Dear professor Athanasios Nenes:

We're appreciated for your valuable comments, which are very useful for improving the quality of this manuscript. Your comments help us better understand the thermodynamic equilibrium between aerosol and gas phase, we learned a lot from these detailed comments. Our responses to the specific points are given below.

Comments

1. Page 1, line 19: "due to the stronger ability…ions". Affinity with the H+ is not the underlying reason (otherwise, increasing HNO3 would also drive acidity up, and it doesn't really). The very low volatility of SO4 compared to the neutralizing cations (mainly NH4) is the reason for the strong acidity associated with SO4 in aerosol. NH4 evaporates to NH3 in achieving equilibrium, and that by nature creates an ion imbalance that leads to H+ production through dissociation of H2O. The appropriate reference for this is Weber et al., 2016.

Response: The statement has been removed from the Abstract.

2. Page 1, line 24: "hydrolysis of … and ALWC". The authors mention hydrolysis of ammonium salts throughout the manuscript, but do not provide any calculations to support this. Even a pure ammonium sulfate particle, when deliquesced, will evaporate some NH4 to the gas phase to produce NH3 – this is the reason for acidity, as mentioned above. LWC variability does lead to a pH unit change for typical variations throughout the day (and this has also been shown before by the Guo et al. studies and others).

Response: The statement "which might be attributed to the limited aerosol liquid water content (ALWC) and hydrolysis of ammonium salts" has been removed from the Abstract, the reasons why aerosol is acidic is interpreted by the thermodynamic equilibrium considerations between aerosol phase and gas phase.

3. Page 3, line 40. "In addition…acid rain". Incorrect statement. Aerosol acidity is decoupled from acid rain pH. The reason being that the water per kg of aerosol "mass" is fixed by the RH – so pH changes are relatively insensitive to changes in absolute aerosol mass, while rain water is decoupled from the aerosol mass – so rainwater pH changes considerably with different aerosol loading. Otherwise the acid rain program would have failed in the US – because aerosol acidity has not gone down over time (e.g., Weber et al., 2016).

Response: According to the theory of 'Greenfield gap'(Greenfield, 1957), the collision efficiency of raindrop on particle between 0.2 and 2.0 μm is very low. It means only the coarse particle can possibly be scavenged by wet precipitation. Furthermore, the concentration of

coarse particle is not high enough to affect the acidity of rain in urban area. The statement has been removed from the revised manuscript. (Page 3, line 34, in the revised manuscript)

Greenfield S M.: Rain scavenging of radioactive particulate matter from the atmosphere. Journal of the Meteorology Sciences, 1957, 14: 115-125.

4. Page 3, line 44. "A net … alkalinity". Hennigan et al., and others have shown that the ion balance derived from observations works when all the ions (even trace ones) are well constrained and the dissociation state of multivalent ions are known. This of course cannot be satisfied for aerosol, so the statement must be erased. The studies quoted (especially Wang et al.) based most of their discussion on ion balances, and therefore are not well-supported.

Response: The statement has been removed from the revised manuscript. The revised statement is "Nevertheless, not all ions (even trace ones) are well constrained in the observations and the dissociation state of multivalent ions are unclear, ion balance and other similar proxies fail to represent the in situ aerosol pH because such metrics cannot accurately predict the H^+ concentration in the aerosol liquid phase (Guo et al., 2015; Hennigan et al., 2015)." (Page 3, line 37-38, in the revised manuscript)

5. Page 3, line 66. "NCP showed". These studies have showed to contain important issues (e.g., Song et al., ACP, 2018; Guo et al., 2017) that does not make the neutral pH inferences likely. I agree that the mildly acidic pH are quite likely, and that it is higher than the pH levels found in other locations, so please modify the sentence accordingly, perhaps removing the references to neutral pH levels.

Response: The statement and references to neutral pH levels has been removed from the revised manuscript. (Page 3, line 58, in the revised manuscript)

6. Page 4, line 66. "particulate matter concentration is very low". pH variations from diurnal variability in RH is always occurring, because the LWC per kg aerosol mass changes drastically with RH. Therefore please remove the "In some countries…very low".

Response: pH diurnal variation is not driven by the particulate matter concentration. The statement has been removed from the revised manuscript. (Page 3, line 64, in the revised manuscript)

7. Page 4, line 79. "size-resolved pH are still rare". That is true, but some studies should be cited here that have done this work.

Response: The works published by Fang et al. (2017) and Craig et al. (2018) have been added in the revised manuscript. (Page 4, line 69, in the revised manuscript)

Fang, T., Guo, H. Y., Zeng, L. H., Verma, V., Nenes, A., Weber, R. J.: Highly acidic ambient particles, soluble metals, and oxidative potential: A link between sulfate and aerosol toxicity, Environ. Sci.

Technol., 51, 2611-2620, 2017.

Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A., Cook, R. D., Dutcher, C. S., and Ault, A. P.: Direct determination of aerosol pH: size-Resolved measurements of submicrometer and supermicrometer aqueous particles, Anal Chem, 90, 11232-11239, 10.1021/acs.analchem.8b00586, 2018.

8. Page 5, line 128. You do not have NH_3, HNO_3 and HCl concentrations. How do you address this when calculating the pH? It is good to make sure people understand this issue.

Response: The state "Gas precursors were not observed during the periods of MOUDI sampling" has been removed from the Section 2.3 in the revised manuscript. The complete method of size-resolved aerosol pH calculation is showed in Section 2.4. (Page 5, line 118, in the revised manuscript)

9. Page 6, line 161-163. Seinfeld and Pandis is a good reference, but it is not clear from there why the DRH is low enough in the NCP to assume metastability. Metastability is supported by the RH history of the particles, and their composition (the likelihood of being in the efflorescence or deliquescence branch of the water uptake curves). I defer to the Song et al., 2018 manuscript and all the discussion in the ACPD form of the manuscript, to see what are the arguments that supports metastability.

Response: As Song et al. (2018) mentioned in their work, there were no observational evidence so far to suggest whether the Beijing winter haze fine particles were in a metastable or stable state. We have referenced some literature and think that the assumption of metastable state is overall reasonable. In the revised manuscript, we try to provide more evidence to support this assumption.

In the ambient atmosphere, the aerosol chemical composition is complicated; hence, the deliquescence relative humidity (DRH) of aerosols is generally low (Seinfeld and Pandis, 2016). Once the particles are deliquescent, crystallization only occurs at a very low RH, which is called hysteresis phenomenon. The efflorescence RH (ERH) of a salt cannot be calculated from thermodynamic principles; rather, it must be measured in the laboratory. For a particle consisting of approximately 1:1 $(NH_4)_2SO_4$: NH_4NO_3, the ERH is around 20%, while for a 1:2 molar ratio it decreases to around 10%. (Shaw and Rood 1990). Recently, NO_3^- dominates the particles in the NCP (Zhao et al., 2013, 2017; Huang et al., 2017; Ma et al., 2017); therefore, we assumed that the particles are in a liquid state (metastable condition). Assumption that particles are in metastable were adopted by numerous studies in the NCP (Liu et al., 2017; Guo et al., 2017; Shi et al., 2017, 2019). (Page 6, line 148-160, in the revised manuscript)

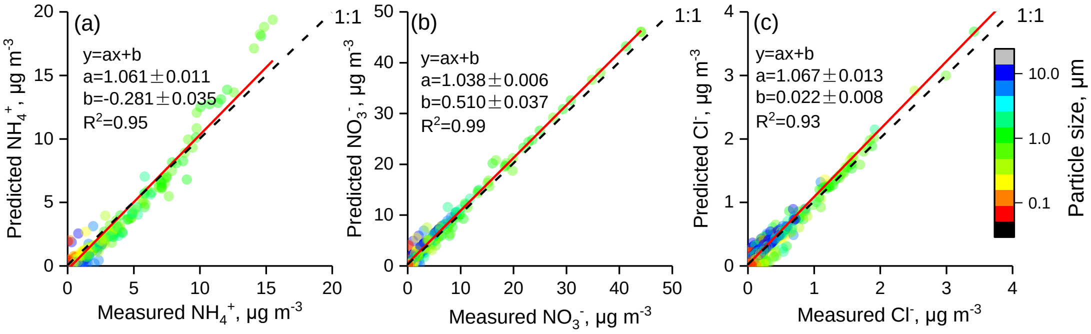
10. Page 6, line 177-182. I'm quite surprised that the partitioning is sensitive to the phase state. What version of ISORROPIA do you use? Are you sure you use the latest version of the code (2.3) with the latest bug fixes? If not, I can provide a copy of the code upon request. The conclusion that pH inferences when the RH is low is also supported by other studies – so it would be good to cite those. Guo et al. JGR (2017) suggest that the lower limit is about 40%, why do you think it's

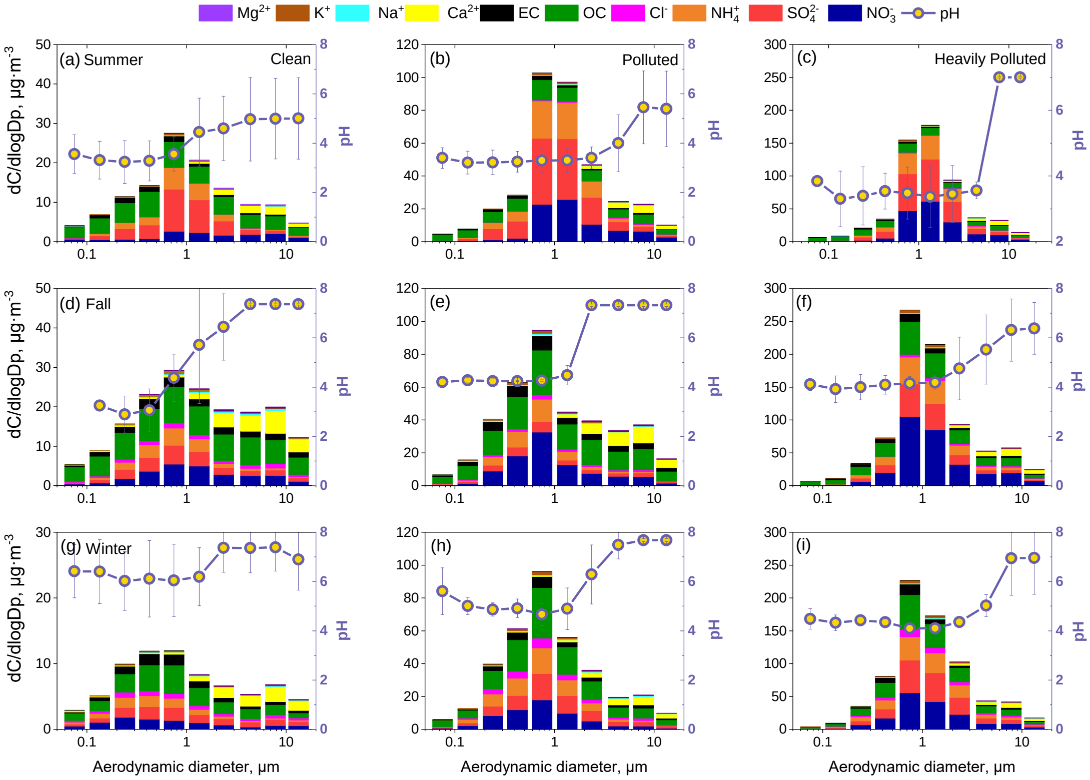
different from the 30% cited in this study?

Response: We have asked Mr. Song and Mr. Shi for the ISORROPIA V2.3 (Win) and recalculated the $PM_{2.5}$ pH at RH≤30 in stable state. We found that when RH was low, the partitioning was still sensitive to the phase state. Because the subcases O7 and P13 are mostly used when the forward metastable mode simulations are performed, while subcases O1 and P1 are mostly used when forward stable mode simulations are performed. Even if Mr. Song revised the errors in the standard ISORROPIA-II for the four subcases (G1, G2, O1, and O2), there are still differences in gas-particle portioning between forward metastable mode and forward stable mode when the RH is low. However, as you mentioned in the comments to Song et al. (2018), when RH is low, the liquid water content becomes very small, $PM_{2.5}$ pH is subject to considerably more uncertain. Therefore, we removed the statement about comparison between stable and metastable, and cited the work of Guo et al. (2017). In this work, we finally set the lower RH limit as 30% due to the overall good agreement between predictions and measurements when RH was high than 30%. (Page 6, line 173-177, in the revised manuscript)

11. Page 7, line 189-191. But you have gas-phase concentration of semi-volatile species with the MARGA. Why not use those? It is much better than the unconstrained iterative procedure of Guo et al. which really works when you have an “idea” of the expected NH3 (or other) levels. This is a major issue of the paper – that it doesn’t seem to constrain the size-resolved pH well because the gas-phase is not constrained well enough.

Response: In the revised manuscript, the gaseous precursor measured by MARGA are used to calculated the size-resolved aerosol pH. Averaged NH_3, HNO_3 and HCl measured by MARGA matched to $PM_{2.5}$ mass concentration levels during the MOUDI sampling periods were input. And the gaseous precursor measured by MARGA are also used to recalculated coarse mode aerosol pH. We are pleased to find that the measured and predicted NO_3^-, NH_4^+, and Cl^- agreed very well in fine-mode particles. The related results about size-resolved aerosol pH have been revised. The overall size distribution of aerosol pH does not change. (Page 7, line 181-195, in the revised manuscript)





12. Page 7, line 208-209. Gas-particle disequilibrium does not assume that you can neglect the gas-phase! Either remove this section, or justify why you can assume this. If you cannot, then you have to revise the section (and related calculations) to accommodate for this.

Response: Related statement has been removed. In the revised manuscript, the gaseous precursor measured by MARGA are also used to calculated coarse mode aerosol pH. (Page 7, line 193, in the revised manuscript)

13. Page 7, line 215. "Nh4 and Ca2". True, but Ca also associated with SO4 and makes insoluble CaSO4 which can strongly depress the amount of soluble materials (hence LWC). You really need to include the hygroscopic ions too (K, Na, Mg).

Response: We're afraid there is a misunderstanding, in the sensitivity analysis, K, Na, Mg, and total chloride are also included in the input files, and we have clarified the statement in the revised manuscript. Here we would like to emphasize the impact of Ca^{2+} on aerosol pH, because Beijing is in North China, vegetation coverage is less than that of Southern China, hence the dust is an important source of particles. (Page 7, line 203-204, in the revised manuscript)

14. Page 8, line 252. ISORROPIA issues an error message whenever there is "too much" Ca, Na, etc. If this is the case, then you need to say this – and basically say there is unneutralized carbonates in the aerosol. In general, these cases are characterized by external mixing – so the bulk pH may be

affected. This needs to be considered in the discussion. If there is unneutralized carbonates, then the pH calculation may need to be revisited.

Response: Thanks for your careful remind, we have checked our calculated results, and no error message was found. The insoluble calcium salt was filtered during the pre-treatment process in sample box of MARGA, the input Ca^{2+} was all obtained from soluble fractions.

In the NCP, the PM2.5 pH spanned 2~7 under clean conditions. Some higher PM2.5 pH values appeared, especially at the end of the haze, and were often companied by the cold-front systems from Siberia, the high wind speed can sweep away air pollutants but raise dust in which the crustal ion species are higher, that is the reason why high aerosol pH usually occurred on clean days. We have revised this statement. (Page 8, line 239-240, in the revised manuscript)

15. Page 9, line 287. "indicating that … particle water". You contradict the statement above, that says composition is the only thing that matters.

Response: Obviously, the statement caused misunderstanding. What we want to express is that $PM_{2.5}$ pH diurnal variation was both driven by meteorological conditions and aerosol composition. We have revised this statement. (Page 9, line 265-267, in the revised manuscript)

16. Page 9, line 290-293. "Specifically … in winter". This discussion is not correct. The liquid water content scales with the aerosol mass when RH < 100% (it's in thermodynamic equilibrium), so LWC does not vary independently from aerosol mass. Therefore, you cannot talk about "more" or "less" seeds that dissolves in liquid water. This discussion is, of course, relevant for clouds – but here you talk about aerosol. So please remove this sentence overall.

Response: The statement has been removed from the revised manuscript.

17. Page 10, line 302. "Theoretically, … release H+". Although highly soluble, HNO3 does not deliquesce to form aqueous aerosol in the troposphere, therefore it cannot by itself "generate" H+. If there is already some aerosol present, the additional HNO3 is too small to cause H+ to form (unless if you are talking about clouds, where the water is orders of magnitude higher than aerosol). What happens with HNO3 is that it needs to co-condense with NH3 or "bind" with Na, K, Ca to form salts that generally are "neutral", so do not generate H+. Given that with the formation of the salt also generates LWC, this leads to the generally observed increase of pH that you see when NO3 increases. This has been extensively discussed in Guo et al., (2018), Shi et al. (2019) and others. Please revise this section accordingly.

Response: Thanks for these comments, we learned a lot from these detailed comments. And we rewrote Section 3.3 to interpret the sensitivity tests results. You can see these statements below or in the revised manuscript. (Page 9, line 284-341, in the revised manuscript)

H_2SO_4 can be completely dissolved in ALWC and in the form of sulfate. As shown in Table 3, HNO_3 also had a high conversion rate to nitrate when RH>30%. Under rich-ammonia conditions (defined and explained in Figure S15), sulfate and nitrate mostly exist in aerosol phase with ammonium. The thermodynamic equilibrium between NH_4^+ and NH_3 makes aerosol acidic (Weber et al., 2016). In the sensitivity tests, we found that elevated SO_4^{2-} is crucial in the increase of H_{air}^+ (Figure S7, S9, S12) and ALWC (Figure S8, S10, S13), and has a key role in aerosol acidity (Figure 7, S11, S14). However, only the $PM_{2.5}$ pH in winter and autumn decreased significantly with elevated TNO_3 (Figure 7, S14). In spring and summer, $PM_{2.5}$ pH changed little with elevated TNO_3. Moreover, when the TNO_3 concentration was low, $PM_{2.5}$ pH even increased with elevated TNO_3 (Figure 7, S11). The effect of TNO_3 on H_{air}^+ and ALWC is similar to that of SO_4^{2-}, that is, the elevated TNO_3 will also result in the increase of H_{air}^+ and ALWC. The difference is that SO_4^{2-} can lead to much higher concentration of H_{air}^+ than TNO_3 due to its low volatility (Figure S7, S9, S12). Thus, the sensitivity of $PM_{2.5}$ pH to TNO_3 is less than that to SO_4^{2-}. Moreover, in spring and summer, more excessive NH_3 could continuously react with the increasing TNO_3 (Table S1), leading to the minimal changes in $PM_{2.5}$ pH with elevated TNO_3. Differently, TNH_3 mass concentration was lower in winter and TNO_3 was higher in autumn (Table S1), which made TNH_3 was not excessive enough and resulted in the decreased $PM_{2.5}$ pH with elevated TNO_3.

In the process of increasing NH_3 concentration in the ammonia–nitric acid–sulfuric acid–water system, NH_3 first reacts with sulfuric acid and consumes a large amount of H^+, and then reacts with HNO_3 to produce ammonium nitrate (Seinfeld and Pandis, 2016). After most nitric acid is converted to ammonium nitrate, it is difficult to dissolve more ammonia into aerosol droplet. The sensitivity tests well describe this mechanism. Changes in TNH_3 in the lower concentration range had a significant impact on H_{air}^+ and $PM_{2.5}$ pH, and variations in TNH_3 at higher concentrations could only generate limited pH changes (Figure 7, S11, S14). The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicates that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral.

In this work, $PM_{2.5}$ pH was lowest in summer but highest in winter, which was consistent with the SO_4^{2-} mass fraction with respect to the total ion content. The SO_4^{2-} mass fraction was highest in summer among the four seasons, with a value of 32.4%±11.1%, but lowest in winter, with a value of 20.9%±4.4%. In recent years, the SO_4^{2-} mass fraction in $PM_{2.5}$ in Beijing has decreased significantly due to the strict emission control measures for SO_2; in most cases, NO_3^- dominates the inorganic ions (Zhao et al., 2013, 2017; Huang et al., 2017; Ma et al., 2017), which could reduce aerosol acidity. A study in the Pearl River Delta of China showed that the in situ acidity of $PM_{2.5}$ significantly decreased from 2007-2012; the variation in acidity was mainly caused by the decrease in sulfate (Fu et al.,2015). The excessive NH_3 in the atmosphere and the high NO_3^- mass fraction in $PM_{2.5}$ is the reason why the aerosol acidity in China is lower than that in Europe and the United States (Guo et al., 2017).

Ca^{2+} is an important crustal ion; in the output of ISORROPIA-II, Ca exists mainly as $CaSO_4$ (slightly soluble). Elevated Ca^{2+} concentrations can increase $PM_{2.5}$ pH by decreasing H_{air}^+ and ALWC (Figure 7 and Figure S7-S14). As discussed in Section 3.1, on clean days, $PM_{2.5}$ pH reached 6~7 when the mass fraction of Ca^{2+} was high; hence, the role of crustal ions on $PM_{2.5}$ pH cannot be ignored in areas or seasons (such as spring) in which mineral dust is an important particle source.

Due to the strict control measures for road dust, construction sites, and other bare ground, the crustal ions in $PM_{2.5}$ decreased significantly in the NCP, especially on polluted days.

In addition to the particle chemical composition, meteorological conditions also have important impacts on aerosol acidity. RH had a different impact on $PM_{2.5}$ pH in different seasons (Figure 7, S11, S14). Elevated RH can enhance water uptake and promote gas-to-particle conversion, resulting in the increased H_{air}^+ and ALWC synchronously for all four seasons. Therefore, the effect of RH on $PM_{2.5}$ pH depends on the differences in the degree of RH's effect on H_{air}^+ and RH's effect on ALWC. In winter, elevated RH could reduce $PM_{2.5}$ pH. However, an opposite tendency was observed in summer. In spring and autumn, RH had little impact on $PM_{2.5}$ pH. Temperature can alter the $PM_{2.5}$ pH by affecting gas-particle partitioning. At higher ambient temperatures, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ all showed a decreased tendency (Figure 8, S16). The volatilization of ammonium nitrate and ammonium chloride can result in a net increase in particle H^+ and lower pH (Guo et al., 2018). Moreover, a higher ambient temperature tends to lower ALWC, which can further decrease $PM_{2.5}$ pH.

18. Page 10, line 307. NH3 "binding H+" doesn't really describe the situation, as the NO3 co-condenses with NH3 to form NH4NO3, either if it is in aqueous or solid phase (in the latter, there is no H+ at all).

Response: Please see our response to comment 17.

19. Page 10, line 315. "which might be attributed to limited ALWC". The aerosol has to be acidic for LWC changes to affect pH. So, in this sense, this segment is incorrect and should be deleted.

Response: The statement has been removed from the revised manuscript.

20. Page 10, line 315-318. "Compared … ions". Comparing the aerosol and cloud pH can be discussed in terms of the large difference in LWC. Because of that, ions (like HSO4) tend to become SO4-, but to talk about "hydrolysis" of ammonium salts is, in itself, not relevant here. Unless of course if I misunderstood the authors – in which case they should actually clarify (with calculations and an explanation) about what they mean and support these statements with numbers.

Response: The statement has been removed from the revised manuscript. The reasons why aerosol is acidic is interpreted by thermodynamic equilibrium considerations between NH_4^+ and NH_3 (Line 287-288 in the revised manuscript).

21. Page 10, line 320. "has a role … conversion process". There are very few locations in the lower troposphere where you have free H2SO4 in the air, most of the forms found are either HSO4 or SO4 salts. Therefore, one can claim that HNO3 and sulfates have comparable "H+ generation capacity" at best. However, the main issue is the relative volatility of the species. HNO3 does not by itself form aerosol (at lower tropospheric conditions), while H2SO4, HSO4 and SO4 salts always are in aerosol form. That, together with the large hygroscopicity of SO4 salts (with the exception of CaSO4)

is the reason why sulfate-rich aerosol can be much more acidic than nitrate-dominated aerosol. This is discussed in numerous references (e.g., Guo et al., 2018).

Response: The statement "Compared with NO3-, SO42- has a key role in aerosol acidity due to its stronger ability to provide H+ during the H2SO4→SO42- conversion process" has been removed from the revised manuscript. The reasons why aerosol is acidic is interpreted by the low volatility of SO42-. (Page 10, line 294-295 in the revised manuscript)

22. Page 10, line 330-331. This is an established fact, please cite the appropriate references here.

Response: The reference published by Guo et al. (2017) has been cited here. (Page 10, line 322 in the revised manuscript)

23. Page 10, line 332-334. Although the statement is correct, it does not really describe the situation in the US. In the SE US, for example, the composition of the aerosol is much more like NH4HSO4 than (NH4)2SO4 (e.g., Weber et al., 2016) – especially in current years where SO4 levels are relatively low. Given this, and that the deliquescence humidity of NH4HSO4 is 40%, while for NH4NO3 is 61.8% at 298K (Seinfeld and Pandis, 2016) and the efflorescence point of both salts is very low. Both of these facts suggest that the LWC (per mass of aerosol) in the US should tend to be higher, actually, than for China. Please correct the statement or erase it.

Response: The statement has been removed from the revised manuscript.

24. Page 11, line 344-345. This statement goes against all studies to date that I know of. True, RH increases partitioning of species like HNO3, but that is usually with co-condensation of e.g., NH3. If H+ increased in the aerosol phase, that would in itself promote evaporation of HNO3. Given that, and the very large increase of LWC with RH all point to an increase in pH, or decrease in H+.

Response: This statement has been revised as below. (Page 11, line 331-336 in the revised manuscript)

RH had different impacts on $PM_{2.5}$ pH in different seasons. In winter, elevated RH could reduce $PM_{2.5}$ pH. However, an opposite tendency was observed in summer. In spring and autumn, RH had little impact on $PM_{2.5}$ pH (Figure 7, S11, S14). Elevated RH can enhance water uptake and promote gas-to-particle conversion, resulting in the increased H_{air}^+ and ALWC synchronously for all four seasons. Therefore, the effect of RH on $PM_{2.5}$ pH depends on the differences in the degree of RH's effect on H_{air}^+ and RH's effect on ALWC.

25. Page 11, line 345-350. This discussion has, in my opinion, the flawed approach of decoupling LWC from H+. Both do not vary independently, because of thermodynamic equilibrium considerations. You can make such discussions in the cloudwater pH, because indeed water is not bound to the aerosol through a thermodynamic constraint (aw=RH).

Response: It is not logical to analyze the impact of ALWC on H_{air}^+, owing to these two parameters are both the outputs of model and not independent. We removed this statement.

Please see the response to comment 17 and 24.

26. Page 12, line 380. "in the fine mode … excessive NH3". The reason why under 1um size you tend to have small variations in pH is because the aerosol is in thermodynamic equilibrium with the gas phase. The pH would remain the same even if there isn't any excess NH3 (e.g., Fang et al., 2017). Besides, the authors do not define what "excess NH3" even means.

Response: The interpretation has been revised as you recommended. (Page 11, line 366-368 in the revised manuscript)

27. Page 13, line 422. "In summary…important". This is not a new finding.

Response: The statement emphasizes that higher RH and lower T are typical meteorological characteristics of haze events in the NCP, which are favourable for the formation of secondary particles. The statement has been revised. (Page 13, line 409-411 in the revised manuscript)

28. Page 13, line 447. Replace "decreased" with "increased"?

Response: This is an unclear expression, which has been revised. (Page 13, line 431-432 in the revised manuscript)

29. Page 13, line 447-449. "Excess … United States". This is already known (e.g. Guo et al., 2017), but it is good that the authors also find this.

Response: The work published by Guo et al., (2017) has been added in the revised manuscript. (Page 10, line 322 in the revised manuscript)

30. Page 14, line 454-453. "pH was still … salts". This is a strongly incorrect statement. The reasons (volatility, and thermodynamic equilibrium considerations) should be stated instead.

Response: The revised interpretation is "the $PM_{2.5}$ pH was still acidic because thermodynamic equilibrium between aerosol droplet and precursor gases" (Page 13, line 437 in the revised manuscript)

Aerosol pH and its driving factors in Beijing

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Abstract

Aerosol acidity plays a key role in secondary aerosol formation. The~~ long-term~~ high-temporal resolution $PM_{2.5}$ pH and size-resolved aerosol pH in Beijing were calculated with ISORROPIA-II. In 2016-2017, the mean $PM_{2.5}$ pH (at relative humidity (RH) > 30%) over four seasons was 4.5±0.7 (winter) > 4.4±1.2 (spring) > 4.3±0.8 (autumn) > 3.8±1.2 (summer), showing moderate acidity. In coarse-mode aerosols, Ca^{2+} ~~and Mg^{2+}~~ played an important role in aerosol pH. Under heavily polluted conditions, more secondary ions accumulated ~~on~~in the coarse ~~particles~~mode, leading to ~~a change in~~ the acidity of the coarse ~~particles~~mode aerosols shifted from neutral to weakly acidic. Sensitivity tests also demonstrated the significant contribution of crustal ions to $PM_{2.5}$ pH. In the North China Plain (NCP), the common driving factors affecting $PM_{2.5}$ pH variation in all four seasons were SO_4^{2-}, TNH_3 (total ammonium (gas+aerosol)), and temperature, while the unique factors were Ca^{2+} in spring and RH in summer. ~~Elevated SO_4^{2-} levels can enhance aerosol acidity due to the stronger ability of SO_4^{2-} to provide hydrogen ions.~~ The decreasing SO_4^{2-} and increasing NO_3^- mass fractions in $PM_{2.5}$ as well as excessive NH_3 in the atmosphere in the NCP in recent years are the reasons why aerosol acidity in China is lower than that in Europe and the United States. The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicated that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was still acidic~~, which might be attributed to the limited aerosol liquid water content (ALWC) and hydrolysis of ammonium salts. Elevated RH values can enhance water uptake and promote gas-to-particle conversion. Therefore, the specific impact of RH on $PM_{2.5}$ pH needs to be determined by the degrees of change in H_{air}^+ and ALWC. Gas-particle partitioning sensitivity tests revealed that the typical high RH values and low temperatures during haze events in the NCP are conducive to the formation of secondary particles.~~ because of the thermodynamic equilibrium between NH_4^+ and NH_3. To reduce nitrate by controlling ammonia, the amount of ammonia must be greatly reduced below excessive quantities.

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

1. Introduction

Aerosol acidity has a significant effect on secondary aerosol formation through the gas-aerosol partitioning of semi-volatile and volatile species (Eddingsaas et al., 2010; Surratt et al., 2010; Pathak et al., ~~2011a~~2011; Guo et al., 2016). Studies have shown that aerosol acidity can promote the generation of secondary organic aerosols by affecting aerosol acid-catalysed reactions (Rengarajan et al., 2011). Moreover, metals can become soluble by acid dissociation under low aerosol pH (Shi et al., 2011; Meskhidze et al., 2003; Fang et al., 2017) or by forming ligands with organic species, such as oxalate, at higher pH (Schwertmann et al., 1991). ~~In addition, high aerosol acidity can lower the buffer capacity and affect the formation of acid rain.~~ The investigation of aerosol acidity is conducive to better understanding the important role of aerosols in acid deposition and atmospheric chemical reactions.

Aerosol acidity is frequently estimated by the charge balance of measurable cations and anions ~~in the aerosol liquid phase. A net negative balance is correlated with acidic aerosols and vice versa (Zhang et al., 2007; Pathak et al., 2011b; Zhao et al., 2017). Generally, a larger ion balance value implies stronger acidity or stronger alkalinity. Nevertheless~~. Nevertheless, not all ions (even trace ones) are well constrained in the observations and the dissociation state of multivalent ions are unclear, ion balance and other similar proxies fail to represent the in situ aerosol pH because such metrics cannot accurately predict the H^+ concentration in the aerosol liquid phase (Guo et al., 2015; Hennigan et al., 2015). To better understand the in situ aerosol pH, the aerosol liquid water content (ALWC) and hydrogen ion concentration per volume air (H_{air}^+) should be determined (Guo et al., 2015).

Most inorganic ions and some organic acids in aerosols are water soluble (Peng, 2001; Wang et al., 2017). Since the deliquescence relative humidity (DRH) and the efflorescence relative humidity (ERH) of mixed salts ~~is~~are lower than that of any single component, ambient aerosols are generally in the form of droplets containing liquid water (Seinfeld and Pandis, 2016). ALWC can be derived from hygroscopic growth factors or calculated by thermodynamic models, and good consistencies in ALWC have been found among these methods (Engelhart et al., 2011; Bian et al., 2014; Guo et al., 2015). However, H_{air}^+ can only be obtained by thermodynamic models, which offer a more precise approach to determine aerosol pH (Nowak et al., 2006; Fountoukis et al., 2009; Weber et al., 2016; Fang et al., 2017). Among these thermodynamic models, ISORROPIA-II is widely used owing to its rigorous calculation, performance, and computational speed (Guo et al., 2015; Fang et al., 2017; Liu et al., 2017; Galon-Negru et al., 2018).

The North China Plain (NCP) is the region with the most severe aerosol pollution in China. Nitrate and sulfate are the major contributors to haze, and their secondary formation processes are determined in large part by aerosol pH (Zou et al., 2018; Huang et al., 2017; Gao et al., 2018). Therefore, understanding the aerosol pH level in this region is extremely important and has recently become a trending topic. ~~Some studies conducted~~Fine aerosol pH reported in the NCP ~~showed that the aerosol acidity was close to neutral (Cheng et al., 2016; Wang et al., 2016; Chi et al., 2017),~~

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~~while in some other studies, fine particles showed moderate acidity~~ (Liu et al., 2017; Song et al., 2018; Shi et al., 2017~~). These results all indicated significantly~~ ; Shi et al., 2019) was higher ~~pH values~~ than ~~those~~that found in the United States or Europe, where aerosols are often highly acidic with a pH lower than 3.0 (Guo et al., 2015, 2016; Bougiatioti et al., 2016; Weber et al., 2016; Young et al., 2013). The differences in aerosol pH in the NCP arise from 1) different methods or different model settings, 2) variations in $PM_{2.5}$ chemical composition in the NCP in recent years, 3) the levels of gas precursors of the main water-soluble ions (NH_3, HNO_3, and HCl), and 4) differences in ambient temperature and ~~relative humidity (~~RH~~). In some countries where the particulate matter concentration is very low,~~. Studies demonstrated that pH diurnal variations are ~~mainly~~largely driven by meteorological conditions (Guo et al., 2015, 2016; Bougiatioti et al., 2016). In the NCP, a comprehensive understanding of the impacts of these factors on aerosol pH is still poor.

Additionally, most studies on aerosol pH focus on PM_1 or $PM_{2.5}$. Knowledge regarding size-resolved aerosol pH is still rare~~.~~ (Fang et al., 2017; Craig et al., 2018). Aerosol chemical compositions are different among multiple size ranges. Among inorganic ions, SO_4^{2-}, NO_3^-, Cl^-, K^+, and NH_4^+ are mainly concentrated in the fine mode except on dusty days (Meier et al., 2009; Pan et al., 2009; Tian et al., 2014), whereas Mg^{2+} and Ca^{2+} are abundant in the coarse mode (Zhao et al., 2017). Aerosol pH can be expected to be diverse among different particle sizes; pH levels at different sizes may be associated with different formation pathways of secondary aerosols.

To better understand the driving factors of aerosol acidity, in this work, the thermodynamic model ISORROPIA-II was utilized to predict aerosol pH in Beijing based on a long-term online high-temporal resolution dataset and a size-resolved offline dataset. The hourly measured $PM_{2.5}$ inorganic ions and precursor gases in four seasons from 2016 to 2017 were used to analyse the seasonal and diurnal variations in aerosol acidity; samples collected by multi-stage cascade impactors (MOUDI-120) were used to estimate the pH variations among 10 different size ranges. Additionally, a sensitivity analysis was conducted to identify the key factors affecting aerosol pH and gas-particle partitioning. The main purposes of this work are to 1) obtain the $PM_{2.5}$ pH level based on ~~long-term~~an online ~~aerosol samples~~measurement, contributing towards a global pH dataset; 2) investigate the size-resolved aerosol pH, providing useful information for understanding the formation processes of secondary aerosols; and 3) explore the main factors affecting aerosol pH and gas-particle partitioning, which can help explain the possible reasons for pH divergence in different works and provide a basis for controlling secondary aerosol generation.

2. Data Collection and Methods

2.1 Site

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

2.2 Online data collection

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Water-soluble ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) in $PM_{2.5}$ and gaseous precursors (HCl, HNO_3, HNO_2, SO_2, and NH_3) in ambient air were measured by an online analyser (MARGA) with hourly temporal resolution during spring (April and May 2016), winter (February 2017), summer (July and August 2017), and autumn (September and October 2017). More details about MARGA can be found in Rumsey et al. (2014) and Chen et al. (2017). The $PM_{2.5}$ and PM_{10} mass concentrations (TEOM 1405DF), hourly ambient temperature and RH were also synchronously obtained. The hourly concentrations of $PM_{2.5}$, PM_{10}, and major secondary ions (SO_4^{2-}, NO_3^-, and NH_4^+) in $PM_{2.5}$, as well as meteorological parameters during the observations, are shown in Figure 1. In the spring, two dust events occurred (April 21 and May 6). In the following pH analysis based on MARGA data, it was assumed that the particles were internally mixed; hence, these two dust events were excluded from this analysis.

Figure 1

2.3 Size-resolved chemical composition

A micro-orifice uniform deposit impactor (MOUDI-120) was used to collect size-resolved aerosol samples with 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 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 in summer, autumn, and winter, respectively. Except for two sets of samples, all the samples were collected in daytime (from 08:00 to 19:00) and nighttime (from 20:00 to 7:00 the next day). One hour of preparation time was allowed for filter changing and washing the nozzle plate with ethanol. The water-soluble ions in the samples were analysed by using ion chromatography (DIONEX ICS-1000). Detailed information about the features of MOUDI-120 and the procedures of sampling, pre-treatment, and laboratory chemical analysis (including quality assurance & quality control) were described in our previous papers (Zhao et al., 2017; Su et al., 2018). ~~Gas precursors were not observed during the periods of MOUDI sampling.~~

2.4 Aerosol pH prediction

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

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

where H_{aq}^+ (mole L^{-1}) is the hydronium ion concentration in the ambient particle liquid water. H_{aq}^+ can also be calculated as H_{air}^+ (μg m^{-3}) divided by the concentration of ALWC associated with inorganic species, $ALWC_i$ (μg m^{-3}). Both the inorganic species and part of the organic species in particles are hygroscopic. However, pH prediction is not highly sensitive to water uptake by organic

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species ($ALWC_o$) (Guo et al., 2015, 2016). In recent years, the fraction of organic matter in $PM_{2.5}$ in the NCP was 20%~25%, which is much lower than that in the United States (Guo et al., 2015). In contrast, approximately 50% of $PM_{2.5}$ in the NCP is inorganic ions (Huang et al., 2017; Zhang et al., 2018; Zhang et al., 2019). The results obtained by Liu et al. (2017) in Beijing showed that the mass fraction of organic matter-induced particle water accounted for only 5% of total ALWC, indicating a negligible contribution to aerosol pH. Hence, aerosol pH can be fairly well predicted by ISORROPIA-II with only measurements of inorganic species in most cases. However, potential errors can be incurred by ignoring $ALWC_o$ in regions where hygroscopic organic species have a relatively high contribution to fine particles.

In ISORROPIA-II, forward and reverse modes are provided to predict ALWC and H_{air}^+. In forward mode, T, RH, and the total (*i.e.*, gas+aerosol) concentrations of NH_3, H_2SO_4, HCl, and HNO_3 need to be input. In reverse mode, equilibrium partitioning is calculated given only the concentrations of aerosol components, RH, and T as input. In this work, the online ion chromatography system MARGA was used to measure both inorganic ions in $PM_{2.5}$ and gaseous precursors. Moreover, the forward mode has been reported to be less sensitive to measurement error than the reverse mode (Hennigan et al., 2015; Song et al., 2018). Hence, ISORROPIA-II was run in forward mode for aerosols in the metastable conditions in this study.

When using ISORROPIA-II to calculate the $PM_{2.5}$ acidity, all particles were assumed to be internally mixed, and the bulk properties were used without considering the variability in chemical composition ~~with~~at a given particle size. In the ambient atmosphere, the aerosol chemical composition is complicated; hence, the deliquescence relative humidity (DRH) of aerosols is generally low (Seinfeld and Pandis, 2016~~), and 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 particles are exposed to a substantially low RH, the state of the particles may change.~~). Once the particles are deliquescent, crystallization only occurs at a very low RH, which is called hysteresis phenomenon. The efflorescence RH (ERH) of a salt cannot be calculated from thermodynamic principles; rather, it must be measured in the laboratory. For a particle consisting of approximately 1:1 $(NH_4)_2SO_4$: NH_4NO_3, the ERH is around 20%, while for a 1:2 molar ratio it decreases to around 10%. (Shaw and Rood 1990). Recently, NO_3^- dominates the particles in the NCP (Zhao et al., 2013, 2017; Huang et al., 2017; Ma et al., 2017); therefore, we assumed that the particles are in a liquid state (metastable condition). Assumption that particles are in metastable were adopted by numerous studies in the NCP (Liu et al., 2017; Guo et al., 2017; Shi et al., 2017; Shi et al., 2019). Figure 2 and Figure S1-S4 show comparisons between the predicted and measured NH_3, HNO_3, HCl, NH_4^+, NO_3^-, Cl^-, $\varepsilon(NH_4^+)$ ($NH_4^+/(NH_3+NH_4^+)$, mol/mol), $\varepsilon(NO_3^-)$ ($NO_3^-/(HNO_3+NO_3^-)$, mol/mol)), and $\varepsilon(Cl^-)$ ($Cl^-/(HCl+Cl^-)$, mol/mol) based on real-time ion chromatography data; all results are coloured with the corresponding RH. The predicted and measured NH_3, NH_4^+, NO_3^-, and Cl^- values are in good agreement: the R^2 values of linear regressions are all higher than 0.94, and the slopes are approximately 1. Moreover, the agreement between the predicted and measured ε(NH_4^+) is better than those of ε(NO_3^-) and ε(Cl^-). The slope of the linear regression between the predicted and measured ε(NH_4^+) was 0.93, 0.91, 0.95, and 0.96 and R^2 was 0.87, 0.93, 0.89, and 0.97 in spring, winter, summer, and autumn, respectively. However, the measured and predicted partitioning of HNO_3 and HCl show significant discrepancies (R^2 values of 0.28 and 0.18, respectively), which may be attributed to the much lower gas concentrations than particle concentrations, as well as the HNO_3 and HCl measurement uncertainties from MARGA (Rumsey et al., 2014). Clearly, more scatter points deviate from the 1:1 line when ISORROPIA-II is operated at RH≤30%, which is highly evident in winter and spring. ~~For data with~~ It should be noted that when RH ~~≤ 30%,~~is low, ALWC becomes very small, $PM_{2.5}$ pH is subject to considerably more uncertain. Guo et al. (2017) suggest that the lower RH limit is about 40%. In this work, due to the overall good agreement between predictions ~~are significantly improved when assuming the aerosols are in stable mode (solid + liquid) (Figure S5-S6)~~ and ~~the aerosol liquid water is almost zero and cannot be used to predict aerosol pH. This behaviour reveals that it is not reasonable to predict aerosol pH using the thermodynamic model~~measurements when ~~the RH is relatively low. Consequently,~~ RH was high than 30%,we only determined the $PM_{2.5}$ pH for data with RH ~~values~~ higher than 30~~% in this work.~~%.

Figure 2

Running ISORROPIA-II in the forward mode with only aerosol component concentrations as input may result in a bias in predicted pH due to repartitioning of ammonia in the model, leading to a lower predicted pH when gas-phase data are not available (Hennigan et al., 2015). ~~In this work, no gas phase was available for size-resolved pH prediction. We determined aerosol pH through an iteration procedure that used the measured particulate species and ISORROPIA-II to predict gas species. Detailed information can be found in Fang et al. (2017) and Guo et al. (2016). In summary, the predicted NH_3, HNO_3, and HCl concentrations from the *i*-1th run were applied to the *i*th iteration until the gas concentrations converged. Based on these iterative gas-phase concentrations, the~~In this work, no synchronous gas phase was available during the MOUDI sampling periods, the gas-phase measurements that were taken by the MARGA in 2017 were therefore applied. Even if the periods are not perfectly aligned, the order of magnitude of NH_3, HNO_3 and HCl during a certain period does not change drastically. Guo et al. (2017) found that even if there is some error in NH_3, pH is less sensitive to it, a factor of 10 change in NH_3 is required to change pH by one unit. Averaged NH_3, HNO_3 and HCl measured by MARGA matched to $PM_{2.5}$ mass concentration levels during the MOUDI sampling periods, together with ion concentrations of samples collected by MOUDI as well as the average RH and T during each sampling period were used to determine the aerosol pH for different size ranges. Similar to calculating the $PM_{2.5}$ pH, it was assumed that all the particles in each size bin were internally mixed and had the same pH.

Comparisons of the ~~iterative and predicted NH_3, HNO_3, and HCl as well as the~~ measured and predicted NO_3^-, NH_4^+, Cl^-~~, ε(NH_4^+), ε(NO_3^-), and ε(Cl^-);~~ for MOUDI samples are shown in Figure 3. ~~A previous study showed that coarse-mode particles could not easily reach equilibrium with~~

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~~gaseous precursors due to kinetic limitations (Dassios et al., 1999; Cruz et al., 2000). Assuming that coarse-mode particles are in equilibrium with the gas phase could result in a large bias between the measured and predicted NO_3^- and NH_4^+ in coarse-mode particles (Fang et al., 2017). Additionally, in this work, assuming that coarse-mode particles are in equilibrium with the gas phase could over-predict NO_3^- and Cl^- and underestimate NH_4^+ in the coarse mode (blue scatters), which could subsequently underestimate the coarse-mode aerosol pH. In contrast to the coarse-mode particles, the measured~~ 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~~ slopes are approximately 1. In the coarse-mode~~ particles, the aerosol pH in~~, the ~~coarse mode~~predicted NH_4^+ was ~~determined by ignoring the gas phase~~lower than the measured NH_4^+ due to the impact of crustal ions.

Figure 3

2.5 Sensitivity of PM$_{2.5}$ pH to SO_4^{2-}, TNO_3, TNH_3, Ca^{2+}, RH, and T

To explore the major influencing factors on aerosol pH, sensitivity tests were performed. In the sensitivity analysis, SO_4^{2-}, TNO_3 (total nitrate (gas+aerosol) expressed as equivalent HNO_3), TNH_3 (total ammonium (gas+aerosol) expressed as equivalent NH_3), Ca^{2+}, RH, and T were selected as the variables since SO_4^{2-} and NO_3^- are major anions in aerosols, NH_4^+ and Ca^{2+} are major cations in aerosols, and Ca^{2+} is generally considered representative of crustal ions. To assess how a variable affects PM$_{2.5}$ pH, the real-time measured values of this variable and the average values of other ~~variables~~species (K, Na, Mg, and total chloride (gas+aerosol) were also included) in each season were input into ISORROPIA-II. The magnitude of the relative standard deviation (RSD) of the calculated aerosol pH can reflect the impact of variable variations on aerosol acidity. The higher the RSD is, the greater the impact, and vice versa. The average value and variation range for each variable in the four seasons are listed in Table S1.

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

3. Results and Discussion

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

The average mass concentrations of PM$_{2.5}$ and major inorganic ions in the four seasons are shown in Table 1. Among all the ions measured, NO_3^-, SO_4^{2-}, and NH_4^+ were the three most dominant species, accounting for 83% ~ 87% of the total ion content. The average concentrations of primary inorganic ions (Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+}) were higher in spring than in other seasons. PM$_{2.5}$ in Beijing showed moderate acidity, with PM$_{2.5}$ pH values of 4.4±1.2, 4.5±0.7, 3.8±1.2, and 4.3±0.8 for spring, winter, summer, and autumn observations, respectively (data at RH $\leq$30% were excluded). The overall winter PM$_{2.5}$ pH was comparable to the result (4.2) found in Beijing by Liu et al. (2017)

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and that (4.5) found by Guo et al. (2017), but lower than that (4.9, winter and spring) in Tianjin (Shi et al., 2017), another mega city approximately 120 km away from Beijing. The $PM_{2.5}$ pH in summer was lowest among all four seasons. The seasonal variation in $PM_{2.5}$ pH in this work was similar to the results in Tan et al. (2018), except for spring, and followed the trend winter (4.11 ± 1.37) > autumn (3.13 ± 1.20) > spring (2.12 ± 0.72) > summer (1.82 ± 0.53).

Table 1

To further investigate the $PM_{2.5}$ pH level under different pollution conditions over four seasons, the $PM_{2.5}$ concentrations were classified into three groups: 0~75 μg m^{-3}, 75~150 μg m^{-3}, and >150 μg m^{-3}, representing clean, polluted, and heavily polluted conditions, respectively. The relationship between $PM_{2.5}$ concentration and pH is shown in Figure ~~S7~~S5. The $PM_{2.5}$ pH under clean conditions spanned 2~7, while those under polluted and heavily polluted conditions was mostly concentrated from 3~5. Table 1 shows that as the air quality deteriorated, the aerosol component concentration, as well as ALWC and H_{air}^+, all increased in each season. The average $PM_{2.5}$ pH under clean conditions was the highest (Table 1), followed by polluted and heavily polluted conditions in spring, summer, and autumn. In winter, however, the average pH under polluted conditions (4.8±1.0) was the highest.

On clean days, ~~a~~some higher $PM_{2.5}$ pH values (>6) ~~was~~appeared and were generally accompanied by ~~a~~ higher mass fraction of crustal ions (Mg^{2+} and Ca~~$^{2+}$), while a~~$^{2+}$). In contrast, lower $PM_{2.5}$ pH (<3) was often accompanied by a higher mass fraction of SO_4^{2-} and lower mass fraction of crustal ions~~;~~, such conditions were most obvious in summer (Figure 4). Under polluted and heavily polluted conditions, the mass fractions of major chemical components were similar, and the difference in $PM_{2.5}$ pH between these two conditions was also small. All of these results indicated that the aerosol chemical composition ~~might~~should be ~~the~~an essential factor that drives aerosol acidity. The impact of aerosol composition on $PM_{2.5}$ pH is discussed in Section 3.4.

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Figure 4

In spring, summer, and autumn, the pH of $PM_{2.5}$ from the northern direction was generally higher than that from the southwest direction, ~~but~~and the higher pH in summer also occurred with strong southwest winds (wind speed >3 m s^{-1}) (Figure 5). Generally, northern winds occur with cold-front systems, which can sweep away air pollutants but raise dust in which the crustal ion species (Ca^{2+}, Mg^{2+}) are higher. In winter, the $PM_{2.5}$ pH was distributed relatively evenly in all wind directions, but we surprisingly found that the pH in northerly winds on clean days could be as low as 3~4, which was consistent with the high mass fraction of SO_4^{2-}~~ on clean days caused by the northern winds.~~.

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Figure 5

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

Obvious diurnal variation was observed based on the long-term online dataset, as shown in Figure 6. To understand the factors that can drive changes in $PM_{2.5}$ pH, the diurnal variations of NO_3^-, SO_4^{2-}, ALWC, and H_{air}^+ were investigated and are exhibited in Figure 6. Generally, ALWC was higher

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during nighttime than daytime and reached a peak near 04:00 ~ 06:00 (local time). After sunrise, the increasing temperature resulted in a rapid drop in RH, leading to a clear loss of particle water, and ALWC reached the lowest level in the afternoon. H_{air}^+ was highest in the afternoon, followed by nighttime, and H_{air}^+ was relatively low in the morning. The low ALWC and high H_{air}^+ values in the afternoon resulted in the minimum $PM_{2.5}$ pH ~~at this time~~. The average nighttime pH was 0.3~0.4 units higher than that during daytime. ~~The~~From the above discussion, we found that both H_{air}^+ and ALWC had significant diurnal variations ~~in~~ , which means that besides chemical composition, the $PM_{2.5}$ pH diurnal variation was also affected by meteorological conditions. This trend is slightly different from the situation from the US: Guo et al. (2015) found that the ALWC diurnal variation was significant and the diurnal pattern in pH was mainly driven by the dilution of aerosol water.~~described here were determined for the cases with an RH higher than 30%.~~

The correlation between NO_3^- concentration and $PM_{2.5}$ pH was weakly positive at low ALWC, and $PM_{2.5}$ pH was almost independent of the NO_3^- mass concentration at higher ALWC values (Figure ~~S8~~S6). In contrast, at a low ALWC level, increasing SO_4^{2-} decreased the pH; at a high ALWC level, a negative correlation still existed between SO_4^{2-} mass concentration and $PM_{2.5}$ pH. SO_4^{2-} had a greater effect than NO_3^- on $PM_{2.5}$ pH.

Figure 6

~~From the above discussion, we found that both H_{air}^+ and ALWC had significant diurnal variations, indicating that aerosol acidity in the NCP was driven by both aerosol composition and particle water. This trend is slightly different from the situation from the US: Guo et al. (2015) found that the ALWC diurnal variation was significant and the diurnal pattern in pH was mainly driven by the dilution of aerosol water. Specifically, in winter, the $PM_{2.5}$ mass concentration in Beijing was several times or even dozens of times higher than that in the US, and the RH was generally low, which means there were more seeds in the limited particle water. Hence, the dilution of H_{air}^+ by aerosol liquid water was quite limited in winter.~~

3.3 Factors affecting $PM_{2.5}$ pH

In this work, the effects of SO_4^{2-}, TNO_3, TNH_3, Ca^{2+}, RH, and T on $PM_{2.5}$ pH were determined through a four-season sensitivity analysis. The common important driving factors affecting $PM_{2.5}$ pH variations in all four seasons were SO_4^{2-}, TNH_3, and T (Table 2), while the unique influencing factors were Ca^{2+} in spring and RH in summer. For ALWC, the most important factor was RH, followed by SO_4^{2-} or NO_3^-. Figure 7 and Figure ~~S9-S16~~S7-S14 show how these factors affect the $PM_{2.5}$ pH, ALWC, and H_{air}^+ over all four seasons.

Table 2

~~Theoretically, elevated TNO_3~~H_2SO_4 can ~~reduce $PM_{2.5}$ pH since~~ be completely dissolved in ALWC and in the form of sulfate. As shown in Table 3, HNO_3~~$\rightarrow NO_3^-$~~ also had a high conversion ~~process can release H^+. However, in~~rate to nitrate when RH>30%. Under rich-ammonia conditions (defined and explained in Figure S15), sulfate and nitrate mostly exist in aerosol phase with ammonium. The thermodynamic equilibrium between NH_4^+ and NH_3 makes aerosol acidic (Weber et al., 2016). In

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the sensitivity tests, we found that elevated SO_4^{2-} is crucial in the increase of H_{air}^+ (Figure S7, S9, S12) and ALWC (Figure S8, S10, S13), and has a key role in aerosol acidity (Figure 7, S11, S14). However, only the $PM_{2.5}$ pH in winter and autumn decreased significantly with elevated TNO_3 (Figure 7, ~~S16~~S14). In spring and summer, $PM_{2.5}$ pH changed little with elevated TNO_3. Moreover, when the TNO_3 concentration was low, $PM_{2.5}$ pH even increased with elevated TNO_3 (Figure 7, ~~S13~~S11). The ~~phenomenon was mainly due to the rich-ammonia condition in the NCP (Figure S18). The sensitivity tests showed that elevated TNH_3 could consume~~ effect of TNO_3 on H_{air}^+ ~~swiftly~~ and ALWC is similar to that of SO_4^{2-}, that is, the elevated TNO_3 will also result in the increase ~~the~~ of H_{air}^+ and ALWC. The difference is that SO_4^{2-} can lead to much higher concentration of H_{air}^+ than TNO_3 due to its low volatility (Figure S7, S9, S12). Thus, the sensitivity of $PM_{2.5}$ pH~~. In this work, the lower TNH_3 mass concentration in winter and higher TNO_3 mass concentration in autumn (Table S1) resulted in decreased $PM_{2.5}$ pH with elevated TNO_3. In~~ to TNO_3 is less than that to SO_4^{2-}. Moreover, in spring and summer, more excessive NH_3 could continuously ~~buffer~~react with the increasing TNO_3~~,~~ (Table S1), leading to the minimal changes in $PM_{2.5}$ pH~~,~~ with elevated TNO_3. Differently, TNH_3 mass concentration was lower in winter and TNO_3 was higher in autumn (Table S1), which made TNH_3 was not excessive enough and resulted in the decreased $PM_{2.5}$ pH with elevated TNO_3.

In the process of increasing NH_3 concentration in the ammonia–nitric acid–sulfuric acid–water system, NH_3 first reacts with sulfuric acid and consumes a large amount of H^+, and then reacts with HNO_3 to produce ammonium nitrate (Seinfeld and Pandis, 2016). After most nitric acid is converted to ammonium nitrate, it is difficult to dissolve more ammonia into aerosol droplet. The sensitivity tests well describe this mechanism. Changes in TNH_3 in the lower concentration range had a significant impact on H_{air}^+ and $PM_{2.5}$ pH, and ~~changes~~variations in TNH_3 at higher concentrations could only generate limited pH changes (Figure 7, ~~S13, S16~~S11, S14). The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicates that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was far from neutral~~, which might be attributed to the limited ALWC. Compared to the liquid water content in clouds and precipitation, the ALWC was much lower; hence, the dilution of H_{air}^+ by aerosol liquid water was limited. Moreover, the hydrolysis of ammonium salts contributes to the release of hydrogen ions.~~

Figure 7

~~Compared with NO_3^-, SO_4^{2-} has a key role in aerosol acidity due to its stronger ability to provide H^+ during the $H_2SO_4 \rightarrow SO_4^{2-}$ conversion process (Figure S9, S11, S14). Hence, elevated SO_4^{2-} is crucial in the increase of H_{air}^+.~~ In this work, $PM_{2.5}$ pH was lowest in summer but highest in winter, which was consistent with the SO_4^{2-} mass fraction with respect to the total ion content. The SO_4^{2-} mass fraction was highest in summer among the four seasons, with a value of 32.4%±11.1%, but lowest in winter, with a value of 20.9%±4.4%. In recent years, the SO_4^{2-} mass fraction in $PM_{2.5}$ in Beijing has decreased significantly due to the strict emission control measures for SO_2; in most

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cases, NO_3^- dominates the inorganic ions (Zhao et al., 2013, 2017; Huang et al., 2017; Ma et al., 2017), which could reduce aerosol acidity. A study in the Pearl River Delta of China showed that the in situ acidity of $PM_{2.5}$ significantly decreased from 2007-2012; the variation in acidity was mainly caused by the decrease in sulfate (Fu et al.,2015). The excessive NH_3 in the atmosphere and the high NO_3^- mass fraction in $PM_{2.5}$ ~~may be~~is the reason why the aerosol acidity in China is lower than that in Europe and the United States~~. In addition, the DRH of NH_4NO_3 is lower than that of $(NH_4)_2SO_4$ (Seinfeld and Pandis, 2016); hence, the particles dominated by NH_4NO_3 can deliquesce at lower RH, which may result in the increase in ALWC.~~ (Guo et al., 2017).

Ca^{2+} is an important crustal ion; in the output of ISORROPIA-II, Ca exists mainly as $CaSO_4$ (slightly soluble). Elevated Ca^{2+} concentrations can increase $PM_{2.5}$ pH by decreasing H_{air}^+ and ALWC (Figure 7 and Figure ~~S9-S16~~S7-S14). As discussed in Section 3.1, on clean days, $PM_{2.5}$ pH reached 6~7 when the mass fraction of Ca^{2+} was high; hence, the role of crustal ions on $PM_{2.5}$ pH cannot be ignored in areas or seasons (such as spring) in which mineral dust is an important particle source. Due to the strict control measures for road dust, construction sites, and other bare ground, the crustal ions in $PM_{2.5}$ decreased significantly in the NCP, especially on polluted days.

In addition to the particle chemical composition, meteorological conditions also have important impacts on aerosol acidity. RH had ~~a~~ different ~~impact~~impacts on $PM_{2.5}$ pH in different seasons~~. Elevated RH can enhance water uptake and promote gas-to-particle conversion.~~ (Figure 7, S11, S14). In winter, ~~the H_{air}^+ increase caused by elevated RH was much larger than the increase in ALWC; hence,~~ elevated RH could reduce $PM_{2.5}$ pH. However, an opposite tendency was observed in summer ~~due to the lower mass concentration of chemical components, and the dilution effect of ALWC on H_{air}^+ was obvious only in summer (Figure 7).~~. In spring and autumn, RH had little impact on $PM_{2.5}$ pH~~ due~~. Elevated RH can enhance water uptake and promote gas-to-~~-~~particle conversion, resulting in the ~~synchronous variation in~~ increased H_{air}^+ and ALWC ~~(Figure S13, S16). The different impacts~~synchronously for all four seasons. Therefore, the effect of RH on $PM_{2.5}$ pH ~~indicated that the higher~~ depends on the differences in the degree of RH's effect on H_{air}^+ and RH~~ during severe haze may increase aerosol acidity~~'s effect on ALWC. Temperature can alter the $PM_{2.5}$ pH by affecting gas-particle partitioning. At higher ambient temperatures, $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$, and $\varepsilon(Cl^-)$ all showed a decreased tendency (Figure 8, S16). The volatilization of ammonium nitrate and ammonium chloride can result in a net increase in particle H^+ and lower pH (Guo et al., 2018). Moreover, a higher ambient temperature tends to lower ALWC, which can further decrease $PM_{2.5}$ pH.

Figure 8

3.4 Size~~ distribution of~~-resolved aerosol pH~~ values~~

Inorganic ions in particles present clear size distributions, and the size-resolved chemical composition can change at different pollution levels (Zhao et al., 2017; Ding et al., 2017; Ding et al., 2018), which may result in variations in aerosol pH. Thus, we further investigated the size-resolved aerosol pH at different pollution levels. According to the average $PM_{2.5}$ concentration

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

Figure 9

The aerosol pH in both~~ the~~ fine mode and coarse mode was lowest in summer among the three seasons, followed by autumn and winter. The seasonal variation in aerosol pH derived from MOUDI data was consistent with that derived from the real-time $PM_{2.5}$ dataset. In summer, the predominance of sulfate in ~~the ~~fine mode and high ambient temperature resulted in a low pH, ranging from ~~1.8~~3.2 to 3.9. The fine-mode aerosol pH in autumn and winter was in the range of 3.9 ~ 5.2~~.4 ~ 6.3~~ and ~~3.5 ~ 6.~~4.7 ~ 5.7, respectively. ~~In~~The fine-mode aerosol pH was overall comparable to the $PM_{2.5}$ pH. Moreover, in the fine mode, the difference in aerosol pH among size bins was not significant~~, probably owing to the excessive NH_3 (Guo~~ because the aerosol is in thermodynamic equilibrium with the gas phase (Fang et al., 2017). Additionally, the size distributions of aerosol pH in the daytime and nighttime were explored and are illustrated in Figure ~~S19~~S17. In summer and autumn, the pH in the daytime was lower than that in the nighttime, while in winter, the pH was higher in the daytime. During the winter sampling periods, SO_4^{2-} ~~and NO_3^-~~mass fraction were obviously higher in the nighttime and led to abundant H_{air}^+~~ in the nighttime.~~$^+$.

The abundance of Ca^{2+} ~~and Mg^{2+}~~ in the coarse mode led to a predicted ~~coarse particle~~aerosol pH approximately at or higher than 7 ~~for all three seasons.~~in autumn and winter. Even if the coarse mode Ca^{2+} mass concentration in the summer was low, the coarse mode aerosol pH was still more than 1 unit higher than the fine mode aerosol pH. The difference in aerosol pH (with and without Ca^{2+}~~ and Mg^{2+}~~) increased with increasing particle size above 1 μm (Figure ~~S20~~S18). Moreover, the coarse-mode aerosols during severely hazy days shifted from neutral to weakly acidic, especially in autumn and winter. As shown in Figure 9, the pH in stage 3 (3.1-6.2 μm) declined from 7.~~8~~4 (clean) to ~~4.~~5.0 (heavily polluted) in winter. The significant decrease in the mass ~~ratios~~ratio of Ca^{2+} ~~and Mg^{2+}~~ in the coarse mode particles on heavily polluted days resulted in the loss of acid-buffering capacity. Furthermore, the different size-resolved aerosol acidity levels may be associated with different generation pathways of secondary aerosols. According to Cheng et al. (2017) and Wang et al. (2017), the aqueous oxidation of SO_2 by NO_2 is key in sulfate formation under a high RH and

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neutral conditions. However, it is speculated that dissolved metals or HONO may be more important for secondary aerosol formation under acidic conditions.

3.5 Factors affecting gas-particle partitioning

Gas-particle partitioning can be directly affected by the concentration levels of gaseous precursors and meteorological conditions. In this work, sensitivity tests showed that decreasing TNO_3 lowered ε(NH_4^+) effectively, which helped maintain NH_3 in the gas phase. Elevated TNH_3 can increase ε(NO_3^-) when TNO_3 is fixed, which means that the elevated TNH_3 altered the gas-particle partitioning and shifted more TNO_3 into the particle phase, leading to an increase in nitrate (Figure 8 and ~~S17~~S16). Controlling the emissions of both NO_x (gaseous precursor of NO_3^-) and NH_3 are efficient ways to reduce NO_3^-. However, the relationship between TNH_3 and ε(NO_3^-) in the sensitivity tests (Figure 8 and ~~S17~~S16) showed that the ε(NO_3^-) response to TNH_3 control was highly nonlinear, which means that a decrease in nitrate would happen only when TNH_3 is greatly reduced. The same result was also obtained from a study by Guo et al. (2018). The main sources of NH_3 emission are agricultural fertilization, livestock, and other agricultural activities, which are all associated with people's livelihoods. Therefore, in terms of controlling the generation of nitrate, a reduction in NO_x emissions is more feasible than a reduction in NH_3 emissions.

RH and temperature can also alter gas-particle partitioning. The equilibrium constants for solutions of ammonium nitrate or ammonium chloride are functions of T and RH. The measurement data also showed that lower T and higher RH contribute to the conversion of more TNH_3, TNO_3, and TCl into the particle phase (Table 3). When the RH exceeded 60%, more than 90% of TNO_3 was in the particle phase for all four seasons. In summer and autumn, ~~lower RH was generally accompanied by higher ambient temperature, and~~ more than half of the TNO_3 and TCl were partitioned into the gaseous phase~~.~~ at lower RH conditions (≤30%). In ~~contrast, in~~ winter~~ and spring~~, low temperatures favoured the ~~reduction~~existence of NO_3^- and ~~volatilization of~~ Cl^-~~;~~ in aerosol phase, and ε(NO_3^-) and ε(Cl^-) were higher than ~~65~~75%, even at low RH~~;~~, ε(NH_4^+) was lower than ε(NO_3^-) and ε(Cl^-). In spring, summer, and autumn, the average ε(NH_4^+) was still lower than 0.3 even when the RH was >60%; this trend was associated with excess NH_3 in the NCP. ~~In summary, higher~~Higher RH and lower temperature are ~~favourable conditions for the formation of secondary particles, which are~~ typical meteorological characteristics of haze events in the NCP (Figure 1~~); hence, gaseous precursor emission control is crucially important~~), which are favourable conditions for the formation of secondary particles.

Table 3.

5. Summary and Conclusions

Long-term high-temporal resolution $PM_{2.5}$ pH and size-resolved aerosol pH in Beijing were calculated with ISORROPIA-II. ~~The model validation results indicated that it is not reasonable to assume aerosols are in a liquid state (metastable) when the RH is lower than 30%.~~ In 2016-2017 in Beijing, the mean $PM_{2.5}$ pH (RH>30%) over four seasons was 4.5±0.7 (winter) > 4.4±1.2 (spring) > 4.3±0.8 (autumn) > 3.8±1.2 (summer), showing moderate acidity. In this work, both H_{air}^+ and ALWC

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had significant diurnal variations, indicating that aerosol acidity in the NCP was driven by both aerosol composition and meteorological conditions. The average $PM_{2.5}$ nighttime pH was 0.3~0.4 units higher than that in the daytime. The $PM_{2.5}$ pH in northerly wind was generally higher than that in wind from the southwest. Size-resolved aerosol pH analysis showed that the coarse-mode aerosol pH was approximately equal to or even higher than 7 ~~for all three seasons~~in winter and autumn, which was considerably higher than the ~~pH of~~ fine ~~particles.~~mode aerosol pH. The presence of Ca^{2+} ~~and Mg^{2+}~~ had a crucial effect on coarse-mode aerosol pH. Under heavily polluted conditions, the mass fractions of Ca^{2+} ~~and Mg^{2+}~~ in coarse particles decreased significantly, resulting in an evident increase in the ~~acidity of the~~ coarse ~~particles~~mode aerosol acidity. The $PM_{2.5}$ pH sensitivity tests also showed that when evaluating aerosol acidity, the role of crustal ions cannot be ignored in areas or seasons (such as spring) where mineral dust is an important particle source. In northern China, dust can effectively buffer aerosol acidity ~~in aerosols or precipitation~~.

The sensitivity tests in this work showed that the common important driving factors affecting $PM_{2.5}$ pH are SO_4^{2-}, TNH_3, and T, while unique influencing factors were Ca^{2+} in spring and RH in summer. ~~In recent years, NO_3^- has generally dominated the inorganic ions in the NCP. However, owing~~Owing to the significantly rich ~~ammonia content~~NH_3 in the atmosphere, the change in ~~the atmosphere in spring and summer, the~~ $PM_{2.5}$ pH ~~in only winter and autumn decreased obviously~~was not significant with the elevated TNO_3~~.~~, especially in spring and summer. Excess NH_3 in the atmosphere and a high NO_3^- mass fraction in $PM_{2.5}$ ~~may be~~is the reason why aerosol acidity in China is lower than that in Europe and the United States. Notably, TNH_3 had a great influence on aerosol acidity at lower concentrations but had a limited influence on $PM_{2.5}$ pH when present in excess. The nonlinear relationship between $PM_{2.5}$ pH and TNH_3 indicated that although NH_3 in the NCP was abundant, the $PM_{2.5}$ pH was still acidic~~, which might be attributed to the limited ALWC and the hydrolysis of ammonium salts~~ due to the thermodynamic equilibrium between aerosol droplet and precursor gases. Higher ambient temperature could reduce the $PM_{2.5}$ pH by increasing ammonium evaporation and decreasing ALWC. RH had different impacts on $PM_{2.5}$ pH in different seasons, which depends on the differences in the degree of RH's effects on H_{air}^+ and RH's effects on ALWC.

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

In recent years, nitrates have dominated $PM_{2.5}$ in the NCP, especially on heavily polluted days. Sensitivity tests showed that decreasing TNO_3 and TNH_3 could lower $\varepsilon(NH_4^+)$ and ~~that decreasing TNH_3 could also lower~~ $\varepsilon(NO_3^-)$, helping to reduce nitrate production. However, the $\varepsilon(NO_3^-)$ response to TNH_3 control was highly nonlinear. Given that ammonia was excessive in most cases, a decrease

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in nitrate would occur only if TNH_3 were greatly reduced. Therefore, in terms of controlling the generation of nitrate, a reduction in NO_x emissions is more feasible than a reduction in NH_3 emissions.

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 analysed the chemical compositions of size-resolved aerosol samples. J D and P Z wrote the manuscript.

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

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

Table 2. Sensitivity of $PM_{2.5}$ pH to SO_4^{2-}, TNH_3, TNO_3, Ca^{2+}, RH, and T. A larger magnitude of the relative standard deviation (RSD) represents a larger impact derived from variations in variables.

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

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Table 1

Spring	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}	
Average	57±42	12.6±14.2	8.4±7.7	6.7±7.2	21±33	3.7E-06±1.5E-05	4.4±1.2
Clean	39±19	6.6±6.5	5.4±3.8	3.6±3.2	13±23	3.2E-06±1.9E-05	4.6±1.4
Polluted	101±21	30.7±14.3	16.2±6.2	15.3±6.0	33±36	3.1E-06±2.9E-06	4.1±0.4
Heavily polluted	199±62	36.4±19.8	29.3±14.0	23.2±12.3	78±60	1.6E-05±5.4E-06	3.7±0.3
Winter	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Average	60±69	13.7±21.0	7.3±8.7	7.3±10.0	35±46	2.2E-05±2.3E-04	4.5±0.7
Clean	22±20	3.6±3.9	2.8±1.8	2.2±2.0	10±16	3.2E-07±4.8E-07	4.5±0.6
Polluted	107±21	18.9±8.6	11.0±5.7	11.0±4.7	41±45	1.9E-05±9.1E-05	4.8±1.0
Heavily polluted	209±39	59.7±21.8	26.2±6.3	29.1±8.7	80±52	7.0E-05±4.7E-04	4.4±0.7
Summer	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Average	39±24	9.5±9.5	8.6±7.5	7.2±5.6	50±68	1.6E-05±1.8E-05	3.8±1.2
Clean	33±18	7.3±6.8	7.0±6.0	5.9±4.0	42±61	1.4E-05±1.6E-05	3.8±1.2
Polluted	87±13	26.5±10.5	20.7±7.0	17.6±4.8	100±88	3.1E-05±2.0E-05	3.5±0.4
Autumn	$PM_{2.5}$	NO_3^-	SO_4^{2-}	NH_4^+	ALWC*	H_{air}^{+*}	pH*
Average	59±48	18.5±19.5	6.5±5.9	8.2±8.2	109±160	8.1E-06±1.1E-05	4.3±0.8
Clean	33±21	7.6±7.4	4.4±4.1	3.8±3.5	49±83	3.8E-06±6.6E-06	4.5±1.0
Polluted	105±21	33.8±11.6	14.3±6.3	16.0±4.6	225±189	1.7E-05±1.2E-05	4.1±0.3
Heavily polluted	174±18	63.4±15.4	25.0±15.9	29.0±5.1	317±236	2.2E-05±1.0E-05	4.1±0.2

[*] For data with RH>30%.

Table 2

Impact Factor	SO_4^{2-}	TNO_3	TNH_3	Ca^{2+}	RH	T
Spring- RSD	12.4%	5.2%	3.9%	7.5%	1.3%	7.0%
Winter- RSD	28.1%	8.4%	27.0%	1.0%	4.1%	6.7%
Summer- RSD	7.9%	3.6%	8.1%	1.9%	8.6%	5.8%
Autumn- RSD	6.0%	3.3%	16.1%	0.8%	2.4%	7.5%

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Table 3

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

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

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

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

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

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

Figure 7. Sensitivity tests of $PM_{2.5}$ pH to SO_4^{2-}, TNO_3, TNH_3, Ca^{2+}, and meteorological parameters (RH and T) in summer (S) and winter (W).

Figure 8. Sensitivity tests of $\varepsilon(NH_4^+)$, $\varepsilon(NO_3^-)$ to TNO_3, TNH_3, RH and T coloured by $PM_{2.5}$ pH in summer (S) and winter (W).

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

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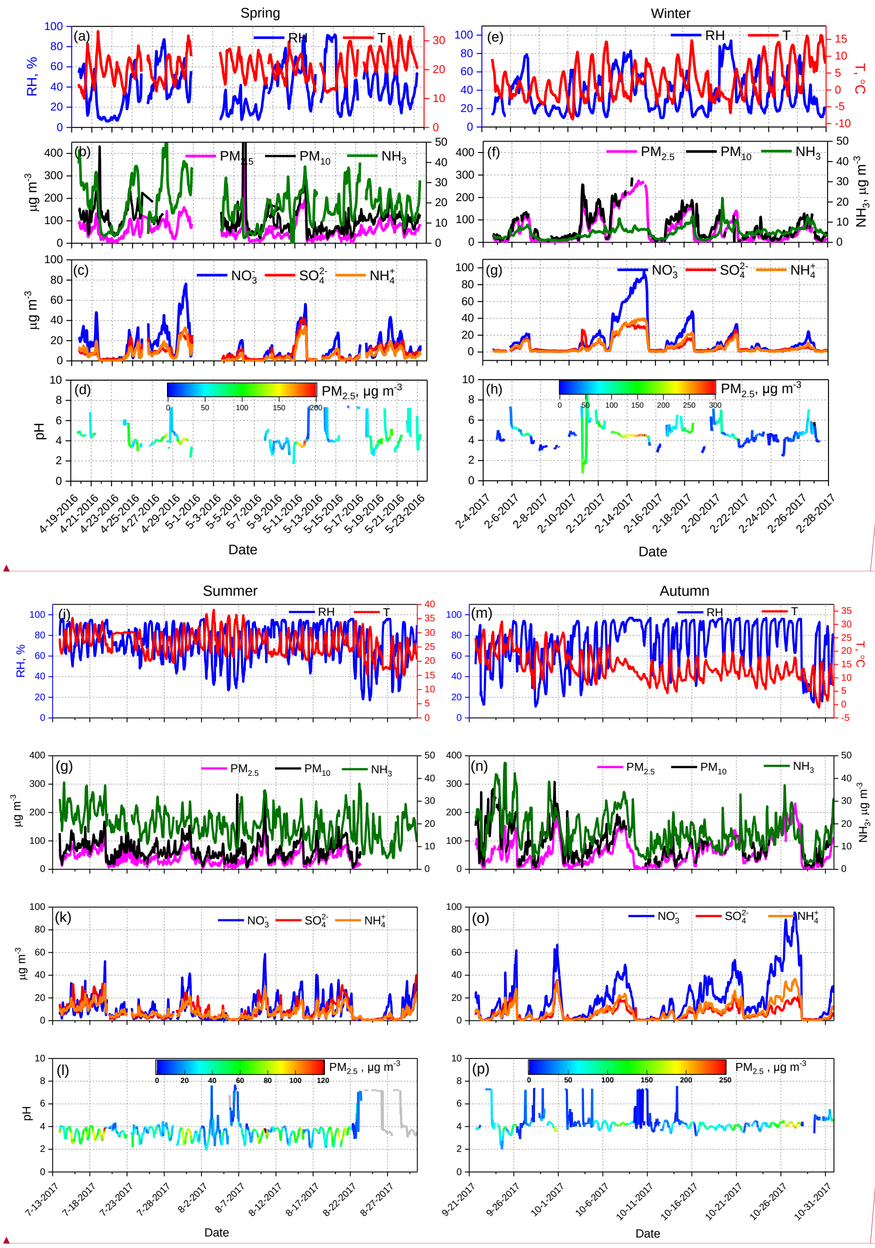

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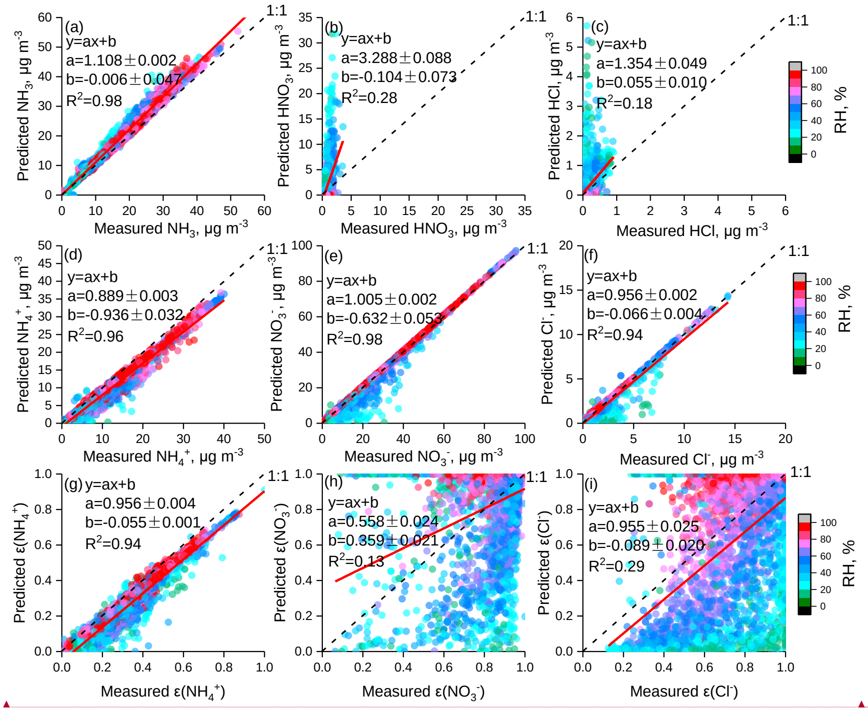

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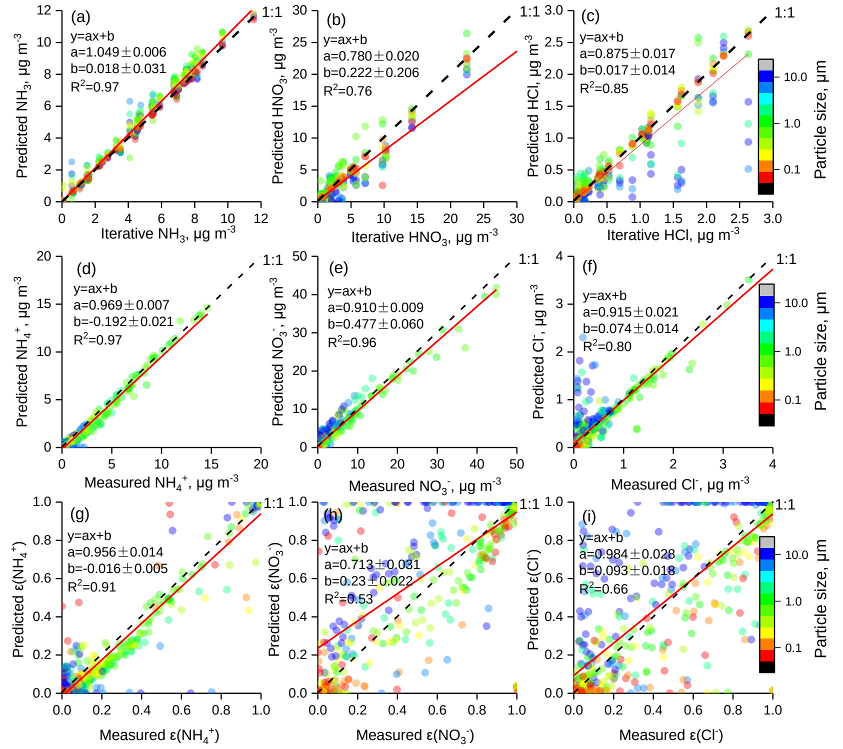

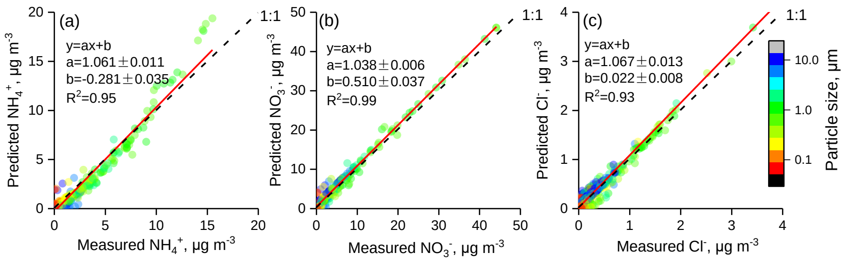

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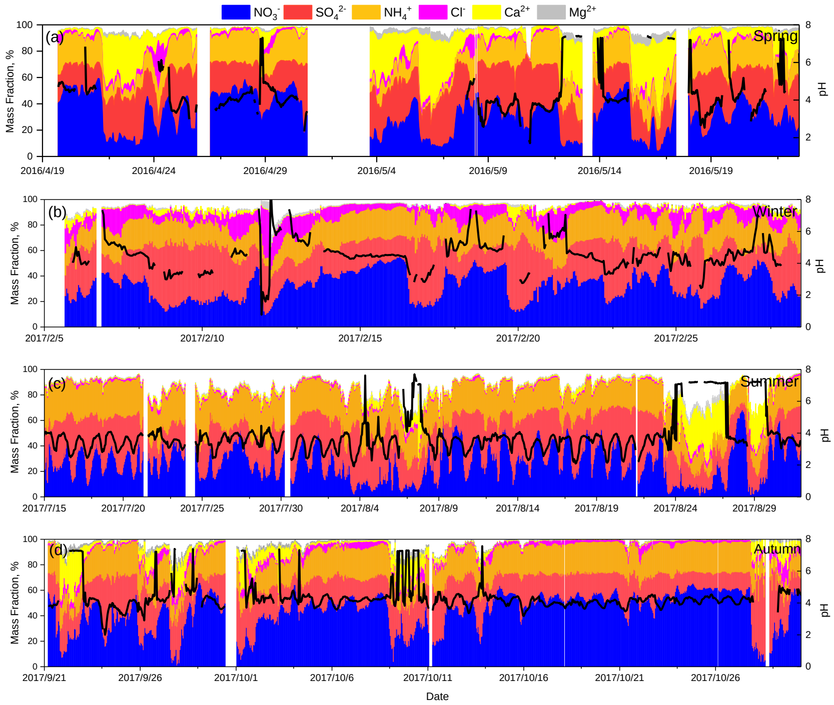

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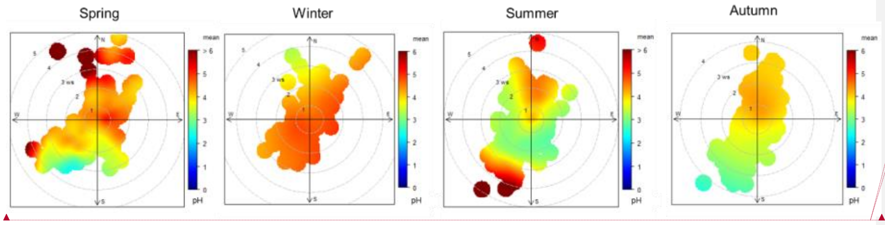

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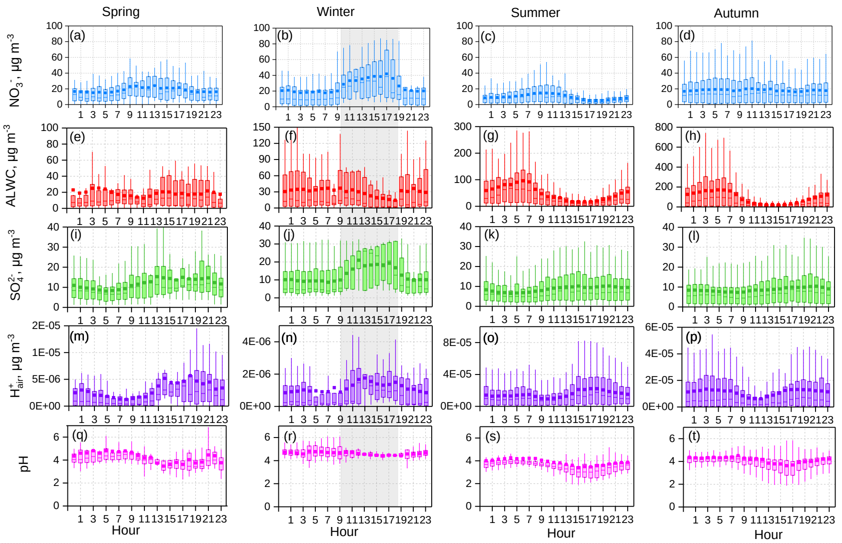

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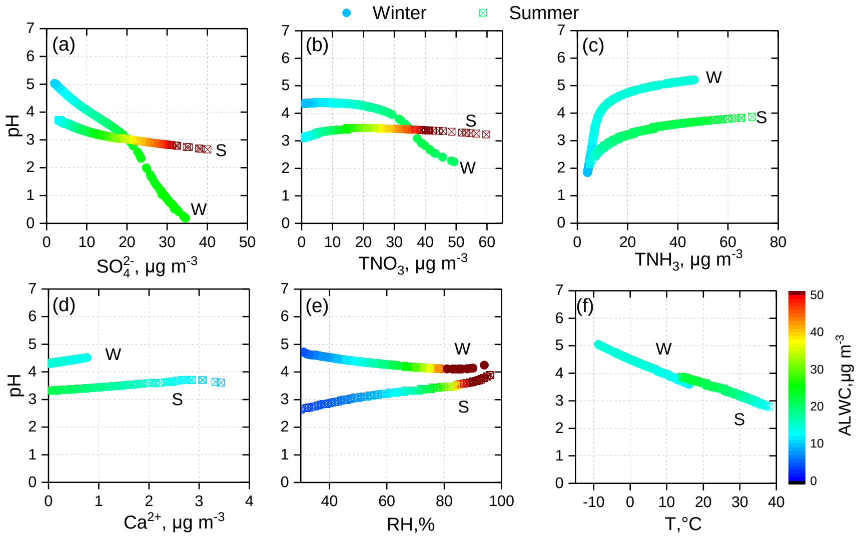

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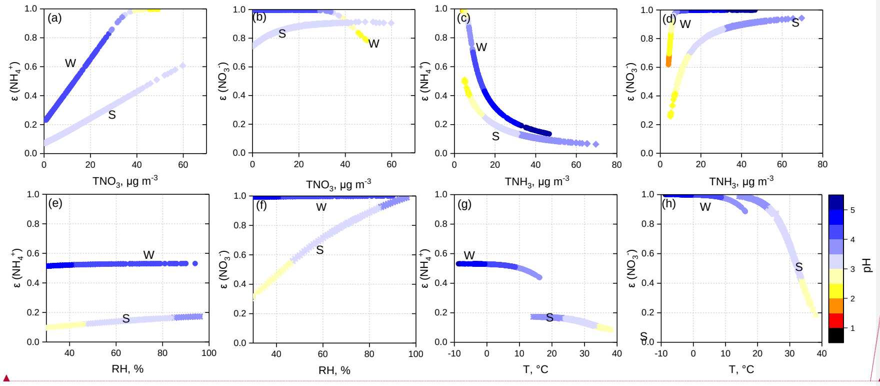

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Figure 8.

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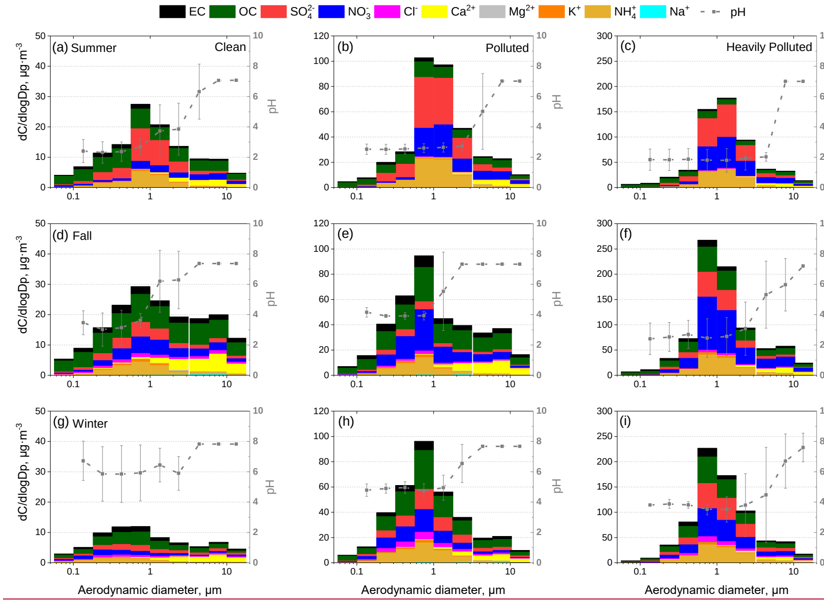

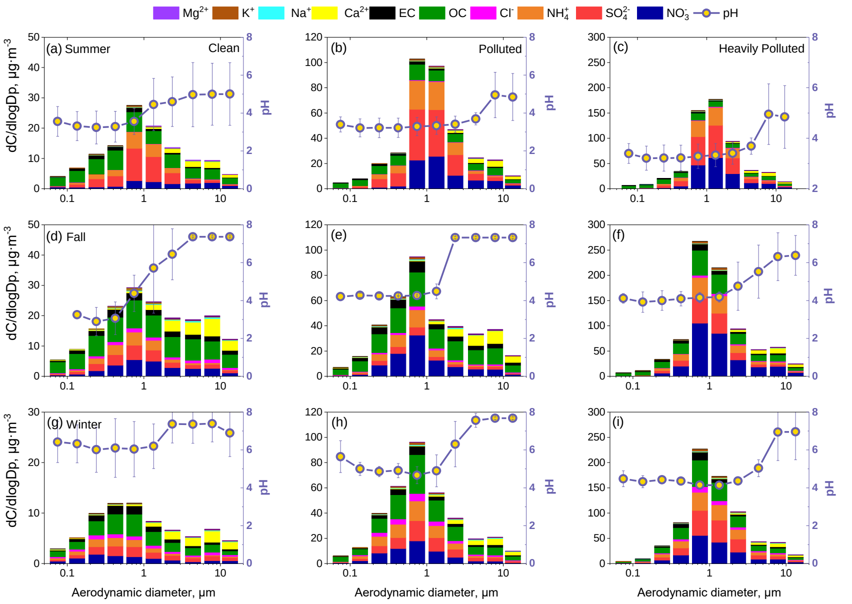
Mg2+
K+
Na+
Ca2+
EC
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Cl-
NH4+
SO42-
NO3-
pH
(a) Summer
Clean
(b)
Polluted
(c)
Heavily Polluted
(d) Fall
(e)
(f)
(g) Winter
(h)
(i)
dC/dlogDp, μg·m-3
pH
Aerodynamic diameter, μm
0.1
1
10

Figure 9.