

## Response to Anonymous Referee #2

Manuscript: *Significant contrasts in aerosol acidity between China and the United States*

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### Comment 1

This manuscript examines differences in aerosol pH between China and the US using both model simulations and network observations. The analysis investigates differences in aerosol pH between the two locations, primarily focusing on composition and concentration differences. Aerosol pH is an important topic and this work is timely and original. It is certainly appropriate for ACP and will be of interest to a broad scientific community. The organization is mostly fine, though some of the discussion is unnecessary (see comments below), and the writing is good. I do have some concerns that need to be addressed before I can recommend the manuscript for publication. My specific comments are below:

#### Response

We thank the reviewer for their review and the overall support. In the revised version, we carefully addressed all the reviewer's comments. We rewrote the model evaluation section to avoid overstatement and added more detailed discussion on model performance and results. As suggested by the reviewer, we also provided discussion about the seemingly contradicting conclusion compared to Zheng's study. The reviewer's suggestion on LWC enlightened us to identify two pathways through which factors affect aerosol pH—the LWC-modifying pathway and the H<sup>+</sup>-modifying pathway. A new section (sect. 3.2.3) was thus added to provide related results and discussion. Some results and discussion in the original version of the manuscript have been moved to Supplementary Information per the reviewer's request. We hope that our revision and this new version of the manuscript have addressed all the reviewer's concerns.

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### Comment 2

I think that the performance of the model is greatly overstated, as summarized in lines 235-237. As the manuscript states, model predictions of aerosol pH are frequently evaluated using comparison of modeled and measured species partitioning (NH<sub>3</sub> and HNO<sub>3</sub> are the most common species used). Figures S3, S4, and S5 show some significant problems predicting key species and parameters (especially  $\epsilon_{\text{NH}_4^+}$  and  $\epsilon_{\text{NO}_3^-}$ ), such that the pH predictions are also questionable in many times/locations. I think that these differences are mostly minimized in the manuscript, or not discussed accurately (e.g., Section 3.1.2). While some of the underlying differences are identified (e.g., the need for better NH<sub>3</sub> emissions in China), the uncertainty in the pH predictions are not acknowledged. I think that the acceptable threshold for pH predictions should be much tighter than +/- 2 pH units (as line 225 – 228 seems to indicate). To address this concern, the manuscript needs to be more transparent and detailed in the discussion of the difficulties predicting both  $\epsilon_{\text{NH}_4^+}$  and  $\epsilon_{\text{NO}_3^-}$ , and how this translates to uncertainty in the pH predictions.

#### Response

We thank the reviewer for their suggestion on the discussion of the model performance. In response to this comment, we revised the model performance section (in lines 223-239) to avoid overstatement and add more transparent and detailed discussion of the difficulties in predicting  $\epsilon_{\text{NH}_4^+}$  and  $\epsilon_{\text{NO}_3^-}$  and how this translates to uncertainty in modeled pH in the model evaluation section as follows,

“Spatially, the model simulations generally capture the observed variations in pH, species concentrations, and partitioning ratios, although there are some notable biases (Figs. S4 and S5). In both China (NCP) and the contiguous US, the modeled  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NH}_3$  are biased low while modeled  $\text{HNO}_3$  is biased high, resulting in low biases in the predicted  $\epsilon(\text{NO}_3^-)$  and  $\epsilon(\text{NH}_4^+)$ . The modeled  $\text{SO}_4^{2-}$  in both countries is biased low. Such low biases have been seen in previous studies (Fountoukis et al., 2013; Theobald et al., 2016) and have been attributed to the spatial mismatch between the observations and simulations due to the coarse resolutions of model grid cells (usually 20–50 km resolution) (Shen et al., 2014; Wang et al., 2014a). Smaller NMBs in the US indicate a better performance, compared to China (NCP). Larger differences between observations and simulations in China (NCP) could also be caused by larger measurement uncertainties as the data in China are collected from different monitoring stations operated by individual research institutions (Wang et al., 2019) and thus lack a unified quality control, compared with data in the US, which come from national monitoring networks (United States Environmental Protection Agency; National Atmospheric Deposition Program). The co-occurrence of low biases in  $\epsilon(\text{NO}_3^-)$ , which causes lower bias in aerosol pH, and low biases in  $\epsilon(\text{NH}_4^+)$  and  $\text{SO}_4^{2-}$ , which cause higher bias in aerosol pH, likely offset each other, resulting in small biases in aerosol pH. Indeed, the simulated average pH values at observation sites ( $3.8 \pm 0.2$  in NCP, China and  $1.8 \pm 0.5$  in the contiguous US) are generally in line with the observed averages ( $4.3 \pm 0.5$  in NCP, China and  $2.6 \pm 0.5$  in the contiguous US) (Fig. 3), although the model shows a moderate low bias in both countries. The larger pH difference in the US than in China is likely due to the low bias in  $\text{TNH}_3$  to which the sensitivity of pH is found to be more pronounced in the US than in China (discussed in detail in Text S1).”

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### Comment 3

This is no fault of the authors, but a significant paper was recently published that must be discussed (Zheng et al., Science 369, 1374–1377 (2020)), especially because the present manuscript presents several contrasting findings compared to Zheng et al. Specifically, Zheng et al. characterizes differences in pH between China and the US, and the reasons for these changes. They find that the two most important factors are temperature and ALW. The present manuscript does account for ALW differences because composition and concentration both affect ALW; however, their analysis does not acknowledge the importance of temperature differences at all. Also, they discuss all of the differences as if composition has the biggest effect (e.g., adding  $\text{NH}_3$  neutralizes the acidic species...), when it may be the effect on ALW that is the most important factor, at least according to Zheng et al. Other studies have also identified the importance of temperature in driving pH differences (Battaglia et al., 2017; Tao and Murphy, 2019). Further, Zheng et al. conclude that NVCs make a very small contribution (on the order of ~5%) to the pH difference between the two regions, which seems to contradict the present study. So, the present manuscript needs to add significant discussion to address similarities and differences between their study and Zheng et al. They should also more broadly discuss other factors that are known to influence pH, such as temperature.

### Response:

Thank you for sharing this recently published Science paper (or Zheng’s paper). Zheng’s paper provided in-depth analysis of the drivers leading to the aerosol pH difference between northern China and the United States based on a multiphase buffer theory that they proposed. Their results as illustrated in Fig. 3 of their paper highlighted aerosol water content (AWC) and temperature as two most important factors explaining the pH difference, which seemingly contradicts our findings that mainly attribute the pH difference to  $\text{TNH}_3$  concentrations and aerosol composition. First of all, we

want to thank the reviewer for raising this interesting question which should definitely be addressed in the current paper. Below we listed the reasons that explain the contrasting conclusions. Corresponding discussion was also reflected in the revised manuscript.

**Temperature.** Zheng's paper compared two scenarios with very distinct conditions. One scenario was set for the conditions in North China Plain (NCP) in winter, and the other was set for the conditions in the southeastern United States in summer (SE-US). Because of the differences in latitude (north for China vs south for the United States) and season (winter for China vs summer for the United States), the difference in temperature between these two scenarios was very large, i.e., **29 K** (269 K for China vs 298 K for the United States) (Table S1 in Zheng's paper). Their purpose was to identify factors leading to the large pH difference between these two specific scenarios (~4.7 units of difference).

Our study compared the annual average pH levels using multiple sites in both countries. In particular, the US sites covers the contiguous United States (not just one site in the southeastern United States). The difference in average temperature between China (NCP) and the contiguous United States is only **2.6 K** (287.4 K in China vs 284.8 K in the United States) (Table S3), which is one order of magnitude lower than the temperature difference in Zheng's study. It is expected that with nearly 30 K difference in temperature in Zheng's settings, the contribution of temperature to pH difference could be much larger than our evaluation.

Our nationwide simulations showed that the temperature difference between the US and China is about 5 K in terms of spatial averages (US minus China) and -1.4 K in terms of population-weighted averages (Table S4). In general, the temperature difference of 29 K between Zheng's scenarios is not representative of the temperature difference between China and the United States on an annual average level.

In response to the reviewer's comment, we added temperature and relative humidity as two additional driving factors of pH into our Multivariable Taylor Series Method (MTSM) analysis. Results were updated correspondingly (see details below). We also evaluated the pH difference between the scenarios adopted in Zheng's study (i.e., NCP and SE-US). The results showed that the temperature accounted for 1.3 units of difference in aerosol pH between their two scenarios (see Figure S9 below), which was in line with what was reported in Zheng's paper (1.6 units).

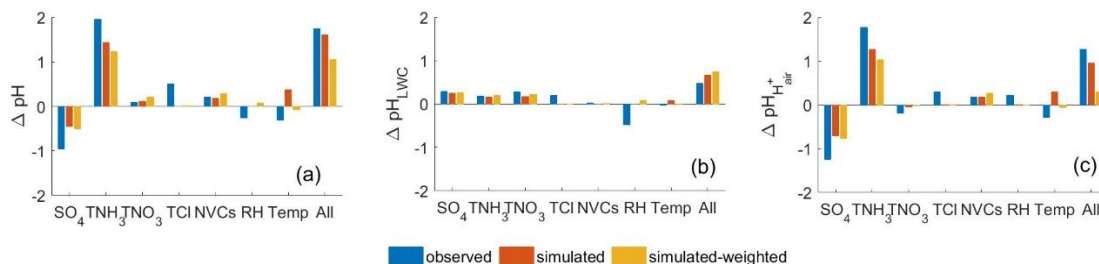
The sentence in line 174 was revised as follows to clarify the inclusion of meteorological variables, *"To separate the contributions of individual components (eight species in total, including Na<sup>+</sup>, SO<sub>4</sub>, TNO<sub>3</sub>, TNH<sub>3</sub>, TCl, Ca<sup>2+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>) and meteorological variables (RH and temperature) to the pH difference ..."*

Results and discussion associated with temperature were added to lines 335-340 as follows, *"Studies have identified an important role of temperature in driving aerosol pH (Battaglia et al., 2017; Tao and Murphy, 2019; Jia et al., 2020). Our MTSM analysis showed that temperature accounted for 0.07–0.39 unit of pH difference between China and the US, which varies by group (Fig. 6). Such relatively small contributions of temperature, compared to those of TNH<sub>3</sub> and SO<sub>4</sub>, are mainly because of the small difference in temperature between these two countries which are at similar latitudes. The difference in the annual average temperature between China and the US is 1.4 K, -5.0 K, and 2.6 K in the observation, non-weighted, and population-weighted groups, respectively (Table S4)."*

The comparison between results of the contribution of temperature is also discussed in a new section (Sect. 3.2.3 in the revised manuscript, two pathways leading to the aerosol acidity difference) in lines 425-435 as follows,

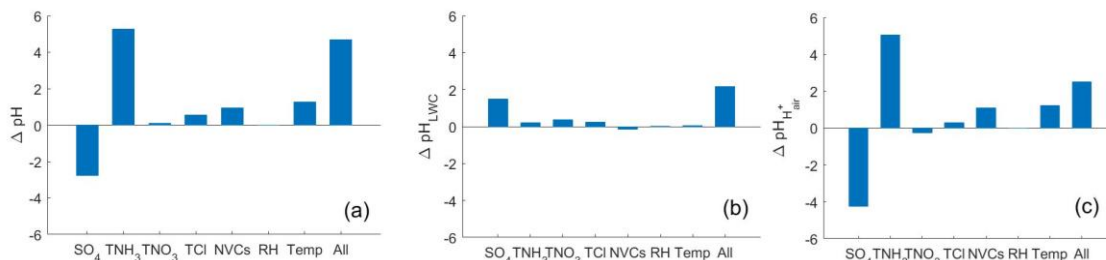
“Our results, showing the importance of both mass concentration associated with LWC and chemical composition associated with  $H_{air}^+$  and a minor role of temperature, seem in some aspects to contradict a previous study (Zheng et al., 2020) which highlighted LWC and temperature instead of chemical composition as the most important factors explaining the pH difference between China (NCP) and the US. We note that the difference in the conclusions is reasonable when considering the differences in the specific cases examined in these two studies. The previous study compared the conditions in NCP in winter with those in the southeastern US in summer (SE-US). Because of the differences in latitude (north for China vs south for the US) and season (winter for China vs summer for the US), the difference in temperature between their scenarios (29 K) was an order of magnitude greater than those in our study which has greater spatial and temporal coverage (2.6 K in the observation group, 5 K in the non-weighted group, and -1.4 K in the population-weighted group). Using MTSM, we evaluate the pH difference between NCP and SE-US scenarios considered in the previous study. The results show that temperature accounts for 1.3 units of difference in aerosol pH between their two scenarios (Fig. S9), in line with what was previously reported (1.6 units).”

Figure 6 was updated as follows to include meteorological factors in response to this comment,



**Figure 6.** Contributions of individual components and meteorological factors to (a) total difference of aerosol pH ( $\Delta pH$ ), (b) the aerosol pH difference through the pathway of LWC ( $\Delta pH_{LWC}$ ), (c) the aerosol pH difference through the pathway of  $H_{air}^+$  ( $\Delta pH_{H_{air}^+}$ ) between China and the United States calculated by Multivariable Taylor Series Method (MTSM) as described in Sect. 2.4. For each factor, the sum of the contributions through the two pathways yields the net contribution of this factor to the aerosol pH difference. The case in the United States is chosen as the starting point, and China as the ending point.

Figure S9 was added to **Supplementary Information** as follows to provide the results from the sensitivity test using Zheng’s settings,



**Fig. S9** Contributions of individual components and meteorological factors to (a) total difference of aerosol pH ( $\Delta pH$ ), (b) through the pathway of LWC ( $\Delta pH_{LWC}$ ), (c) through the pathway of  $H^+_{air}$  ( $\Delta pH_{H^+_{air}}$ ) calculated by Multivariable Taylor Series Method (MTSM) between the NCP scenario and the US-SE scenario in Zheng’s study (Zheng et al., 2020). For individual factors, the sum of the contributions through the two pathways yields the net contribution of this factor to aerosol pH. The case in the United States is chosen as the starting point, and China as the ending point.

**Aerosol liquid water content (LWC).** The reviewer’s comment is well taken. As pointed out by the reviewer, the present manuscript does account for LWC differences because concentration, composition, and meteorology all affect LWC. In the revised paper, we added more analyses and discussion regarding LWC in response to the reviewer’s comment. Specifically, we used MTSM to identify factors contributing to LWC difference as what we have done for pH. Our simulations showed a LWC difference of **8.2  $\mu\text{g}\cdot\text{m}^{-3}$**  between China (NCP) and the contiguous United States in group “observation” in our study and **340  $\mu\text{g}\cdot\text{m}^{-3}$**  between Zheng’s scenarios (NCP minus US-SE). In both simulations, MTSM identified  $\text{SO}_4^{2-}$ ,  $\text{TNO}_3$ , and TCl as three most important components leading to the LWC difference (Fig. 6, Fig. S7, Fig. S9). Relative humidity (RH) in our cases played an important role (Fig. 6). RH levels were identical between Zheng’s scenarios and thus didn’t contribute to any LWC difference (Figure S9).

The much larger LWC difference between Zheng’s scenarios than that between ours was mainly driven by the differences in pollutants concentrations. For example, the  $\text{SO}_4$  concentration is as high as  $156 \mu\text{g}\cdot\text{m}^{-3}$  in Zheng’s NCP scenario, while only  $9.2 \mu\text{g}\cdot\text{m}^{-3}$  in ours. Such differences in concentrations are reasonable, given that Zheng’s paper selected a severe haze event occurring in Beijing in winter 2013 as the scenario for China (NCP), while we used annual average levels over NCP in 2017 as our case for China (NCP). Note that winter 2013 was a period when air pollution reportedly reached record high levels across the northern China. Since 2013, China has launched strict controls on air pollutant emissions, and  $\text{PM}_{2.5}$  levels decreased significantly between 2013 and 2017 (Zhang et al., 2019). Therefore, Zheng’s NCP scenario should be more representative of short-term haze events in pre-2013 period, while our China (NCP) case should be more representative of annual average levels in recent years.

Inspired by the reviewer, we noted that there are two pathways through which factors affect aerosol pH—by modifying aerosol LWC and by modifying  $H^+$ . As pH is calculated as  $[\log_{10}(\text{LWC}) - \log_{10}(\text{H}_{\text{air}}^+) - 3]$  (LWC and  $\text{H}_{\text{air}}^+$  are expressed as mass per unit volume of air,  $\mu\text{g m}^{-3}$ ), no matter how complex the aerosol system is, the linkage between a perturbation in input factors and the change in pH is either through the change in LWC or in  $\text{H}_{\text{air}}^+$  or both. Based on this view, we updated Figure 6 to include these two pathways associated with LWC and  $H^+$ , respectively, (see Figure 6b and c as given above). Related results and discussion were provided in Section 3.2.3 as follows,

**“3.2.3 Two pathways leading to the aerosol acidity difference**

As aerosol pH is calculated as  $[\log_{10}(\text{LWC}) - \log_{10}(\text{H}_{\text{air}}^+) - 3]$ , all mechanisms affecting aerosol pH must be through the modification of LWC,  $\text{H}_{\text{air}}^+$ , or both (LWC and  $\text{H}_{\text{air}}^+$  are expressed as mass per unit volume of air,  $\mu\text{g m}^{-3}$ ). We quantitatively separate the contributions of individual factors to the China-US pH difference into the LWC-modifying pathway and the  $\text{H}_{\text{air}}^+$ -modifying pathway (Fig. 6). To achieve this, we use MTSM to quantify the contributions of individual factors to the differences in  $\log_{10}(\text{LWC})$  and  $[-\log_{10}(\text{H}_{\text{air}}^+) - 3]$ , respectively, between the two countries, with the same approach as we did for pH (LWC and  $\text{H}_{\text{air}}^+$  are two output variables directly predicted by ISORROPIA). The results show that both the changes in LWC and  $\text{H}_{\text{air}}^+$  lead to increases in aerosol pH when conditions change from those in the US to China.

Given that LWC increases with aerosol mass concentration (Song et al., 2019), higher component concentrations in China than in the US increase LWC and, thus, increase aerosol pH (Fig. 6b). Through the LWC-modifying pathway, changes in  $\text{SO}_4$ ,  $\text{TNH}_3$ , and  $\text{TNO}_3$  lead to increases in pH (0.15–0.3) (Fig. 6b), which are consistent in all three groups. Compared to other groups, the observation group represents a higher pH increase due to Cl and a higher pH decrease due to RH (Fig. 6b), mainly because of the larger differences in Cl concentrations and RH for this group than for other groups (Table S4).

Through the  $\text{H}_{\text{air}}^+$ -modifying pathway, the effects of individual factors on pH changes vary (Fig. 6c). Increases in acidic components ( $\text{SO}_4$  and  $\text{TNO}_3$ ) increase  $\text{H}_{\text{air}}^+$  and thus decrease aerosol pH (Fig. 6c). Increases in  $\text{TNH}_3$ , TCl, and NVCs, on the other hand, decrease  $\text{H}_{\text{air}}^+$  and increase aerosol pH (Fig. 6c). By increasing  $\text{H}_{\text{air}}^+$ , increased  $\text{SO}_4$  decreases pH by 0.7–1.2 units, showing a much stronger acidic capacity than another acidic component,  $\text{TNO}_3$ , which only decreases pH by 0.17–0.27 units (Fig. 6c). Compared to the US, China is in a  $\text{TNH}_3$ -rich condition. The molar ratios of  $[\text{TNH}_3] / (2 \times [\text{SO}_4] + [\text{TNO}_3] + [\text{TCl}])$  in China vs. in the US are 3 vs. 1.4, 2.0 vs. 1.0, and 2.4 vs. 1.5 in the observation, non-weighted, and population-weighted groups, respectively. Changing the conditions from the US to China,  $\text{TNH}_3$  plays the most important role in neutralizing the acidic components and driving the pH increase in the  $\text{H}_{\text{air}}^+$ -modifying pathway (Fig. 6c).

For individual factors, the net changes in pH are a result of the combination of the two pathways. For example, increased  $\text{SO}_4$  increases LWC and  $\text{H}_{\text{air}}^+$  simultaneously. The increase in LWC increases aerosol pH, while the increase in  $\text{H}_{\text{air}}^+$  decreases aerosol pH. All three groups suggest that the effect of  $\text{H}_{\text{air}}^+$  on pH overwhelms that of LWC on pH, leading to a net decrease in pH from an  $\text{SO}_4$  increase (Fig. 6). Increased  $\text{TNH}_3$  increases pH in both pathways, adding up to a larger increase in pH (Fig. 6). Increased  $\text{TNO}_3$  through these two pathways, however, is associated with opposite effects on pH which are comparable in magnitude and thus tends to offset each other (especially in the observation group) (Fig. 6). This explains the aforementioned small change in pH from the  $\text{TNO}_3$  increases. Combining all the factors, both pathways increase aerosol pH (Fig. 6b and c), resulting in the large difference in aerosol acidity between these two countries (Fig. 6a).

To facilitate a follow-up sensitivity test to link the two pathways with mass concentration and chemical composition, we define the total mass concentration as the sum of the mass concentrations of all the seven input components (i.e.,  $\text{Na}^+$ ,  $\text{SO}_4$ ,  $\text{TNH}_3$ ,  $\text{TNO}_3$ , TCl,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ ), including both gas and particle phases, and the chemical composition as the composition of the seven components in the aerosol (gas + particle) system. The observation group shows that the total mass concentration in China is 8.4 times that in the US, and the chemical composition in China is richer in  $\text{TNH}_3$  than that in the US (as illustrated by the ratios of  $[\text{TNH}_3] / (2 \times [\text{SO}_4] + [\text{TNO}_3] + [\text{TCl}])$  mentioned above). It has been found that both LWC and  $\text{H}_{\text{air}}^+$  are affected by mass concentration and aerosol composition (Guo et al., 2015; Xie et al., 2019; Zheng et al., 2020). To investigate how the differences in mass concentration and composition between China and the US is associated with the LWC- and  $\text{H}_{\text{air}}^+$ -

modifying pathways and consequently the pH difference, we first increase the mass concentrations of individual input components in the US case by a constant factor of 8.4, whereby we get an intervening case representing the overall pollution level as in China but with the chemical composition feature as in the US (Table S4, sensitivity test). From the intervening case, we then shift the composition of the US case to that of China (Table S4, sensitivity test). Note that throughout this sensitivity test, meteorological conditions are held constant. The first step by increasing the mass concentration yields an increase of 1.02 units in the aerosol pH which is mainly achieved through the LWC-modifying pathway (1.06 units) instead of the  $H_{air}^+$ -modifying pathway (-0.04 unit) (Fig. S7 (a), (b), (c)). The second step by changing the chemical composition shows a further increase of 0.76 units in the aerosol pH which is mainly achieved through the  $H_{air}^+$ -modifying pathway (0.88 units), whereas the LWC-modifying pathway (-0.11 unit) plays a minor role (Fig. S7 (d), (e), (f)). This sensitivity test reveals that the LWC-modifying pathway is mainly associated with the change in mass concentration, and the  $H_{air}^+$ -modifying pathway is mainly associated with the change in chemical composition.

The increased pH in the first step is surprising as we initially thought that the pH should be unchanged before and after multiplying the concentration of each component with a constant factor. Further investigation shows that, during the first step, increased aerosol concentration drives more fractions of  $TNO_3$  and  $TNH_3$  partitioning into particle phases— $\epsilon(NH_4^+)$  and  $\epsilon(NO_3^-)$  increase from 0.4 and 0.6 to 0.6 and 0.98, respectively. Therefore, although the chemical composition of the aerosol system keeps constant, the particle composition changes. This repartitioning can be explained by the Henry's Law,  $[A_{aq}] = H_A p_A$ , where  $[A_{aq}]$  is the aqueous-phase concentration of A in the unit of moles per liter water,  $p_A$  is the partial pressure of A in the gas phase, and  $H_A$  is the Henry's law coefficient (Seinfeld and Pandis, 2006). In the first step after multiplying the constant factor, assuming no repartitioning,  $p_A$  increases due to the increased concentration of A in the gas phase, while  $[A_{aq}]$  remains largely constant because of the simultaneous increases in LWC and particle-phase A concentration ( $c_A$ ), given that  $[A_{aq}]$  is proportional to  $c_A \cdot LWC^{-1}$  (note that LWC and  $c_A$  are expressed as mass per unit volume of air, and  $[A_{aq}]$  is expressed as moles per unit volume of water). According to the Henry's Law, more gas-phase A will dissolve in water, and thus, the total A in the system shift toward the particle phase after the multiplication of the constant factor. Due likely to the weak acidic capacity of  $NO_3^-$  which is overwhelmed by  $NH_4^+$ , the particle is ultimately neutralized by the increased  $NH_4^+$  in the first step.

We find that by increasing the concentration of every component by a constant factor, the magnitude and direction of the resulting change in pH are sensitive to the fraction of  $TNH_3$  in the aerosol system while insensitive to the ratio of  $SO_4$  to  $TNO_3$ . Based on an  $NH_4^+ - SO_4^{2-} - NO_3^- - H_2O$  system, we conduct a series of sensitive tests to investigate the change in aerosol pH in response to the multiplication of a constant factor of 8.4 (Fig. S8). The change in pH reduces gradually from 1.2 units to 0.8 unit when the  $TNH_3$  mass fraction of the system decreases from 67% to 27% (Fig. S8). With further decreases in the  $TNH_3$  fraction, the increase in pH diminishes rapidly, becomes negative when the  $TNH_3$  mass fraction is lower than 25%, and is -0.6 when the  $TNH_3$  mass fraction is 17% (Fig. S8). Under a constant  $TNH_3$  mass fraction, the change in pH remain generally constant across a wide range of the mass ratios of  $SO_4$  to  $TNO_3$  (from 5:1 to 1:5) (Fig. S8). In populated continental regions, mass fractions of  $TNH_3$  are often found high (Bencs et al., 2008; Behera and Sharma, 2010; Zheng et al., 2015; Cheng et al., 2016; Guo et al., 2017b), and the pH increase rather than decrease in response to the multiplication is thus expected.

Such an assessment by tracking pathway- and step-specific contributions provides a better understanding of the pH difference between China and the US. We show that through the LWC-modifying pathway, the increases in aerosol components consistently lead to increases in pH, and that

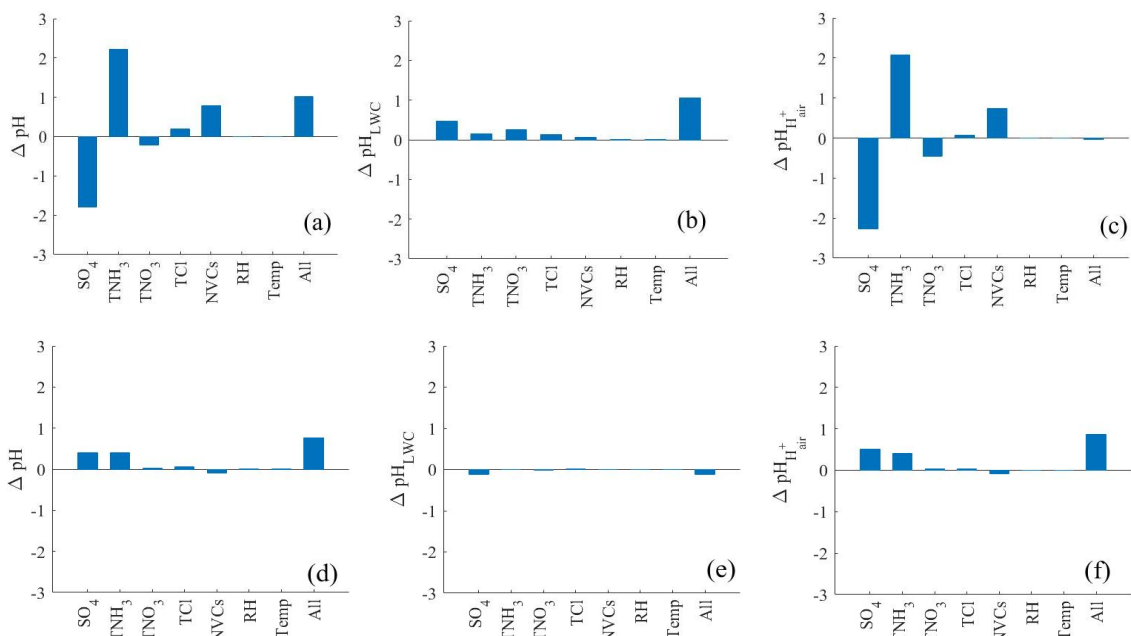
through the  $H_{air}^+$ -modifying pathway, the effects of different components on pH vary in direction. If the LWC-modifying pathway dominated the pH changes over the  $H_{air}^+$ -modifying pathway, aerosol mass concentrations would be the main factor driving the aerosol acidity difference between China and the US, and one could simply attribute the difference in aerosol acidity to the fact that China is more polluted than the US. In contrast, if the  $H_{air}^+$ -modifying pathway dominated, chemical composition would be the dominant factor, and the compound profiles of precursors emissions, which affect the availability of the corresponding aerosol components in the air, would play an important role. While there has been debate about whether mass concentration or chemical composition plays a more important role in determining aerosol pH (Cheng et al., 2016; Guo et al., 2017a; Pye et al., 2020; Zheng et al., 2020), our results suggest that both are important in explaining the China-US pH difference (Fig. 6b and c). The three groups are not consistent with each other in which pathway contributes more than the other to the pH difference, but they all suggest that the two pathways are comparable in terms of their effects on aerosol pH (Fig. 6b and c).

Our results, showing the importance of both mass concentration associated with LWC and chemical composition associated with  $H_{air}^+$  and a minor role of temperature, seem in some aspects to contradict a previous study (Zheng et al., 2020) which highlighted LWC and temperature instead of chemical composition as the most important factors explaining the pH difference between China (NCP) and the US. We note that the difference in the conclusions is reasonable when considering the differences in the specific cases examined in these two studies. The previous study compared the conditions in NCP in winter with those in the southeastern US in summer (SE-US). Because of the differences in latitude (north for China vs south for the US) and season (winter for China vs summer for the US), the difference in temperature between their scenarios (29 K) was an order of magnitude greater than those in our study which has greater spatial and temporal coverage (2.6 K in the observation group, 5 K in the non-weighted group, and -1.4 K in the population-weighted group). Using MTSM, we evaluate the pH difference between NCP and SE-US scenarios considered in the previous study. The results show that temperature accounts for 1.3 units of difference in aerosol pH between their two scenarios (Fig. S9), in line with what was previously reported (1.6 units).

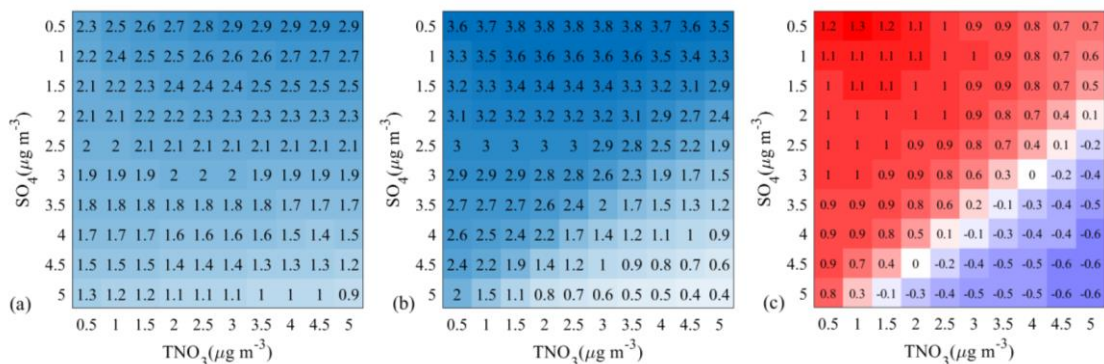
In addition, ISORROPIA simulations show a LWC difference of  $8.2 \mu\text{g}\cdot\text{m}^{-3}$  between China (NCP) and the contiguous US in the “observation” group in our study and  $340 \mu\text{g}\cdot\text{m}^{-3}$  between the scenarios considered in the previous study. The much larger LWC difference in the previous study compared to ours is mainly driven by the differences in pollutant concentrations. For example, the  $\text{SO}_4$  concentration is as high as  $156 \mu\text{g}\cdot\text{m}^{-3}$  in the NCP scenario in the previous study but only  $9.2 \mu\text{g}\cdot\text{m}^{-3}$  in our study. Such differences in concentrations are reasonable, given that the previous study selected a severe haze event occurring in Beijing in winter 2013 as the scenario for China (NCP), while we use annual average levels over NCP in 2017 as our case for China (NCP). Note that winter 2013 was a period when air pollution reportedly reached record high levels across northern China (Wang et al., 2014b; Li et al., 2016). Since 2013, China has launched strict controls on air pollutant emissions, and  $\text{PM}_{2.5}$  levels have decreased significantly between 2013 and 2017 (Zhang et al., 2019). Therefore, the NCP scenario in the previous study should be more representative of short-term haze events in the pre-2013 period, while our China (NCP) case should be more representative of annual average levels in recent years.”

Figs. S7 and S8 mentioned in this section are provided in Supplementary information as follows,





**Fig. S7 Step-specific contributions of individual factors to the pH difference between China and the US.** (a), (b), and (c) show the contributions of individual components and meteorological factors to (a) total difference of aerosol pH ( $\Delta pH$ ), (b) through the pathway of LWC ( $\Delta pH_{LWC}$ ), (c) through the pathway of  $H^+_{air}$  ( $\Delta pH_{H^+_{air}}$ ) between the US case and an intervening case with the concentrations of all components in the US case multiplied by a constant factor of 8.4. The former is chosen as the starting point, and the latter is chosen as the ending point. (d), (e), and (f) show the contributions of individual components and meteorological factors to (d) total difference of aerosol pH ( $\Delta pH$ ), (e) through the pathway of LWC ( $\Delta pH_{LWC}$ ), (f) through the pathway of  $H^+_{air}$  ( $\Delta pH_{H^+_{air}}$ ) between the intervening case and the China case. The former is chosen as the starting point, and the latter is chosen as the ending point. The inputs are shown in Table. S4, sensitivity test.



**Fig. S8 Sensitivity tests showing the pH changes in response to different levels of  $SO_4$  and  $TNO_3$  in an  $NH_4^+-SO_4^{2-}-NO_3^- -H_2O$  aerosol system.** (a) The pH of an aerosol with fixed  $TNH_3$  ( $2 \mu g m^{-3}$ ) and varied  $SO_4$  and  $TNO_3$  (from  $0.5 \mu g m^{-3}$  to  $5 \mu g m^{-3}$ ) (b) The pH after multiplying all the inputs in (a) by a factor of 8.4. Note that the  $SO_4$  and  $TNO_3$  levels shown along the axes are the initial levels before multiplication. (c) pH differences between (b) and (a) (b minus a).

**Nonvolatile cations (NVCs).** Thank you for pointing this out. We found a mistake in our previous calculation where  $Ca^{2+}$  was wrongly treated. With the  $Ca^{2+}$  treatment being corrected, the

contributions of NVCs were on average one quarter of the previous contributions and therefore, became minor. The results on NVCs were updated throughout the manuscript, as specified below.

The sentences in lines 325-327 (lines 307-313 in the original version) was revised as “*Other cations, mainly NVCs, have a relatively small effect (0.2, 0.2, and 0.3 in group “observation”, “simulation”, “simulation-weighted”, respectively), which is consistent with a previous study (Zheng et al., 2020).*”

The sentence in line 329 (line 316 in the original version), “...was fully offset by  $\text{TNH}_3$  and NVCs” was revised as “...*is fully offset by  $\text{TNH}_3$ .*”

The sentence in line 428 in the original version, “The MTSM method further shows a significant contribution of NVCs on the pH difference,” was removed.

We thank the reviewer again for providing this constructive comment and insightful suggestions.

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#### **Comment 4**

Finally, there is quite a bit of space (both figures and discussion) dedicated to analyses that don't seem to add much to the manuscript. For example, Line 350 describes the process for segregating the data into different groups to further examine the effects of  $\text{TNH}_3$ . This was a good idea, however, the results (shown in Fig. 8) don't add any new insight to our current understand of aerosol pH. I would say the same is true for Fig. 11 and the associated discussion, and for the analysis of the  $\text{TNO}_3/\text{TSO}_4$  molar ratios. I would strongly suggest moving these figures and discussion to the Supporting Information, especially in light of the added discussion and possible analyses needed to address the above comments.

#### **Response**

We thank the reviewer for providing this suggestion. In response to this comment, **Section 3.2.3 Effects of ammonium on aerosol pH, 3.2.4 The relationship between sulfate/nitrate and aerosol pH**, and Figures 7-11 in the original manuscript were moved to **Supplementary Information (Text 1, Text 2 and Figs. S10-S14)**. The following sentence was added to lines 333-334 to provide a link.

*“More detailed analyses and discussions on the effects of  $\text{TNH}_3$ ,  $\text{TNO}_3$ , and  $\text{SO}_4$  on aerosol pH can be found in Supplementary Information.”*

**Abstract** and discussion in the main text were updated correspondingly.

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#### **Comment 5**

Line 51: delete the period appearing in the middle of the sentence.

#### **Response:**

Deleted.

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#### **Comment 6**

Line 62-63: what are large-scale measurements?

#### **Response**

To avoid confusion, “large-scale” was removed in the revised version.

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#### **Comment 7**

Line 93. I question the stated accuracy of the AMoN  $\text{NH}_3$  measurements – especially given the variability between duplicate samples reported by the network.

**Response:**

Thanks so much for pointing this out. We are sorry for making this mistake. In response to this comment, the sentence was revised as follows (lines 91-95 in the revised manuscript),

*“The accuracy of CASTNET measurements has been assessed through the analysis of reference and continuing calibration verification samples with a criterion of 95-105% (except  $\text{NH}_4^+$ , whose accuracy criterion is 90-110%) (United States Environmental Protection Agency, 2012). Detailed information about data quality is available in the CASTNET Quality Assurance Report-Annual 2011 (United States Environmental Protection Agency, 2012). A previous study demonstrated that the  $\text{NH}_3$  concentrations measured by the passive AMoN samplers are comparable to annular denuder systems (as a reference system) with a mean relative percent difference of -9% (Puchalski et al., 2015).”*

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**Comment 8**

Line 97: “Its” should not be capitalized

**Response:**

Corrected in the updated manuscript. Thank you.

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**Comment 9**

Provide the criteria for identifying outliers, and the number of outliers excluded from the respective datasets.

**Response**

Thank you for the suggestion. In this study, we selected data very carefully. Provided continuous measurements, there should be 5840 cases in China because we have daily data in one-year period at 16 monitoring sites. However, data in many cases are missing due to the interruption during measurements (e.g., there are no data in January at monitoring sites 1, 3, 4, 5). Therefore, the first step was to remove the cases with missing data of any of the measured species. In this step, 3136 cases were left. Then we identified the outliers as the data beyond the scope of three times the median absolute deviations (MAD) from the median for each component. We removed the cases with any component identified as an outlier. Eventually, we got 1766 cases with valid data of all components. Although we removed a large number of cases in this process, the remaining data covered most of the time in a year and generally distributed evenly by months (see Table S3 below).

In response to this comment, we added description of this data selection process in the main text in lines 100-108 as follows,

*“We derive daily average concentrations of gaseous species including  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{HCl}$  and of particle species including  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and NVCs from hourly observational data at 16 monitoring sites for use in pH calculation. These monitoring sites are clustered in NCP in eastern China (Fig. S2c). Due to the lack of data quality information, we first process the data by removing unreasonable data points. We define a set of valid data containing all the measured components in one day as one case. We first remove cases with one or more missing components. In this step, 2704 of 5840 cases are removed. We then identify data points that are more than three median absolute deviations from the median as outliers and remove cases with any component identified as an outlier. Eventually, 1766 cases remain for subsequent analyses. Although we remove many cases in this process, the remaining cases cover most of the days in a year and are evenly distributed by month (Table S3).”*

Table S3 was added to Supplementary Information as follows,

**Table S3 Distribution of observational cases in China in each month (with outliers removed)**

Month	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Number of cases	104	144	176	157	268	184	182	111	30	45	134	231

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**Comment 10**

Line 158-159: specify if sulfate was also adjusted.

**Response**

In response to this comment, the sentence in line 162 (line 158-159 in the original version) was revised as follows to clarify that sulfate was not adjusted.

*“In order to avoid this potential bias, we use modified  $Ca^{2+}$  concentration for pH calculations while keeping  $SO_4^{2-}$  concentration unchanged...”*

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**Comment 11**

Line 241-241: need to acknowledge that most of the pH predictions over China cannot be evaluated due to limitations in observational data.

**Response**

In response to this comment, the following sentence was added in line 260 to clarify this point, *“It should be noted that due to the scarcity of observational data, the pH estimates in southern and western China are not evaluated.”*

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**Comment 12**

Line 251-252: these correlations are weak, so the description of a “significant positive correlation” is misleading.

**Response**

Statistically, to determine whether the correlation between variables is “significant”, we compare the  $p$  value with a significant level ( $\alpha$ ) (<https://support.minitab.com/en-us/minitab-express/1/help-and-how-to/modeling-statistics/regression/how-to/correlation/interpret-the-results/>). Typically,  $\alpha$  can be 0.05 or 0.01.

As given in the sentence in lines 269-270 (lines 251-252 in the original version), the  $p$  values are less than 0.0001 (lower than either 0.05 or 0.01). Therefore, the correlations mentioned here are significant. In the revised sentence, we added the word “statistically” before “significant” and provided  $\alpha$  as follows,

*“This finding is further confirmed by the statistically significant positive correlation, ...(China:  $r=0.42$ ,  $p<0.0001$ ; the United States:  $r=0.28$ ,  $p<0.0001$ ) ( $\alpha=0.01$ ).”*

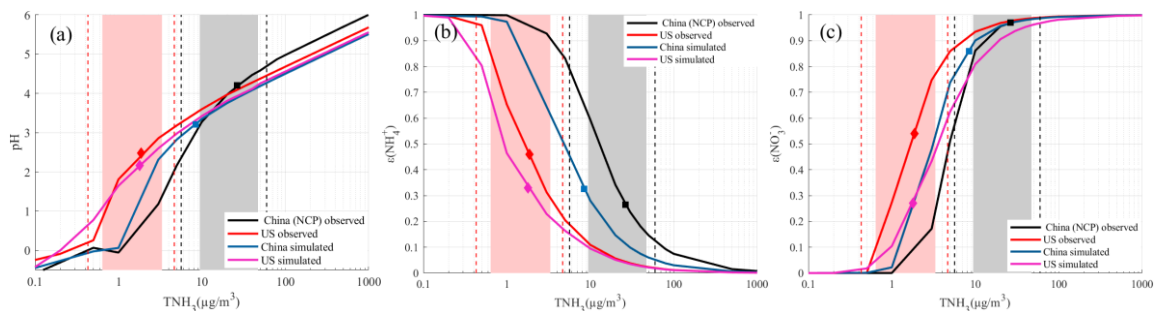
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**Comment 13**

Line 325: “this could be due to higher biases in  $H^+$  concentration by ISORROPIA in ammonia poor conditions” – I don’t follow this explanation?

**Response**

Sorry for the confusion. After checking the input of that figure, we found that we did not use the most updated input where we modified the  $Ca^{2+}$  concentration as we mentioned in Sect. 2.3, line 164. After the modification, the pH change is more stable, so we deleted the original statement. Fig. 7 (Fig. S10 in the updated manuscript) was updated as follows,



**Fig. S10 Responses of pH,  $\epsilon(\text{NH}_4^+)$  and  $\epsilon(\text{NO}_3^-)$  to the change of  $\text{TNH}_3$  from  $0.1$  to  $1000 \mu\text{g}\cdot\text{m}^{-3}$  while keeping all other components constant at their annual average levels.** The shaded areas show the  $\text{TNH}_3$  concentration ranges that covers 75% of the observed cases, the dashed lines show the 5th and 95th percentiles of the observed cases. The squares and diamonds mark the average  $\text{TNH}_3$  levels in China and the United States, respectively.

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### Comments 14

Line 457: awkward as written

### Response

This sentence was removed from the revised manuscript. The language of the manuscript has been checked by two native English speakers.

Again, we thank the reviewer for their overall support and thoughtful suggestions. These suggestions have helped improve the quality of the paper substantially.

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