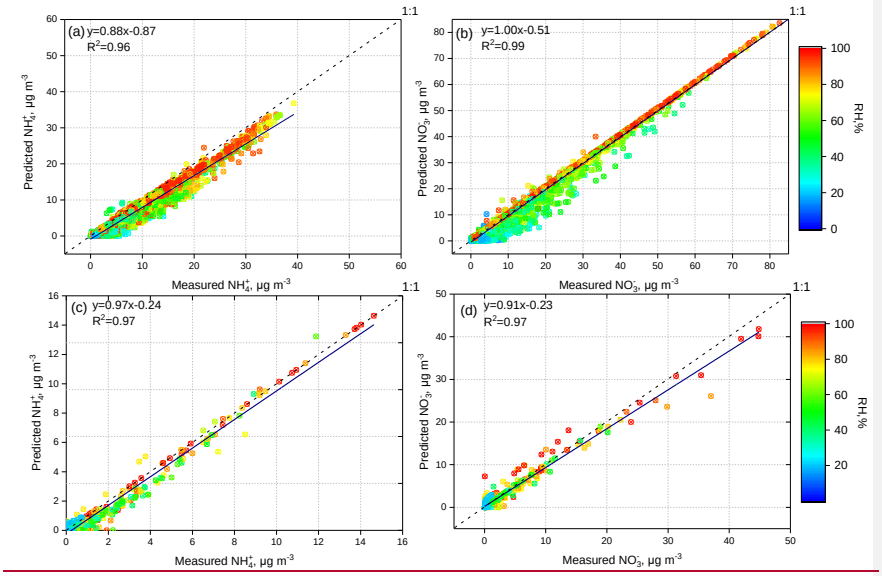

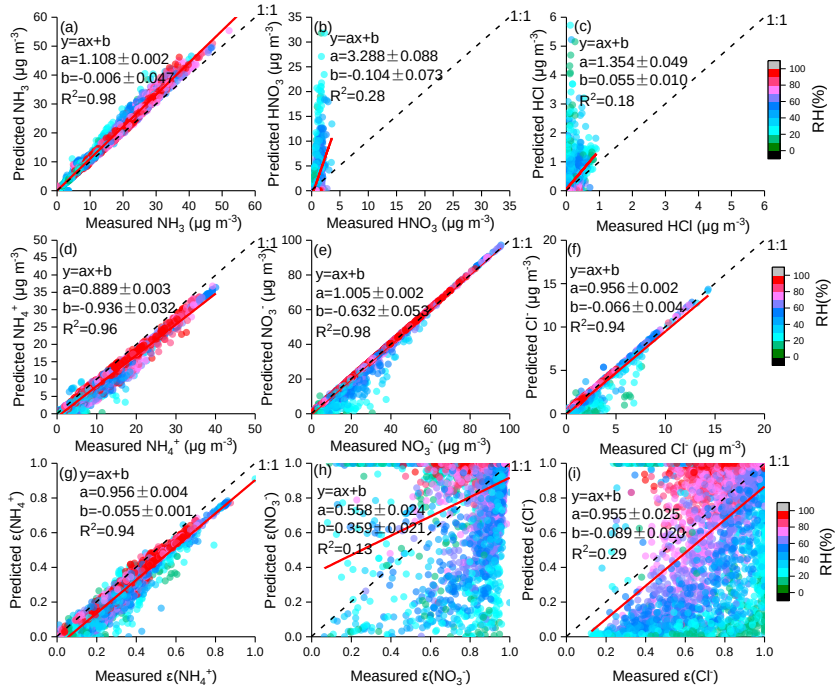

Figure 2.

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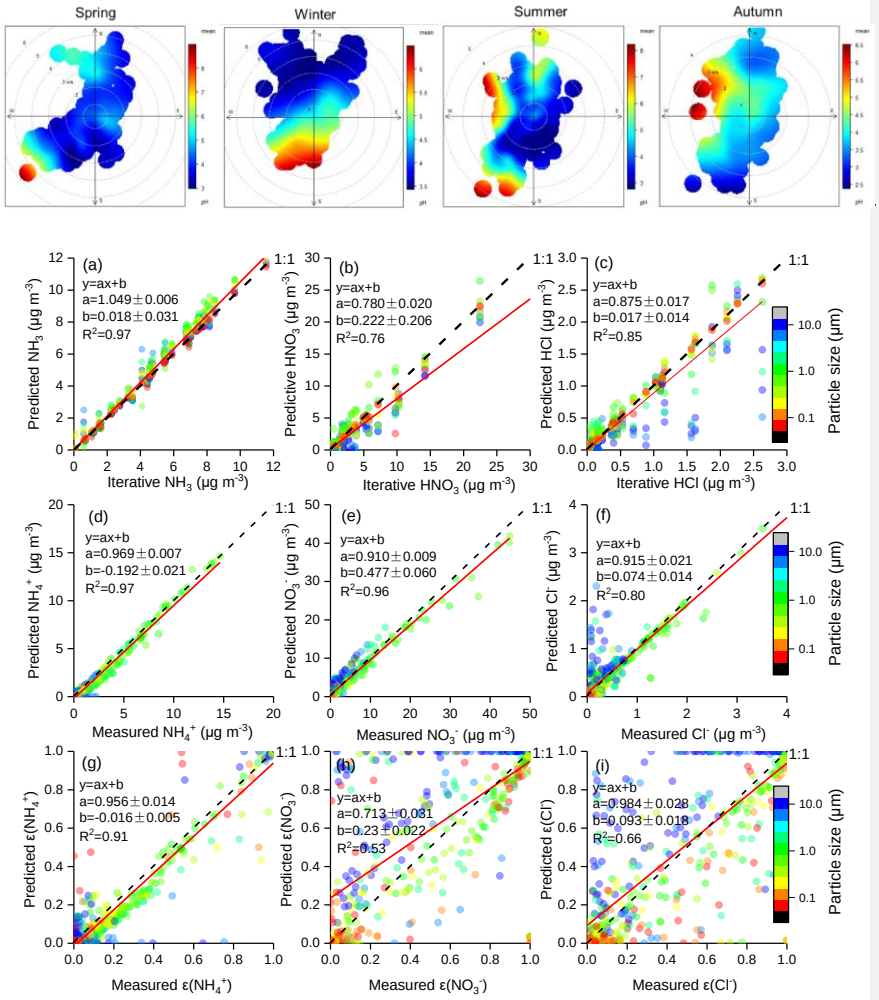

Figure 3.

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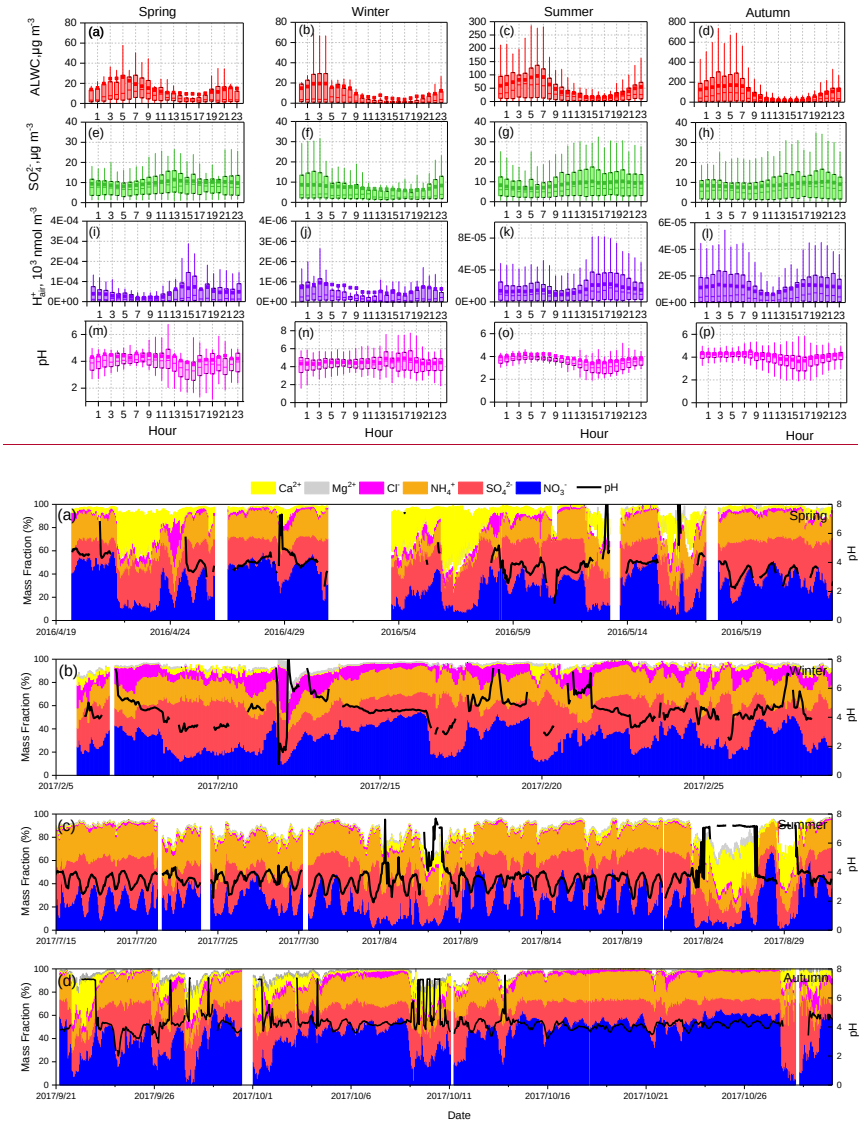
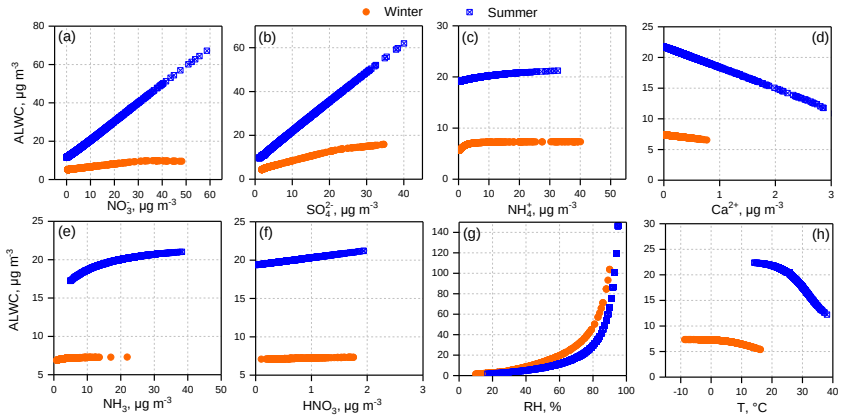
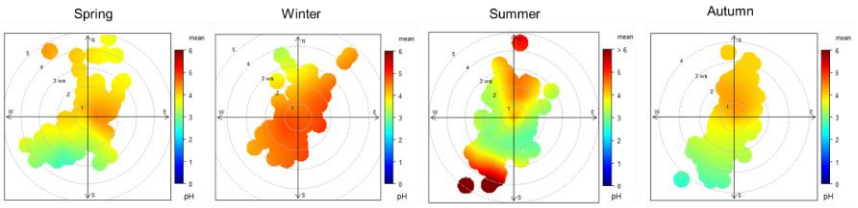

Spring
Winter
Summer
Autumn
ALWC,μg m-3
SO42-,μg m-3
Hion, 10-3 nmol m-3
pH
Hour
Ca2+
Mg2+
Cl-
NH4+
SO42-
NO3-
pH
Mass Fraction (%)
Date

Figure 4.





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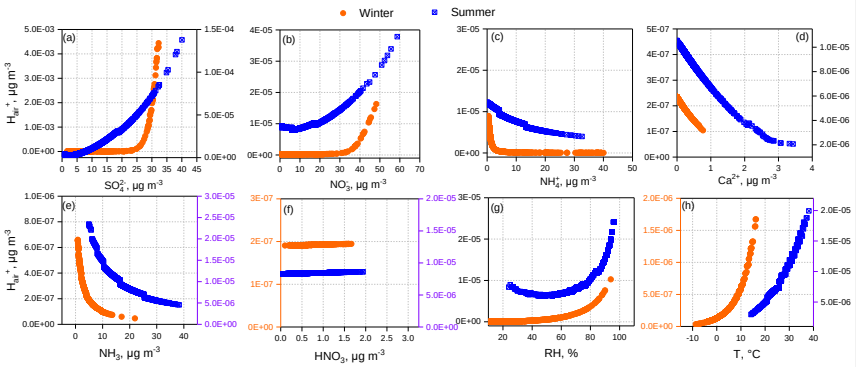

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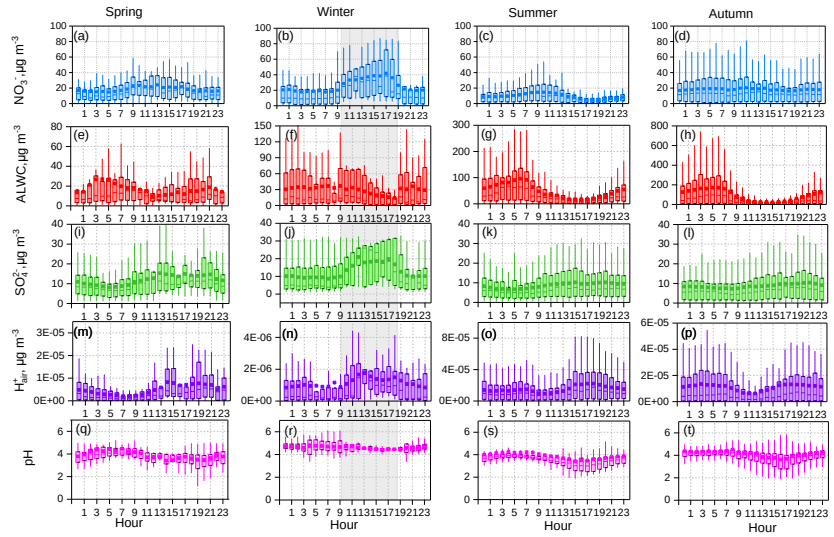

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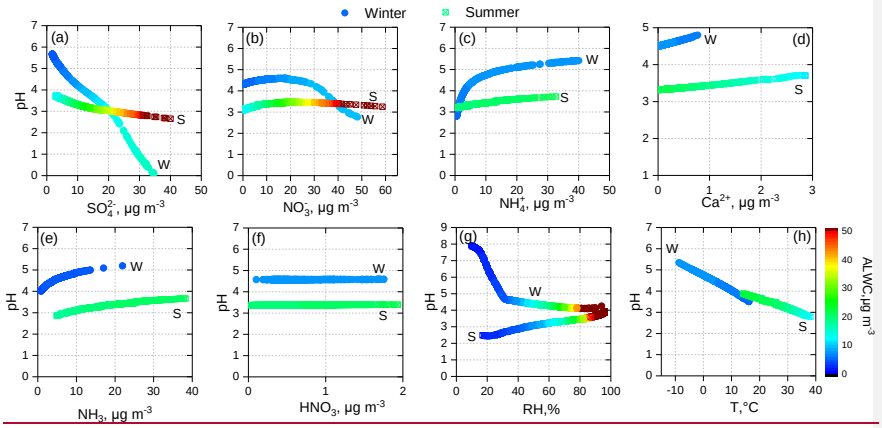

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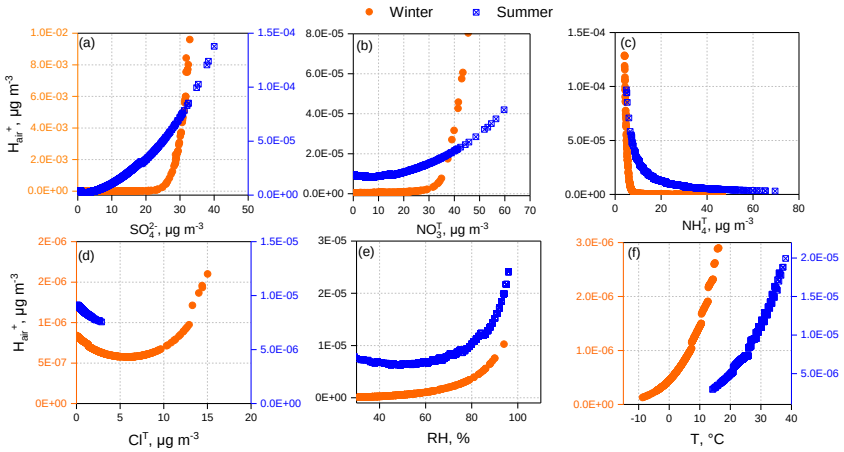

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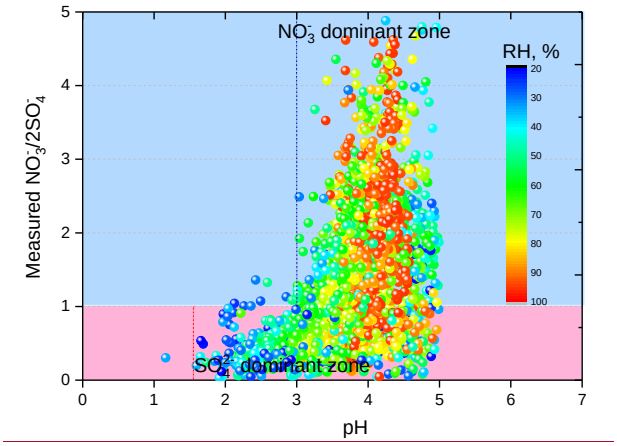

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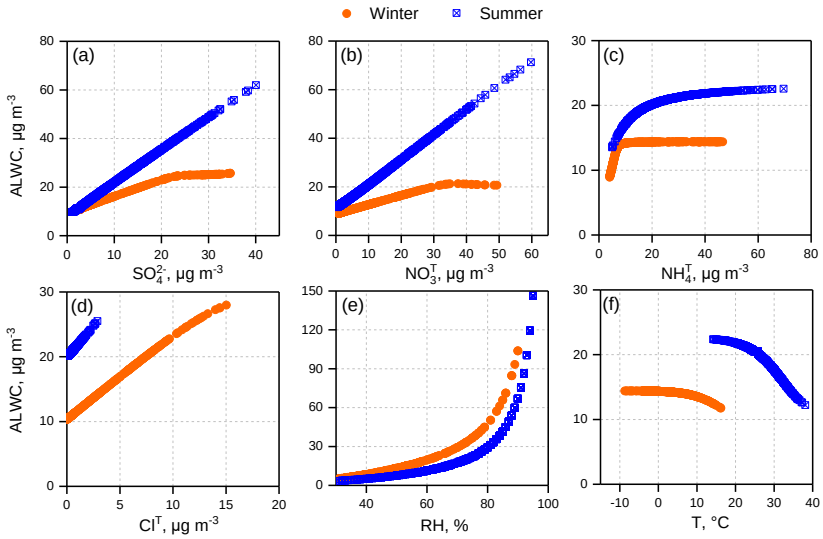

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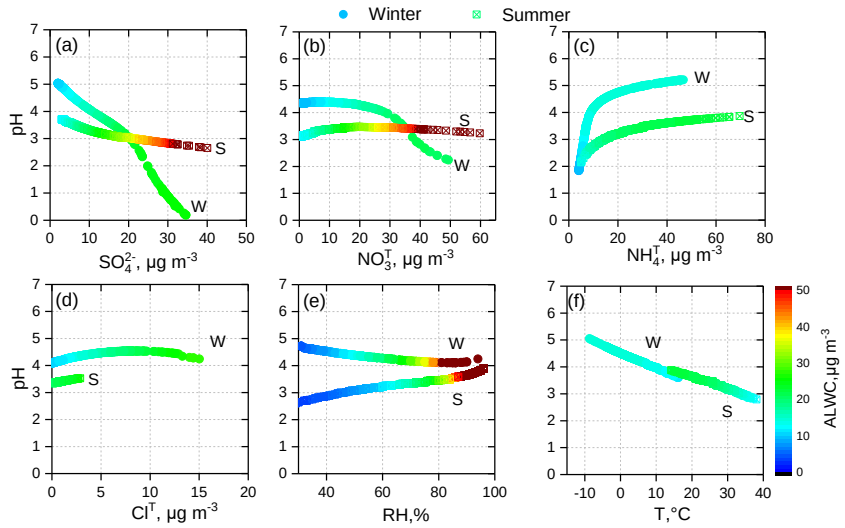

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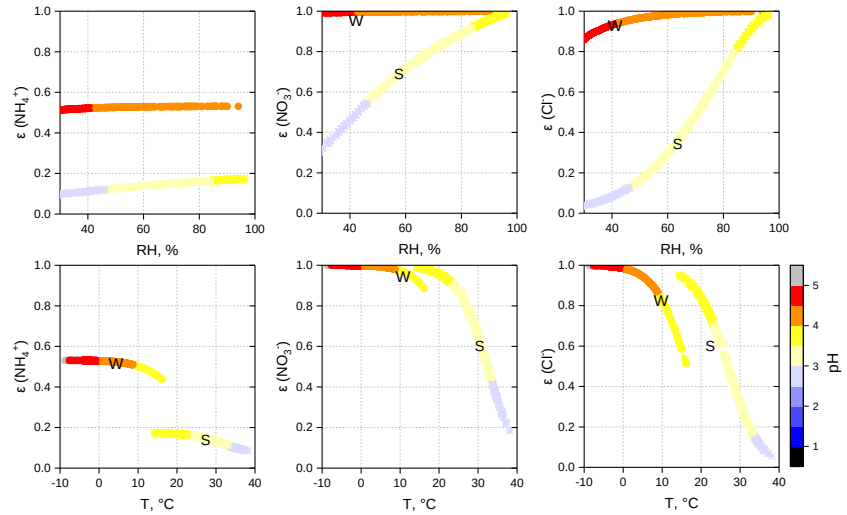

ε (NH4+)
ε (NO3-)
ε (Cl-)
RH, %
T, °C
W
S
pH

Figure 10.

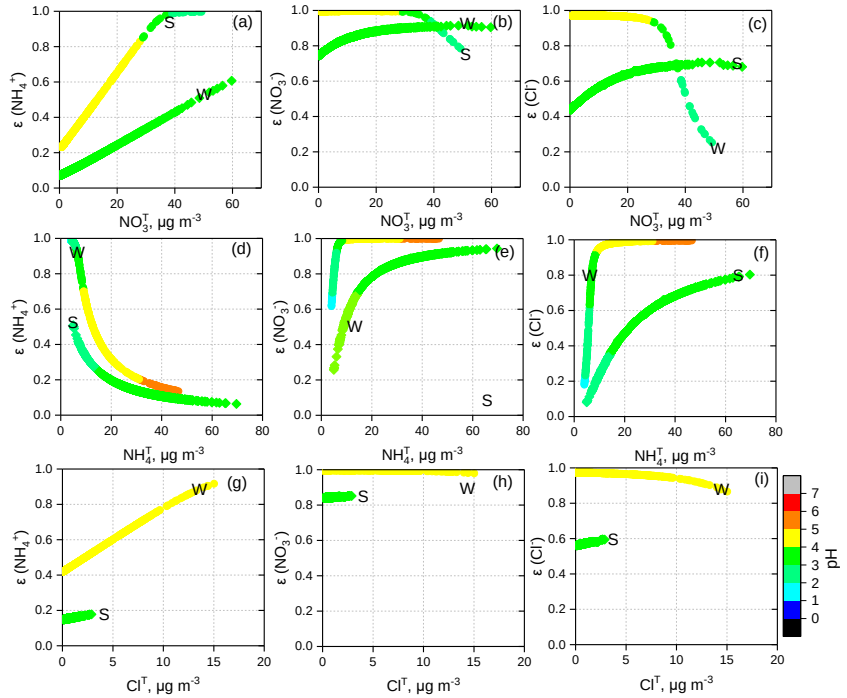
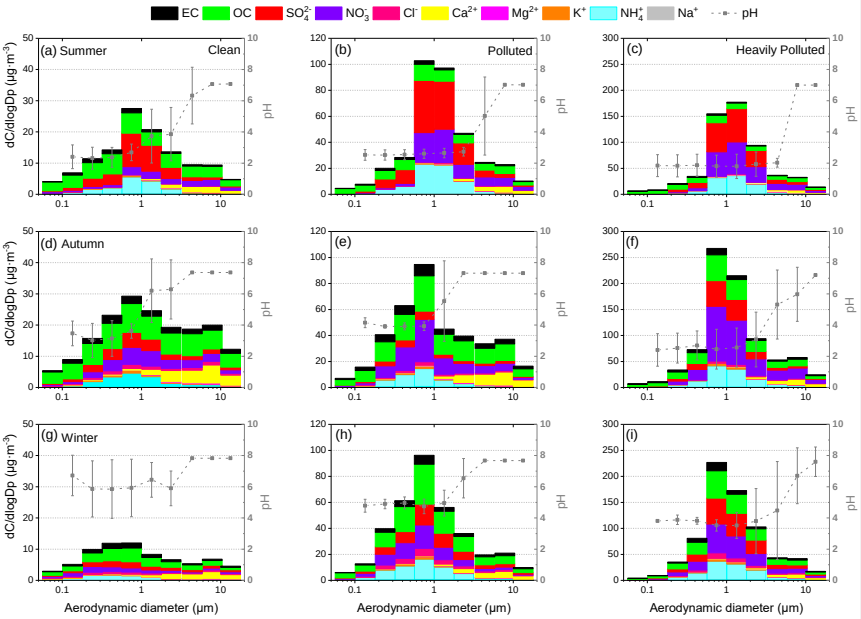

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
NO3T, μg m-3
NH4T, μg m-3
ClT, μg m-3
ε (NH4+)
ε (NO3-)
ε (Cl-)
W
S
pH

Figure 11.



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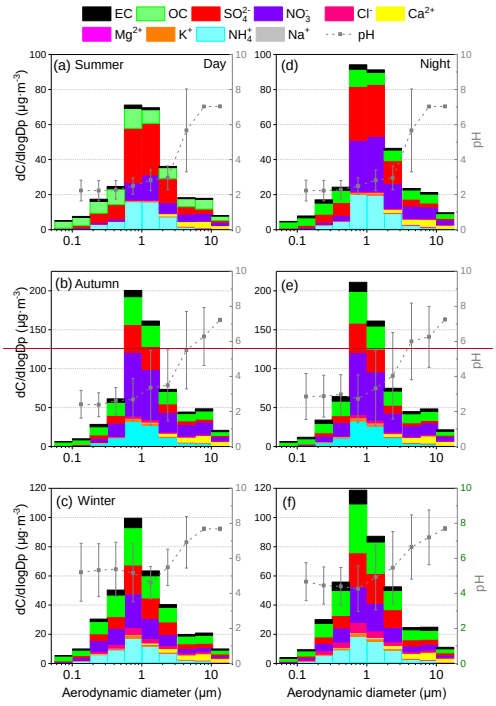
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OC
SO_4^{2-}
NO_3^-
Cl^-
Ca^{2+}
Mg^{2+}
K^+
NH_4^+
Na^+
pH
(a) Summer
Day
(d)
Night
(b) Autumn
(e)
(c) Winter
(f)
dC/dlogDp (μg·m^{-3})
pH
Aerodynamic diameter (μm)

Figure 10.