

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^- , $\varepsilon(\text{NH}_4^+)$ ($\text{NH}_4^+ / (\text{NH}_3 + \text{NH}_4^+)$, mol/mol), $\varepsilon(\text{NO}_3^-)$ ($\text{NO}_3^- / (\text{HNO}_3 + \text{NO}_3^-)$, mol/mol), and $\varepsilon(\text{Cl}^-)$ ($\text{Cl}^- / (\text{HCl} + \text{Cl}^-)$, 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 $\text{NH}_3/\text{NH}_4^+$, $\text{HNO}_3/\text{NO}_3^-$,

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 NH₃, HNO₃, HCl, NH₄⁺, NO₃⁻, Cl⁻, $\epsilon(\text{NH}_4^+)$ (NH₄⁺/(NH₃+NH₄⁺), mol/mol), $\epsilon(\text{NO}_3^-)$ (NO₃⁻/(HNO₃+NO₃⁻), mol/mol), $\epsilon(\text{Cl}^-)$ (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 NH₃, NH₄⁺, NO₃⁻, Cl⁻ were pretty well. However, measured and predicted partitioning of HNO₃ and HCl showed significant discrepancies (R² 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 \leq 30%, which is much evident in winter and spring. For data with RH \leq 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%.

A new section (Section 3.3 Gas-particle separation) was added in the revised manuscript. Table 2 exhibited the measured $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{Cl}^-)$ at different RH levels. The measured $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{Cl}^-)$ increased with the elevated RH in all four seasons, indicating more NH₄^T, NO₃^T, and Cl^T were partitioned into particle phase at higher RH. In winter and spring, NO₃^T and Cl^T were dominated by particle phases. Whereas in summer and autumn, more than half of the NO₃^T and Cl^T were partitioned into the gaseous phase. When the RH reaches above 60%, more than 90% of NO₃^T and 70% of Cl^T were in the particle phase for all four seasons. Compared with $\epsilon(\text{NO}_3^-)$ and $\epsilon(\text{Cl}^-)$, the $\epsilon(\text{NH}_4^+)$ was pretty lower, which may attribute to the higher NH₃ mass concentration in the atmosphere. In winter, the average $\epsilon(\text{NH}_4^+)$ were much higher than that in other seasons with the

relatively lower NH_3 mass concentration.

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 HNO_3 not affect pH, but changes in NH_3 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 reappportioned 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 $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{Cl}^-)$ 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.

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.

T: At high ambient temperature, $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, and $\epsilon(\text{Cl}^-)$ all showed a decreased tendency (Figure 10 and S19). And NH_4^+ , NO_3^- , and Cl^- were volatilized partially, the procedure of $\text{NH}_4^+ \rightarrow \text{NH}_3$ released one H^+ to particle phase, whereas the procedure of $\text{NO}_3^- \rightarrow \text{HNO}_3$ and $\text{Cl}^- \rightarrow \text{HCl}$ 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 $(\text{NH}_4)_2\text{SO}_4$ resulted in a net increase in particle H^+ and lower pH. In addition, molality-based equilibrium constants (H^*) of $\text{NH}_3\text{-NH}_4^+$ partitioning decreased faster with increasing temperature when compared with that of $\text{HNO}_3\text{-NO}_3^-$ 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.

SO₄²⁻: 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 $40 \mu\text{g m}^{-3}$ 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 fraction in total ions. The SO_4^{2-} mass fraction in total ions in summer was highest among four seasons with $32.4\% \pm 11.1\%$, whereas it was lowest in winter with $20.9\% \pm 4.4\%$.

NO₃^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^+ ($\epsilon(\text{NH}_4^+) \approx 1$). 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 $\varepsilon(\text{NH}_4^+)$ 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 $\varepsilon(\text{NH}_4^+)$ in the sensitivity analysis showed that decreasing NO_3^{T} could lower the $\varepsilon(\text{NH}_4^+)$ effectively (Figure 11 and S20), which helps NH_3 maintain in the gas phase.

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 $\varepsilon(\text{NO}_3^-)$ and $\varepsilon(\text{Cl}^-)$ 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 $\varepsilon(\text{NO}_3^-)$ in the sensitivity analysis (Figure 11 and S20) showed that the $\varepsilon(\text{NO}_3^-)$ 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.

The ratio of $[\text{TA}]/2[\text{TS}]$ provides a qualitative description for the ammonia abundance, where $[\text{TA}]$ and $[\text{TS}]$ are the total (gas + aqueous + solid) molar concentrations of ammonia and sulfate. The rich-ammonia is defined as $[\text{TA}] > 2[\text{TS}]$, while if the $[\text{TA}] \leq 2[\text{TS}]$, then it is defined as poor-ammonia (Seinfeld and Pandis, 2016). In this work, the ratio of $[\text{TA}]/2[\text{TS}]$ 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.

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 $\mu\text{g m}^{-3}$, 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 NO₃^T, higher Cl^T could decrease the aerosol pH.

Ca²⁺: In fine particles, Ca²⁺ mass concentration was generally low. In the output of ISORROPIA-II, Ca existed as CaSO₄ (slightly soluble). Elevated Ca²⁺ concentration could increase the aerosol pH by decreasing H_{air}^+ and ALWC (Figure. S18), the decreased H_{air}^+ results from the buffering capacity of Ca²⁺ to the acid species, while the decreased ALWC result from the weak water solubility of CaSO₄. As discussed in Section 3.1, on clean conditions, the aerosol pH could reach 6~7 when the mass fraction of Ca²⁺ 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.

Table 2. The averaged ambient temperature and $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ at different ambient RH levels in four seasons.

	RH	T, °C	$\epsilon(\text{NH}_4^+)$	$\epsilon(\text{NO}_3^-)$	$\epsilon(\text{Cl}^-)$
Spring	$\leq 30\%$	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	$\leq 30\%$	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
	≤ 30 %	35.6± 0.4	0.06±0.02	0.35±0.20	0.39±0.17
Summer	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
	≤ 30 %	21.7± 7.5	0.07±0.06	0.49±0.25	0.45±0.21
Autumn	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

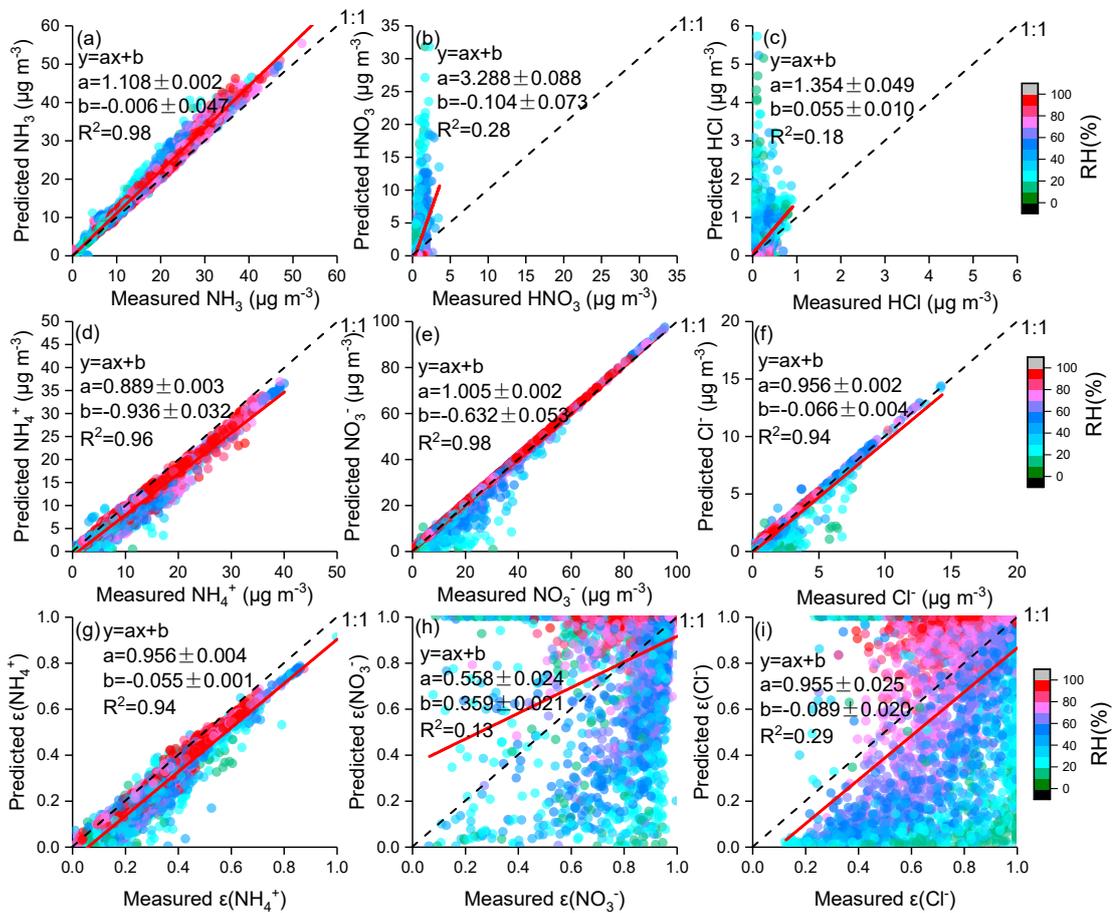


Figure 2. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by RH. In this Figure, the real-time data in four seasons were put together, and the comparisons for each season were shown in Figure S1-S4.

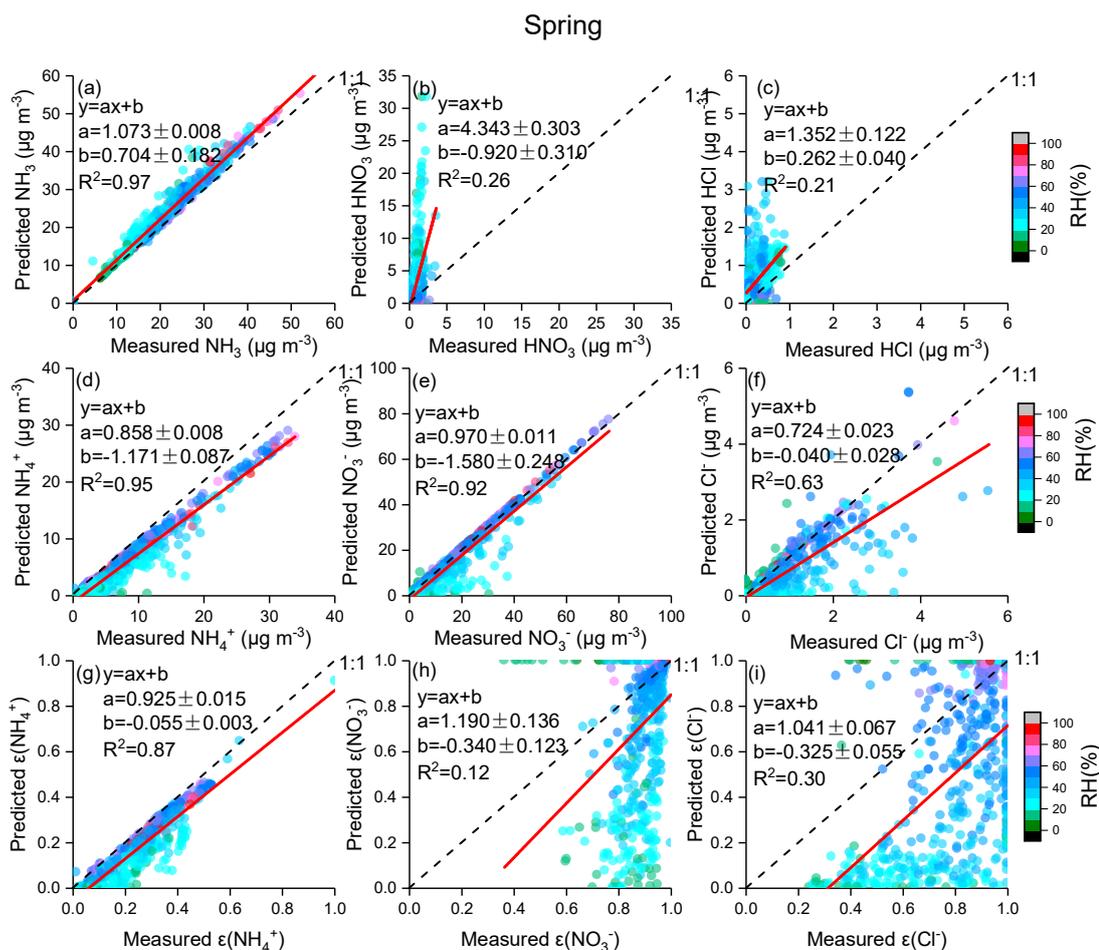


Figure S1. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by RH in spring.

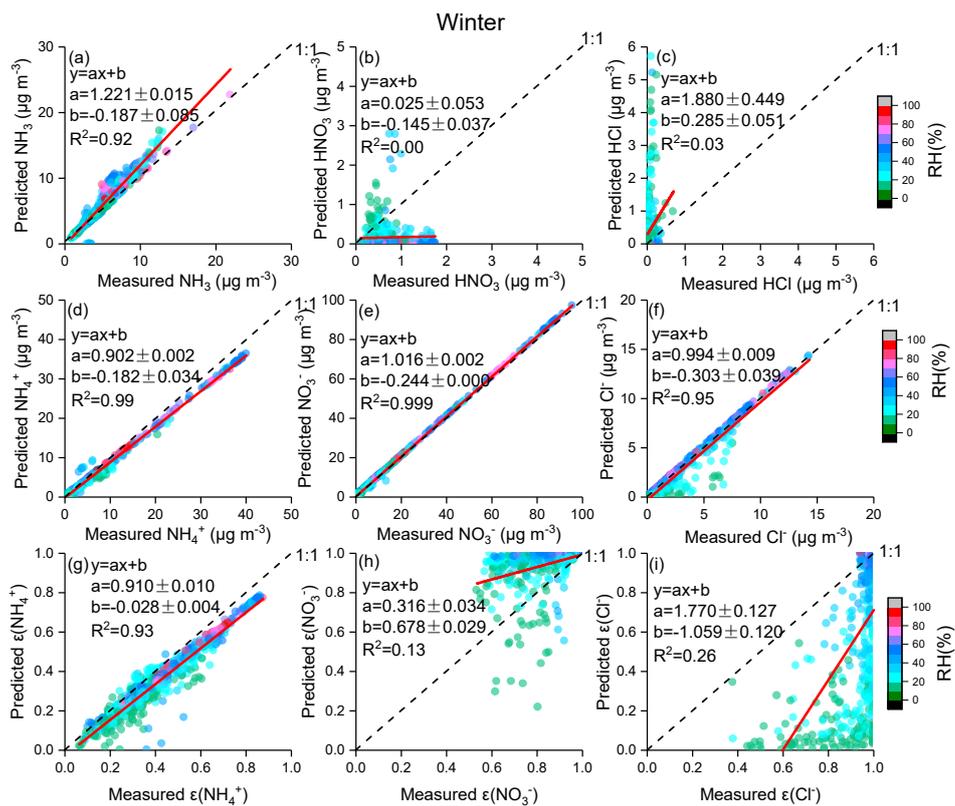


Figure S2. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by RH in winter.

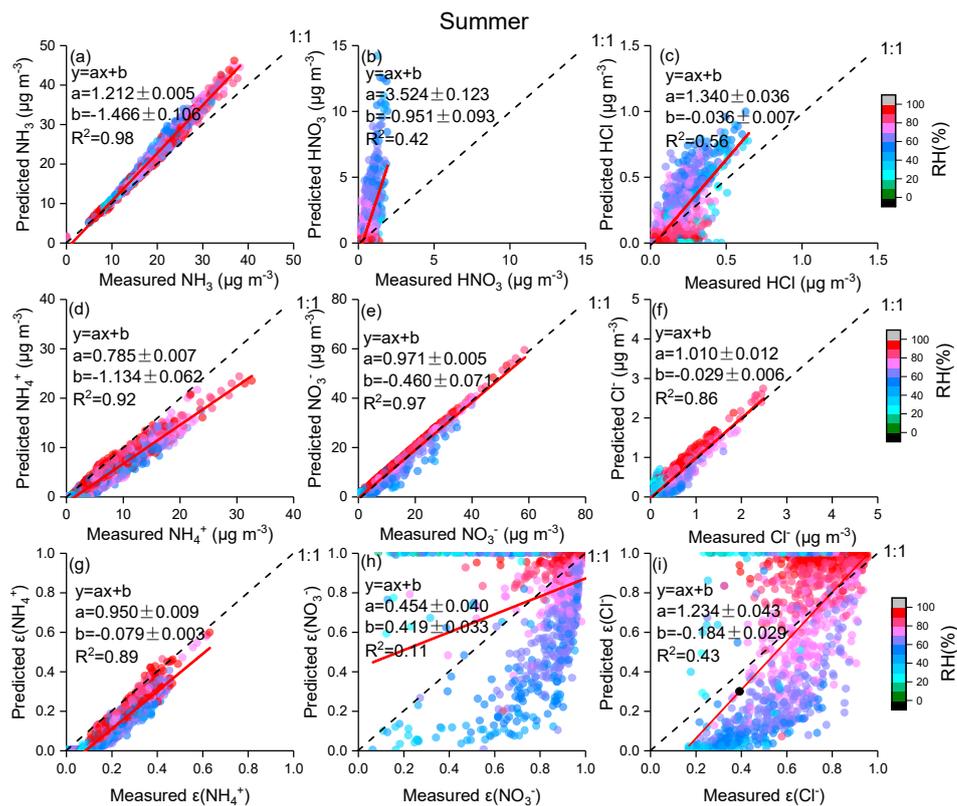


Figure S3. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by RH in summer.

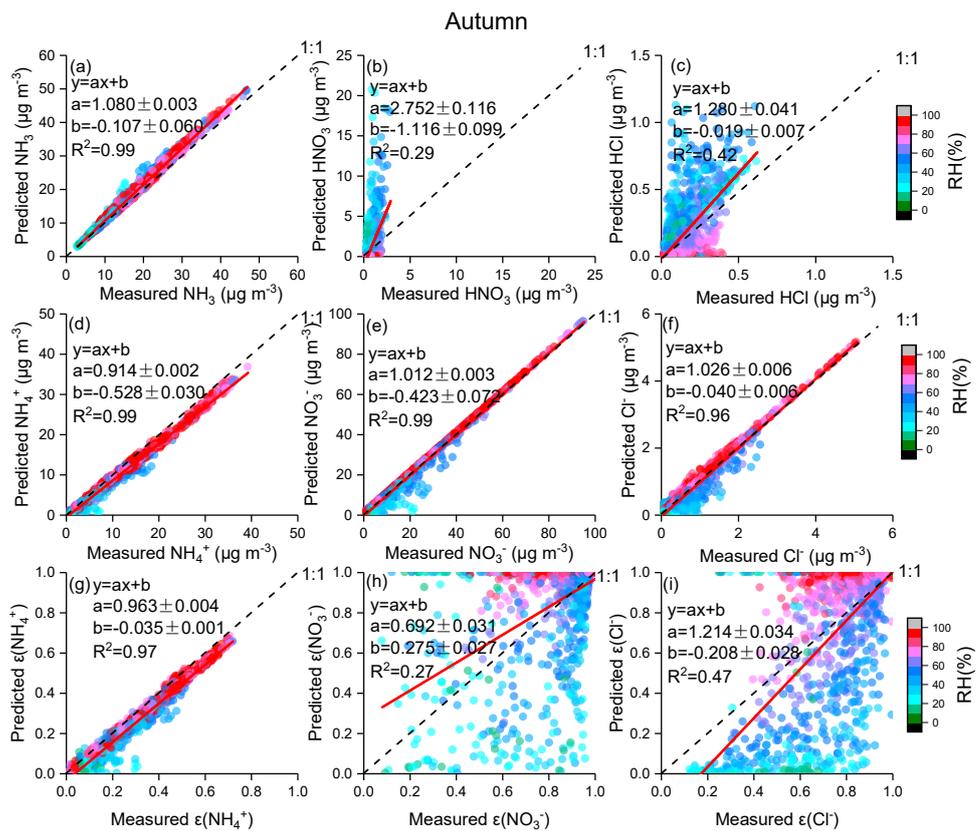


Figure S4. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by RH in autumn.

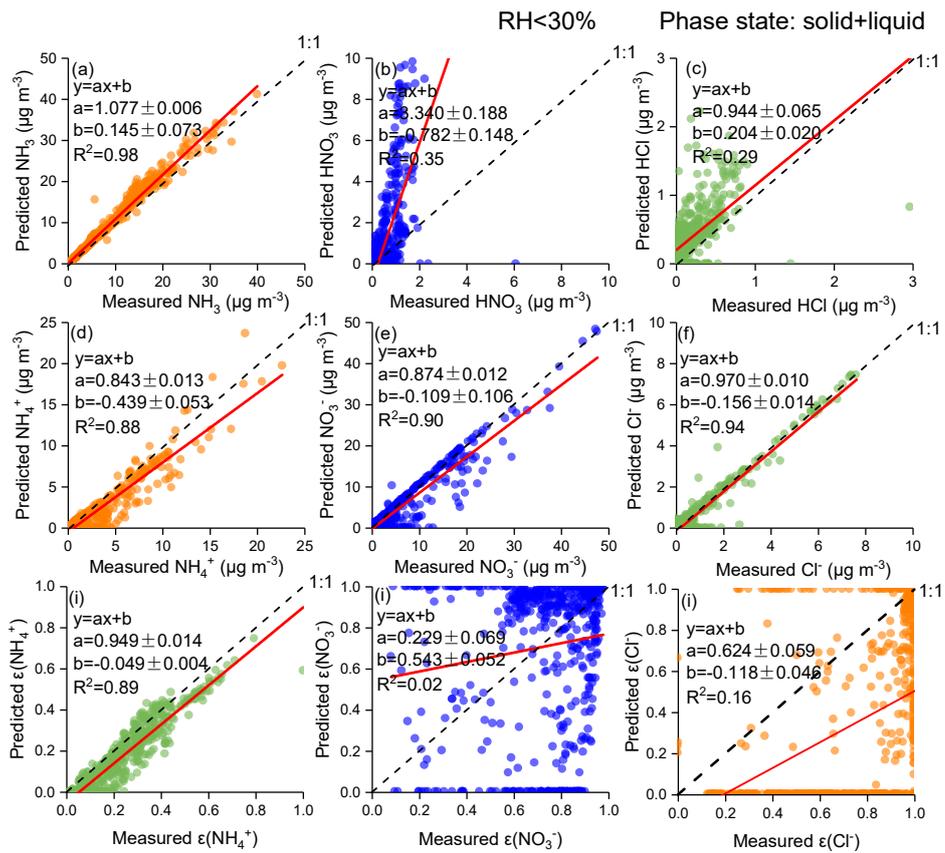


Figure S5. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ at the $\text{RH} \leq 30\%$, the ISORROPIA-II runs in stable mode (solid + liquid).

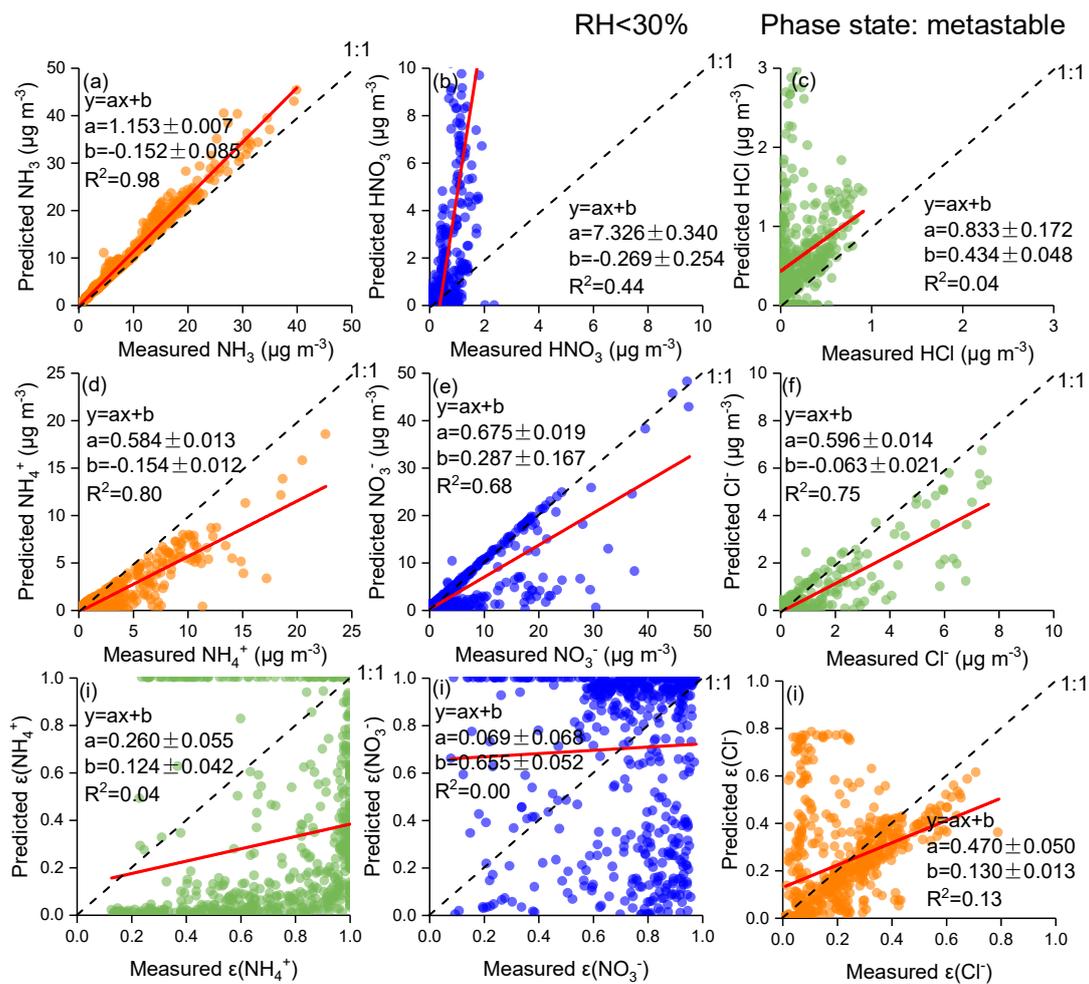


Figure S6. Comparisons of predicted and measured NH_3 , HNO_3 , HCl , NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ at the $\text{RH} \leq 30\%$, the ISORROPIA-II runs in metastable mode.

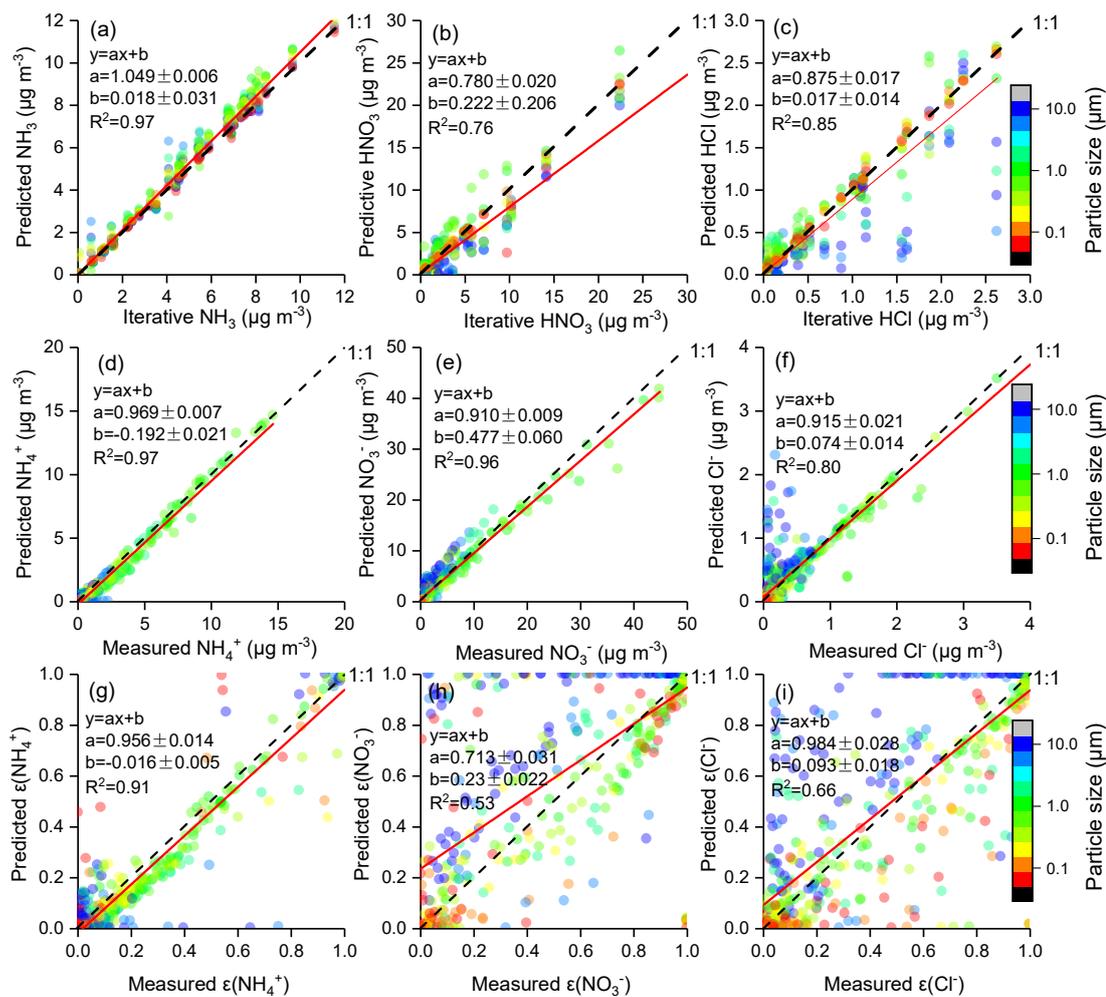


Figure 3. Comparisons of predicted and iterative NH_3 , HNO_3 , HCl , as well as the predicted and measured NH_4^+ , NO_3^- , Cl^- , $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ colored by particle size. In this Figure, all MOUDI data were put together.

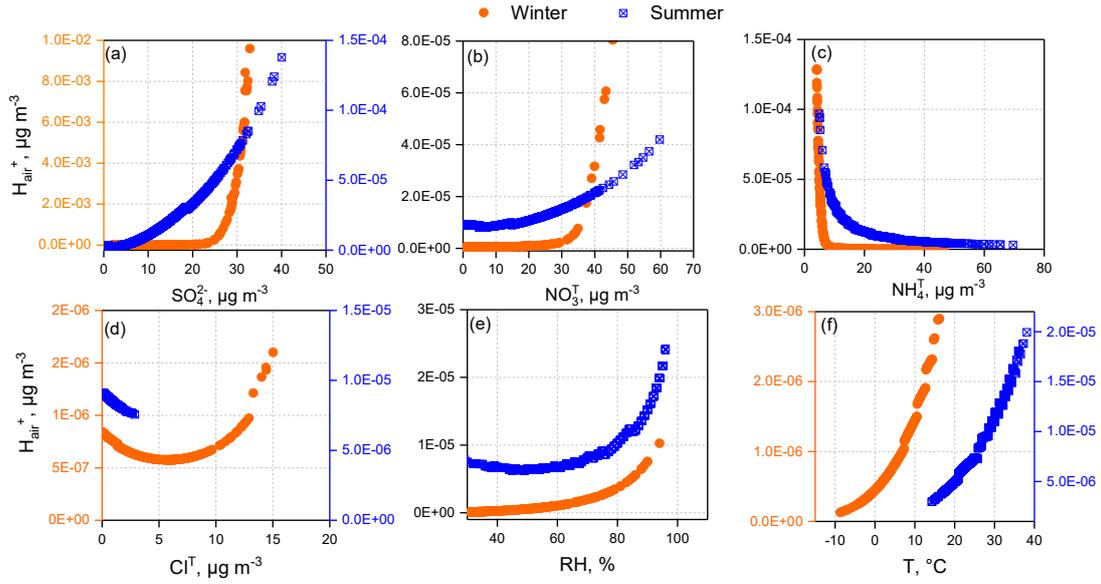


Figure 7. Sensitivities of H_{air}^+ to SO_4^{2-} , NO_3^T , NH_4^T , Cl^T , as well as meteorological parameters (RH, T) in summer and winter.

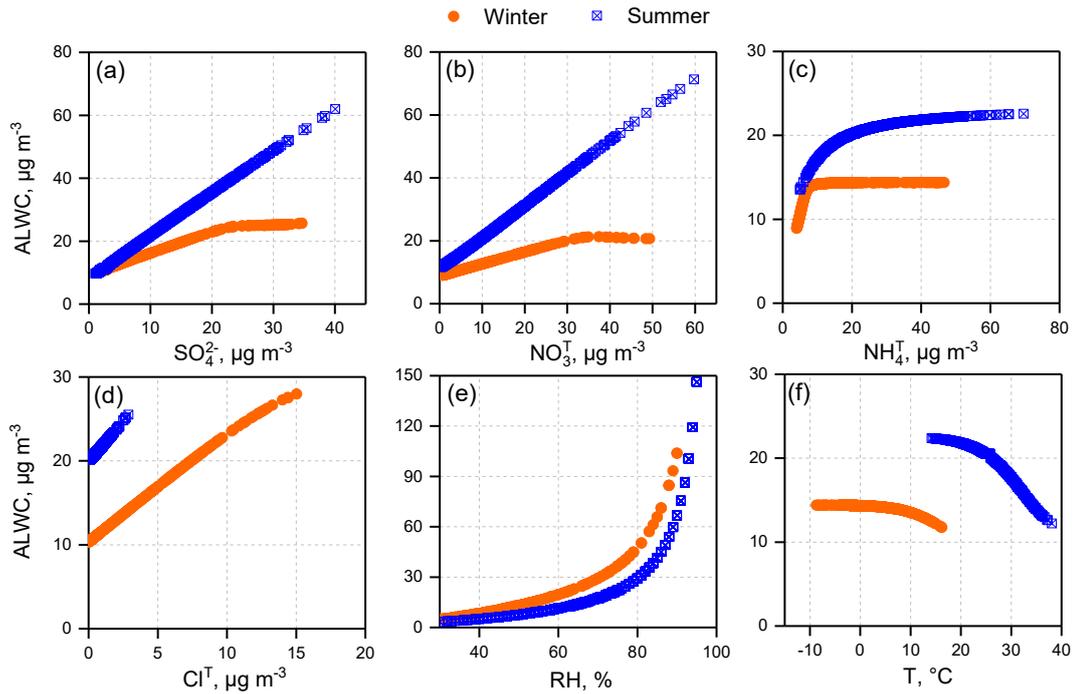


Figure 8. Sensitivities of ALWC to SO_4^{2-} , NO_3^T , NH_4^T , Cl^T , as well as meteorological parameters (RH, T) in summer and winter.

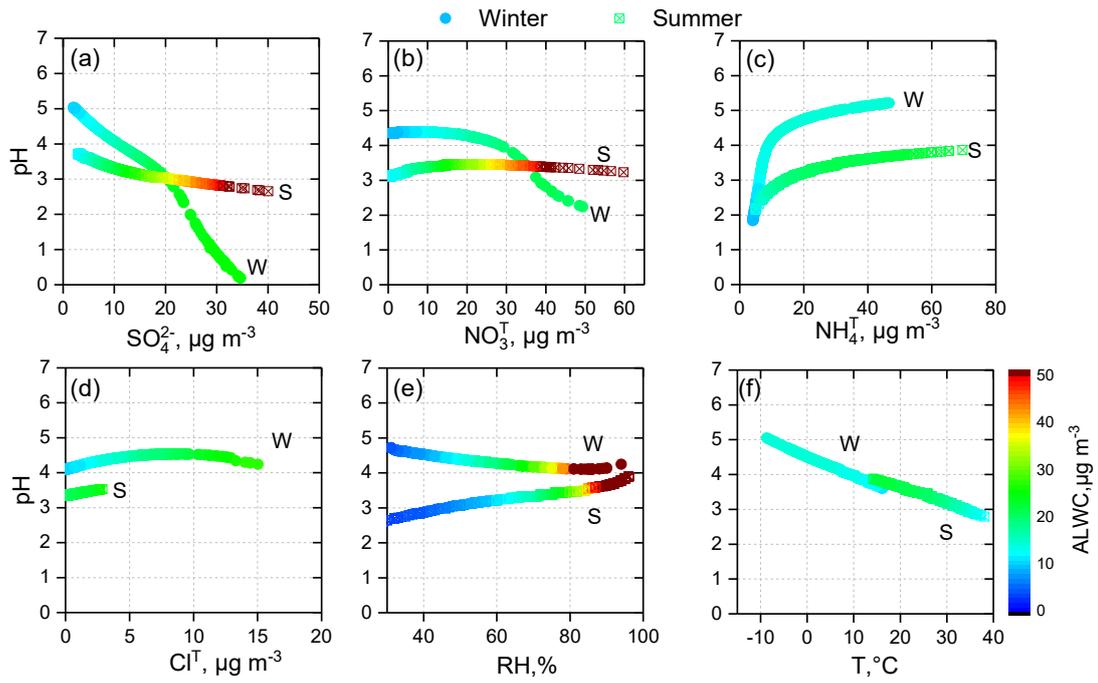


Figure 9. Sensitivities of aerosol pH to SO_4^{2-} , NO_3^T , NH_4^T , Cl^T , as well as meteorological parameters (RH, T) in summer and winter.

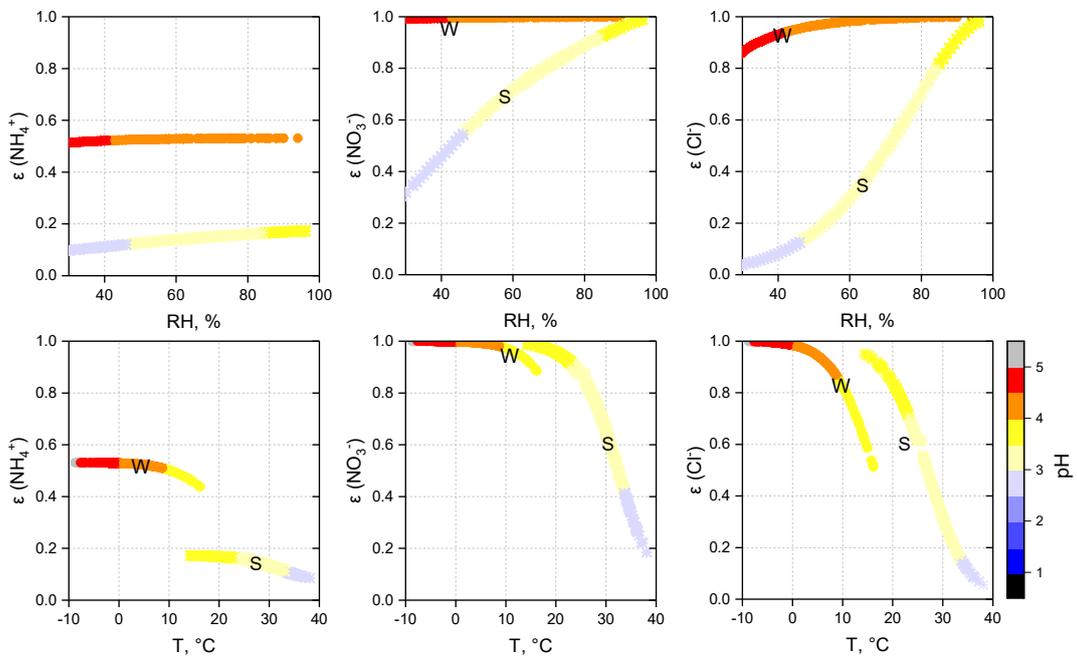


Figure 10. Sensitivities of $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ to RH and T colored by aerosol pH in summer and winter.

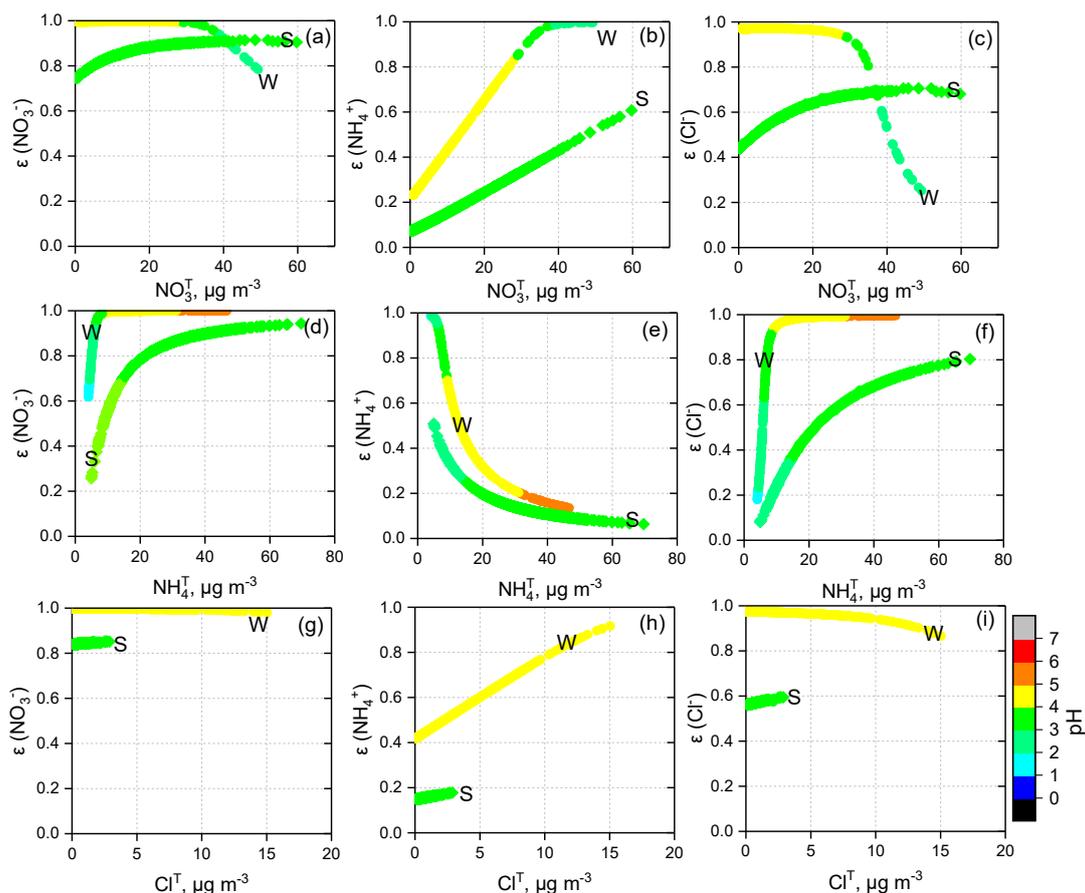


Figure 11. Sensitivities of $\epsilon(\text{NH}_4^+)$, $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ to NO_3^{T} , NH_4^{T} , Cl^{T} colored by aerosol pH in summer and winter.

Specific Comments:

1. Line 37 change specials to species

Response: In the revised manuscript, the word “specials” has been changed to “species”

2. Line 202 and following, it is not just lack of NH_3 data that can affect predicted pH, what about HNO_3 , 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.

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 partitioning procedure more NH_4^+ was partitioned into the gas phase and led to the low aerosol pH for fine mode particles.

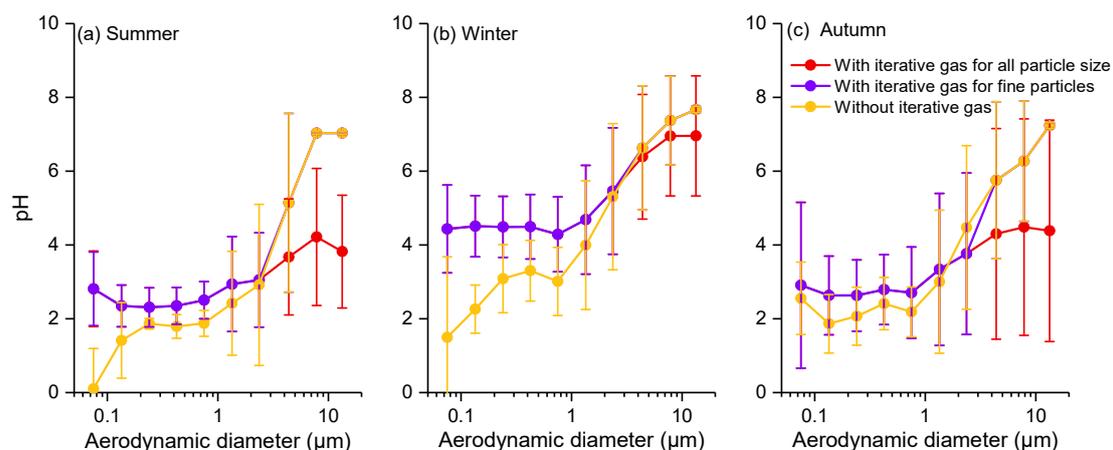


Figure R1 The averaged size-resolved aerosol pH in three seasons predicted with three assumptions: (1) predicted with no iterative gases, (2) predicted assuming lack of equilibrium with gas phase for coarse mode particles, (3) predicted assuming all particles in equilibrium with the gas phase.

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 “southern” 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 $100 \mu\text{g m}^{-3}$), the impact of dilution of ALWC to the H_{air}^+ was more significant.

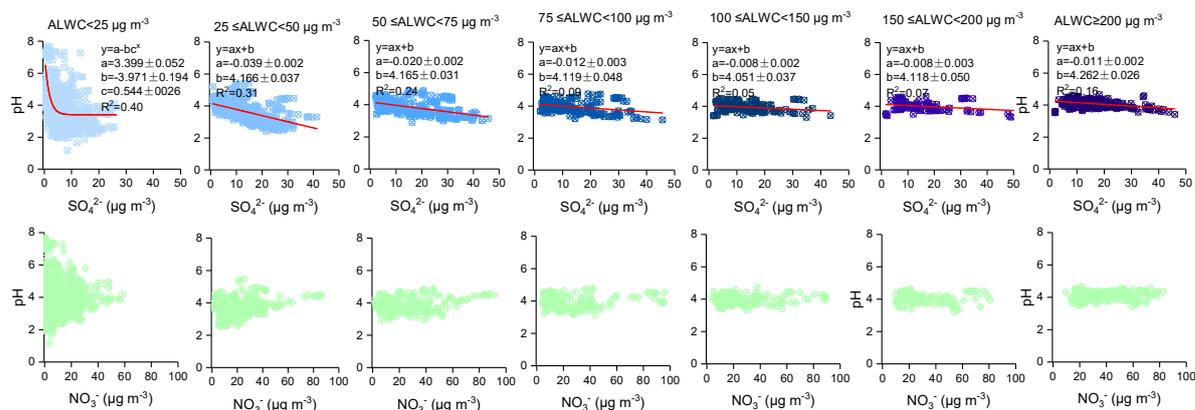


Figure S10. The relationship between SO_4^{2-} and NO_3^- mass concentration and aerosol pH at different ALWC levels.

9. Line 327, provide a physical explanation for the U shape dependency of H^+ on NO_3^-

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 NH_3 and H^+ over broad NH_3 concentration ranges? I.e., will increases in NH_3 always lead to higher dissolved NH_3 ? 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 ($\epsilon(NH_4^+)$, $\epsilon(NO_3^-)$, $\epsilon(Cl^-)$) 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 NO_3^- . The authors discuss the trends they observe in the sensitivity analysis and NO_3^-/SO_4^{2-} , 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 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 NO₃⁻ mass concentration, high NO₃⁻ 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 NH₄^T was nonlinear. NH₄^T in lower range had a significant impact on aerosol pH (Table S2), and higher NH₄^T generated limited pH change (Figure 9, S14, S17). Elevated NH₄^T could reduce H_{air}⁺ exponentially and slightly increase ALWC when the other input parameters were held constant. As the NH₄^T increases, H_{air}⁺ are consumed swiftly during the dissolution of NH₃ and the further reaction with SO₄²⁻, NO₃⁻, and Cl⁻. And the elevated NH₄^T increased the ε(NO₃⁻) and ε(Cl⁻) when NO₃^T and Cl^T were fixed (Figure 11 and S20), which means the elevated NH₄^T alters the gas-particle partition and shifts more NO₃^T and Cl^T into particle phase, leading to the deliquescence of additional nitrate and chloride and increase of ALWC.

Although NH₃ 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.

In our opinion, the ALWC, H_{air}⁺, aerosol pH, ε(NH₄⁺), ε(NO₃⁻), and ε(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. The relationship between $\epsilon(\text{NO}_3^-)$, $\epsilon(\text{Cl}^-)$ 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 $\epsilon(\text{NO}_3^-)$ and $\epsilon(\text{Cl}^-)$ varies from 0 to 100%.

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 $\text{NO}_2 + \text{SO}_2$ 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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