Responses to the reviewers

Title: Role of ammonia on fine-particle pH in agricultural regions of China: Comparison between urban and rural sites.

We thank both reviewers for reading the manuscript and providing detailed comments. We have carefully considered all comments and changed the manuscript accordingly.

Response to Reviewer 1

General Comments:

This manuscript presents simultaneous measurements of inorganic aerosol composition and key gas-phase species (NH3, HCl, HNO3) at two urban and three rural sites in Henan Province, China. The measurements occurred during the winter and capture one of the well-documented winter haze episodes. The focus of the manuscript is modeling aerosol pH at the urban-rural sites, and performing sensitivity tests to characterize the factors that most control pH during such polluted conditions. This is a novel and valuable data set that can add important insight to our understanding of aerosol pH. The topic is appropriate for ACP and will be of interest to a broad audience. The manuscript organization and figure quality are generally good, however certain elements of the presentation – namely the English usage – require improvements throughout to bring it up to publication quality. Several analyses and/or results require clarification, and a number of key references are missing. These comments are detailed below.

Thank you for your careful reading of our paper and valuable comments and suggestions. We believe that we have adequately addressed your comments. To facilitate your review, we used yellow highlights for your comments, and red color indicating our own corrections in the manuscript.

Specific Comments:

Missing from the manuscript is a discussion of measurement uncertainty and statistical significance of the various analyses. For example, throughout the manuscript (line 27-78, 194-195, 203-204, 228-229, 250-254, 260-261) concentrations or values at the five sites are compared and ranked. In some cases, the differences appear to be quite small, and are not likely statistically significant if uncertainty and measurement variability are taken into account.

Response: Thanks for the comment. We have added the uncertainty of each instrument based on references or instrument manuals (line 127-145), and pH uncertainty was evaluated by calculating the input data in two extreme scenarios (see Section 2.4). Considering the measurement uncertainty and statistical significance, we have modified the comparison between urban and rural sites instead of the rank

of five sites in the revised version (line 247-250, 252-255, 369-271).

Figures 5, 6, and 7 and the associated discussion in Section 3.3 need clarification. It is not clear how the different sensitivity analyses were performed (What was held constant? What was varied? Which conditions were used for the base simulations?). In some cases, the interpretations also require clarification: e.g., the authors use "%RSD" – how is this actually defined? It seems in the text that they interpret %RSD as actual pH values instead of a percentage, but this could just reinforce the point that this discussion needs to be improved. On the point of RSD, the description in the text does not seem consistent with what is plotted in Fig. 5 or Fig. 7.

> **Response:** Sorry for the misunderstanding. We have added a paragraph to describe the sensitivity tests and explain the use of RSD (line 275-289, 310-315): "To explore the dominant factors that determine the local particle pH level and resulting in the high pH at rural sites, sensitivity tests of pH to chemical species (i.e., TNH_x, TH_2SO_4, TNO_3, TCl, TNa, K^+, Ca^{2+}, and Mg^{2+}) and meteorological parameters (i.e., T and RH) were performed. Firstly, the real-time measured values of a variable (e.g., TNH_x,) and the average values of other parameters (i.e., TH_2SO_4, TNO_3, TCl, TNa, K^+, Ca^{2+}, Mg^{2+}, T and RH) during Case 2 were input into ISORROPIA-II to identify the major factor for local $PM_{2.5}$ pH (Ding et al., 2019), and the results are listed in Table 4 and Fig. S10. In addition, a given range for a variable for all sites with corresponding average values of other parameters was simulated to assess the different effects of this variable among five sites (Fig. 5 and S11). The chosen variation range for each variable was close to the observed minimum and maximum values (Table S4), which aims to better reflect the actual ambient conditions of observation periods. The degree of sensitivity was represented as the relative standard deviation (%RSD) of the re-calculated pH values. RSD calculates the absolute value of the coefficient of variation, which helps us to determine how small or large is the standard deviation when compared to the mean of the re-calculated pH data set. Therefore, when the re-calculated pH data set has a higher RSD value, this variable can change the pH easier and is more important for local pH."

As stated above, the manuscript requires editing for grammar, English usage, and punctuation. Since this is an issue throughout the manuscript, specific areas for improvement are not identified in 'Technical Corrections'.

> **Response:** We have sought a professional expert to edit our revised manuscript for better flow and readability as well as for correcting some grammatical and editorial errors. In addition, this paper has been re-checked using a professional language editing service (Essaystar Group), Editing Certificate will be provided upon request. Hope it has been improved by correcting the English usage in the revised version.

A number of key references are missing. These need to be cited and the discussion enhanced to include the context they provide. To Sections 3.3 and 3.4 add discussion of Weber et al. (2016), Vasilakos et al. (2018),

and Nenes et al. (2019). On the meteorological effects on pH, add discussion of Battaglia et al. (2017) and Tao and Murphy (2019). For recent discussions of aerosol pH importance, definitions, and reported ambient levels, add discussion of Pye et al. (2019). Line 67 refers to several other studies that have examined aerosol pH in agricultural regions of China – the present results should be contrasted with these prior studies.

Response: Thanks. We have cited the above-mentioned papers and enhanced the discussion in Sections 3.3 and 3.4. (Line 56-58, 69-72, 81-82, 291-296, 302-306, 384-385)

Original line 67 (line 79 in the revised version) refers to nearly none of the studies that have examined aerosol pH in agricultural regions of China. In fact, until now, we do not have found a paper focused on the $PM_{2.5}$ acidity in agricultural regions of China. Moreover, we add the discussion about the difference of pH at rural sites between the present results and previous studies in the USA (line 252-253).

The discussion of Fig. 3 (line 208-218) needs revision. For Figures 3d, 3e, and 3f, the authors discuss the strong anti-correlated relationships, but why are these separated by case 1, 2, and 3? This is the same location and the measurements are all within a few week span, so the differences in slope and intercept are curious. Discussion of the physical meaning should be provided (e.g., what explanation is there for the greater sensitivity of H+ to pH in case 1?). It would probably be more instructive to combine these into one plot. For Figures 3g, 3h, and 3i, what explanation do the authors have for a linear relationship between H+ and TWSII on a semi-log plot? For a given TWSII concentration, the H+ level appears to vary by several orders of magnitude, which seems to agree with Guo et al. (2015), Hennigan et al. (2015) and Murphy et al. (2017).

Response: Thanks for the suggestion. We have combined the figures 3d, 3e, and 3f into one plot (Fig. S4) and the figures 3g, 3h, and 3i were replaced by Table S2. In addition, we added the underlying reasons for the variations of H^+ for a given TWSII concentration (line 259-261): "Particle hydronium ion aqueous concentration depends on both the presence of ions and the amount of particle AWC (Guo et al., 2015). Moreover, H^+_{air} was closely associated with the NH_3 mixing ratios, and higher NH_3 always corresponded to lower H^+_{air} (Liu et al., 2017)".

The results in Figure S2 need much more discussion. This is not just limited to the HCl and HNO3 results, though more explanation should be provided. Typically, the model predictions of pH are validated by the predictions of NH3/NH4+, HCl/Cl-, and HNO3/NO3- partitioning in lieu of direct pH measurements. In addition to the problems with HCl and HNO3 at all sites, it looks like there are systematic differences in NHx partitioning between the model and measurements at the U-ZZ and R-PY sites. Why is that and what does this mean for the associated pH predictions at these sites?

Response: Thanks for the comments. We have enhanced this discussion (line 198-208): "Correlations between the predicted and measured HNO_3 and HCl are weak. Similar problems were found in the northeast U.S. and Beijing. These discrepancies were potentially due to measurement uncertainties

brought about by low gas concentrations, the interference of coarse-mode particles, non-volatile cation measurement artifacts, uncertainties in the thermodynamic constants, and kinetic limitations to mass transfer (Ding et al., 2019, Haskins et al., 2018; Pye et al., 2019; Liu et al., 2017). Pye et al. (2019) suggested that ISORROPIA-II yields a mean activity coefficient of (H^+, Cl^-) that may result in the higher predicted HCl concentration. HNO_3 can be partition to both fine and coarse modes, thereby affecting predicted fine-mode nitrate concentrations (Nah et al., 2018). The best semi-volatile species for evaluation of pH modeling depend on the fraction of the gas phase. In this work, most of the HNO_3 and HCl concentrated in the particle phase, and thus they are not suited to test the model (Guo et al., 2016).".

In addition, we have added the discussion about the differences in NH_x partitioning between the model and measurements at the U-ZZ and R-PY sites (line 185-197): "The variations of slopes of NH_4^+ (Fig. S2b) and NH_3 (Fig. S2e) between U-ZZ and R-PY sites are probably attributed to the unbalanced charge of input WSIIs (see Text S1 for more details of calculation) with average equivalent ratios (Fig. S3) of 0.99 ± 0.13 (U-ZZ) and 1.20 ± 0.12 (R-PY). However, Song et al. (2018) explained that the ion balance was not a key factor for pH calculation in the forward mode, because the forward mode calculations account for additional constraints imposed by the partitioning of semi-volatile species. To verify this, we adjusted the measured NH_4^+ concentration, which was most sensitive to pH modeling (see Section 3.3), to fit the ion balance, and reran the pH calculation. As shown in Fig. S4, modeled NH_4^+ and NH_3 concentrations have better performance ($r = 0.99$, $0.94 < slope < 1.06$) with input concentrations at both sites than before. However, re-predicted pH values change slightly, and these deviations are included in the range of pH uncertainty discussed in Section 2.4. Therefore, little variations between the predicted and measured NH_4^+ and NH_3 concentrations at the five sites are acceptable for pH calculation." Moreover, the reason why the charge of ion was unbalance has been discussed in Text S1: "In addition to the measurement uncertainties, equivalent ratios lower than 1 might be attributed to the loss of cations from the volatilization of ammonium and unmeasured hydrogen ions (Meng et al., 2016). Equivalent ratios higher than 1 were most likely caused by water-soluble organic anions, CO_3^{2-} and HCO_3^- contents that were not detected in chemical analysis (Tian et al., 2018)".
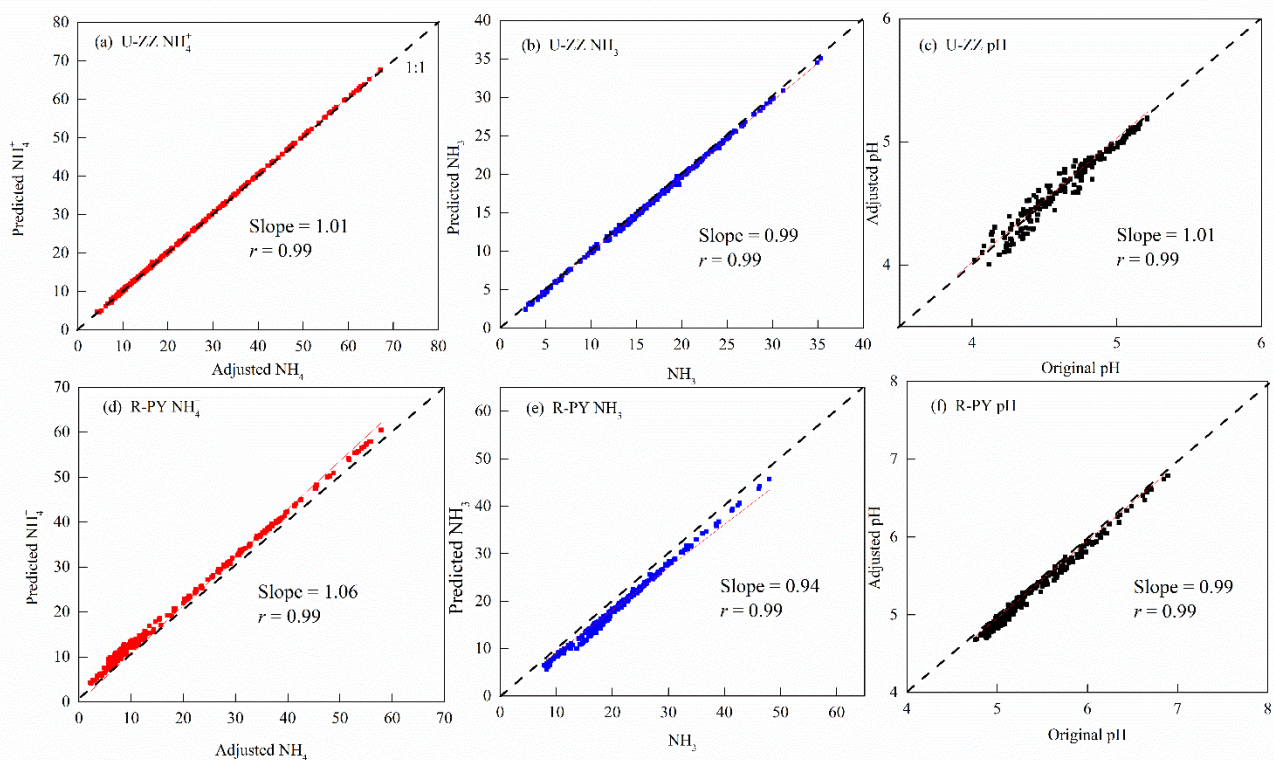
Fig. S4 Comparison between the predicted and input NH_4^+ (a, d) and NH_3 (b, c) concentrations, the original and adjusted pH (c, f) of U-ZZ and R-PY sites after adjusting the measured NH_4^+ concentrations to fit the ion balance.

Technical Corrections:

A map of the five sites should definitely be included – either in the main manuscript or supplemental.

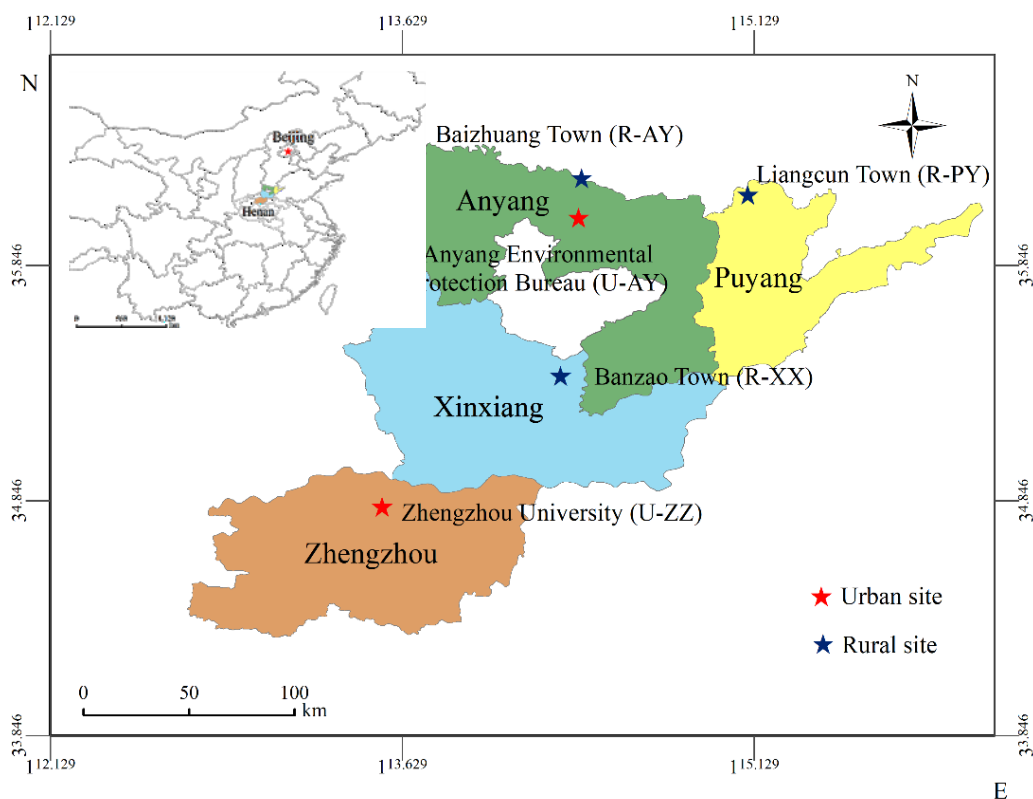**Response:** A map has been supplied in the supplemental materials (Fig. S1).

Line 152: 'distraction' is not the right term here.

Response: The "distraction" has been modified to "interference".

Fig. S5 needs improvement: the scale is not evident from the figures, nor is the relative locations and proximity of the five different sites.

Response: A new figure has been supplied to present the trajectory frequencies for each site during three cases with detail discussions in Text S2.
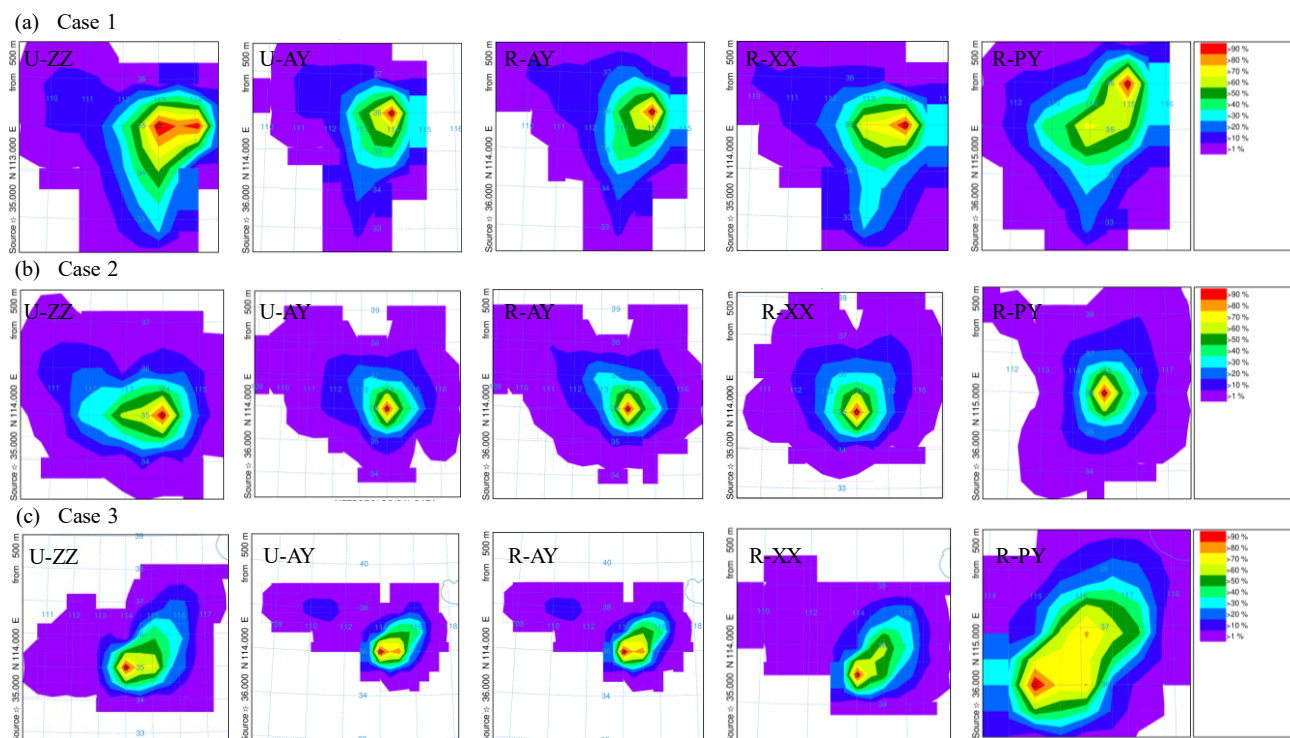
Fig. S5 Trajectory frequencies of typical periods at the five sites during Cases 1(a), 2(b), and 3(c). The color scale bar represents the percentage of trajectories passing through each grid to total trajectories.

Line 238-239: I don't see where sensitivity of pH to crustal species was analyzed?

Response: We have added the discussions on crustal species (line 296-302, 302-325): "TNa, TCl, and crustal ions (i.e., K^+, Ca^{2+}, and Mg^{2+}) have less influence on the predicted pH values, because these species were at low concentrations, together accounting for lower than 10 % of TWSIIs. However, in typical pollution events (e.g., sandstorm) or areas (e.g., coastland), the role of crustal dust and sea spray in particle pH cannot be ignored, when the mass fraction of these ions were high (Allen et al., 2015; Vasilakos et al., 2018). Because the low volatility of these cations allows them to preferentially neutralize sulfates over NH_3 and elevate particle pH (Guo et al., 2018; Vasilakos et al., 2018)", and "The crustal cations and sea spray have limited effects on pH, but a 10-fold increase in these species still can increase predicted pH values by about 0.1 units".

Line 262-263: yes, but these are presumably correlated?

Response: This sentence has been modified to "Excess-NHx concentrations might drive the pH values of rural sites higher than those of urban sites". (Line 371-372)

Line 270-271: this comment is misguided - see Weber et al (2016) for more context and explanation.

Response: This comment has been removed.

Line 286: suggest removing 'obviously'.

Response: Done.

Lines 291-292: what is the physical meaning of these equations?

Response: These equations have been deleted and discussions on these equations have been cut down.

Line 298-299: this sentence is confusing – I suggest re-writing.

Response: This sentence has been removed.

Line 306: I'm not sure the evidence supports this statement. What about meteorology? Also, differences in local vs. regional emissions would need to be accounted for.

Response: This sentence has been modified to (line 374-378): "As discussed in Sections 3.1 and 3.3, the differences of pH among three cases indicate that the underlying influence of regional transport on local particle pH cannot be neglected by differing chemical components of PM2.5 and meteorological conditions. In particular, the median pH values (Table S2) of Case 1, during when the air masses transported from the south of sampling regions, increased by 0.2–0.9 units than those during Cases 2 and 3".

Line 333: consider changing 'promote' to 'perturb'?

Response: Done.

Response to Reviewer 2

Wang et al. analyzed a novel dataset of inorganic aerosol constituents and their gaseous precursors as well as organic aerosol constituents in a province in central China with heavy agricultural activity. They used ISORROPIA, an inorganic thermodynamic aerosol model, and previously published methods to estimate aerosol pH for the observed particles. The measurements were made with state of the art instruments and the modeling was carefully evaluated. They positioned their work in the broader context of aerosol acidity work very well.

Thank you for your careful reading of our paper and the valuable comments and suggestions. To facilitate your review, we used green highlights for your comments, and red color indicating our own corrections in the manuscript.

The analysis sought to elucidate differences between the pH and the pH sensitivity to aerosol constituents

between urban and rural sites. In this aspect of the work, more care could be taken. First, a map with the key emissions and measurement locations marked would help readers unfamiliar with the area characterize the results. Secondly, the differences between the urban and rural sites appears to be fairly random and small. The authors draw conclusions about the rankings between sites or the degree of difference in the aerosol pH sensitivities based on these measurements. Without understanding the uncertainties in the measurements and the accuracy of calibrations between the five instruments, their conclusions seem poorly supported. With the addition of estimated uncertainty on the measurements as well as evidence of the calibration of the instruments against a standard, the authors would be better able to support their conclusions if they remain valid. Finally, relative standard deviation as are presentation of sensitivity of aerosol pH to total ammonia is unfamiliar to me. This metric seems dependent on the range of values selected for the parameters of interest (e.g., total sulfate, temperature) and is difficult to interpret. Please consider using aunit-based sensitivity analysis approach that would indicate the influence of each parameter without respect to the observed range of each influential parameter.

Response: First, a map has been supplied in the supplemental materials (Fig. S1) with the key emissions listed in Table 2.
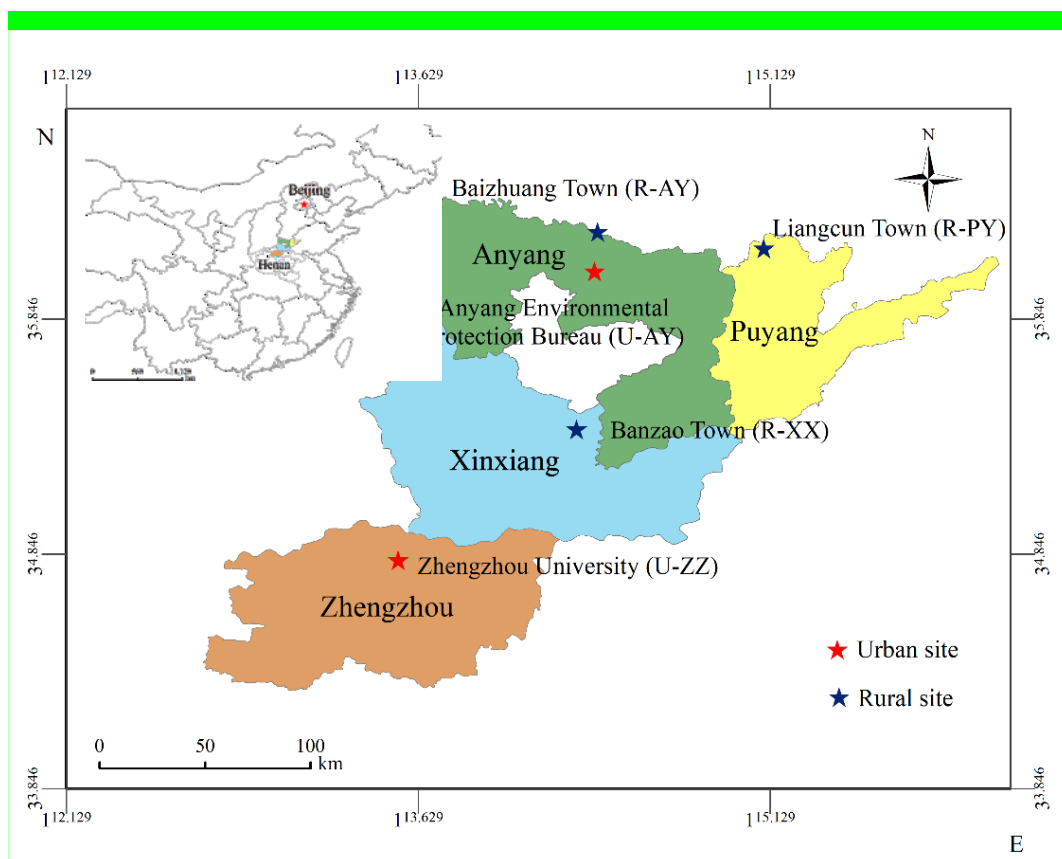

Fig. S1 Locations of the five monitoring stations in Henan Province, China (i.e., urban sites at Zhengzhou (U-ZZ) and Anyang (U-AY), rural sites at Anyang (R-AY), Xinxiang (R-XX), and Puyang (R-PY)). © 2019 National Geomatics Center of China. All rights reserved.

Secondly, we have added the uncertainty of each instrument based on references or instrument

manuals (line 127-145), and pH uncertainty was evaluated by calculating the input data in two extreme scenarios (see Section 2.4). Considering the measurement uncertainty and statistical significance, we have modified the comparison between urban and rural sites instead of the rank of five sites in the revised version (line 247-250, 252-255, 369-271).
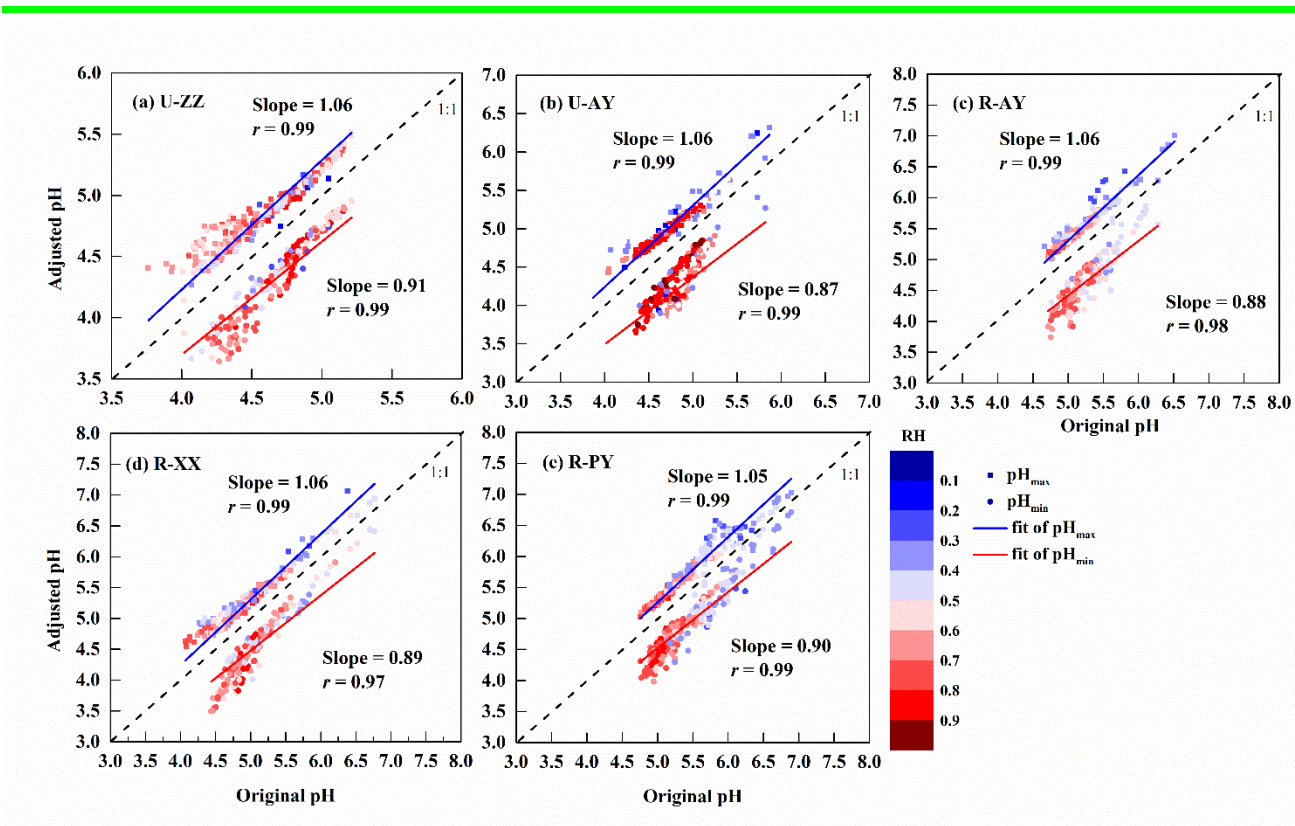

Fig. 1 pH uncertainties of the five sites based on two extreme scenarios of measurement uncertainty. The color scale bar represents RH values. Cations and organic carbon concentrations (OC) were adjusted up to within their maximum positive uncertainties, anions, relative humidity (RH) and temperature (T) were adjusted down within their maximum negative uncertainties, which represented the pH_{max} case; for pH_{min} case, cations and OC concentrations were adjusted down, and anions, RH and T were adjusted up.

Finally, we have added a paragraph to describe the sensitivity tests and explain the use of RSD (line 275-289, 310-315): "To explore the dominant factors that determine the local particle pH level and resulting in the high pH at rural sites, sensitivity tests of pH to chemical species (i.e., TNH_x, TH_2SO_4, TNO_3, TCl, TNa, K^+, Ca^{2+}, and Mg^{2+}) and meteorological parameters (i.e., T and RH) were performed. Firstly, the real-time measured values of a variable (e.g., TNH_x,) and the average values of other parameters (i.e., TH_2SO_4, TNO_3, TCl, TNa, K^+, Ca^{2+}, Mg^{2+}, T and RH) during Case 2 were input into ISORROPIA-II to identify the major factor for local $PM_{2.5}$ pH (Ding et al., 2019), and the results are listed in Table 4 and Fig. S10. In addition, a given range for a variable for all sites with corresponding average values of other parameters was simulated to assess the different effects of this variable among five sites (Fig. 5 and S11). The chosen variation range for each variable was close to the observed minimum and

maximum values (Table S4), which aims to better reflect the actual ambient conditions of observation periods. The degree of sensitivity was represented as the relative standard deviation (%RSD) of the re-calculated pH values. RSD calculates the absolute value of the coefficient of variation, which helps us to determine how small or large is the standard deviation when compared to the mean of the re-calculated pH data set. Therefore, when the re-calculated pH data set has a higher RSD value, this variable can change the pH easier and is more important for local pH."

Specific Comments

A. Text

29-31 These two ideas are not independent. Please choose to state one or the other.

Response: These two ideas have been modified (line 28-31).

41 Typicallly, the phase is included in the subscript (e.g., "NH3(g)/NH4(aq)+").

Response: Thanks for the suggestion. This sentence has been modified (line 44-45).

42 "element" should be "elements".

Response: Done.

102 "electron" is unclear here.

Response: Sorry for the misunderstanding, "electron" has been changed to "electronic factories".

174 Case 2 seems to have different meteorological episodes within it. Consider splitting the lower RH and corresponding lower concentration days into a fourth episode.

Response: Thanks for the comment. The durations of the lower RH and corresponding lower concentration days during Case 2 were short, particularly at U-AY, R-AY, R-XX, and R-PY (Fig. S6) of which only lasted approximately 8 h. In addition, we excluded data with RH < 30 %, a condition where predicted to observed partitioning of nitrate between the gas and particle phase are in weak correlation, and thus uncertainties in the pH prediction are expected to be high (Ding et al., 2019; Guo et al., 2016). Therefore, there is no adequate data to be classified into a fourth episode.

209-10 This conclusion is simply based on Equation 1. Please consider removing the log-linear dependence from Figure 2 and this sentence. This correlation exists because of the calculation.

Response: Thanks for your suggestions. Figure 2 has been replaced by Fig. S9 in revised manuscript to support the conclusion of "predicted pH values present better correlations with H^+_{air} concentrations rather than AWC" (line 257-258).

213-5 This statement makes it difficult to see that Case 3 is being compared with Case 1. Consider making the single sentence into two sentences.

Response: This sentence has been simplified to "The pH values (Table S2) of the five sites during

Cases 2 and 3 were comparable but slightly lower than those in Case 1". (Line 256-257)

221 Perhaps the back trajectories in the SI indicate the degree of influence from transport, but it may be helpful to include a summary of the influences in the description of the cases if this information will be referenced in the discussion.

Response: Thank you for the comments. A new figure has been supplied to present the trajectory frequencies for each site during three cases with detail descriptions in Text S2.

264 "figure" should be "Figure".

Response: Done.

289 "liner" should be "linear"

Response: Done.

B. Figures and Tables

Fig 1 & 2 Please add uncertainty shading or bars to the inorganic constituent measurements and to ammonia. If you could please propagate that uncertainty to aerosol pH, the aerosol pH difference across sites could be evaluated.

Response: We have added the uncertainty shading in Fig. 2. Particle pH uncertainty was evaluated by calculating the input data in two extreme scenarios (see Section 2.4), and uncertainty shading of pH for each site has been presented in Fig. S8.
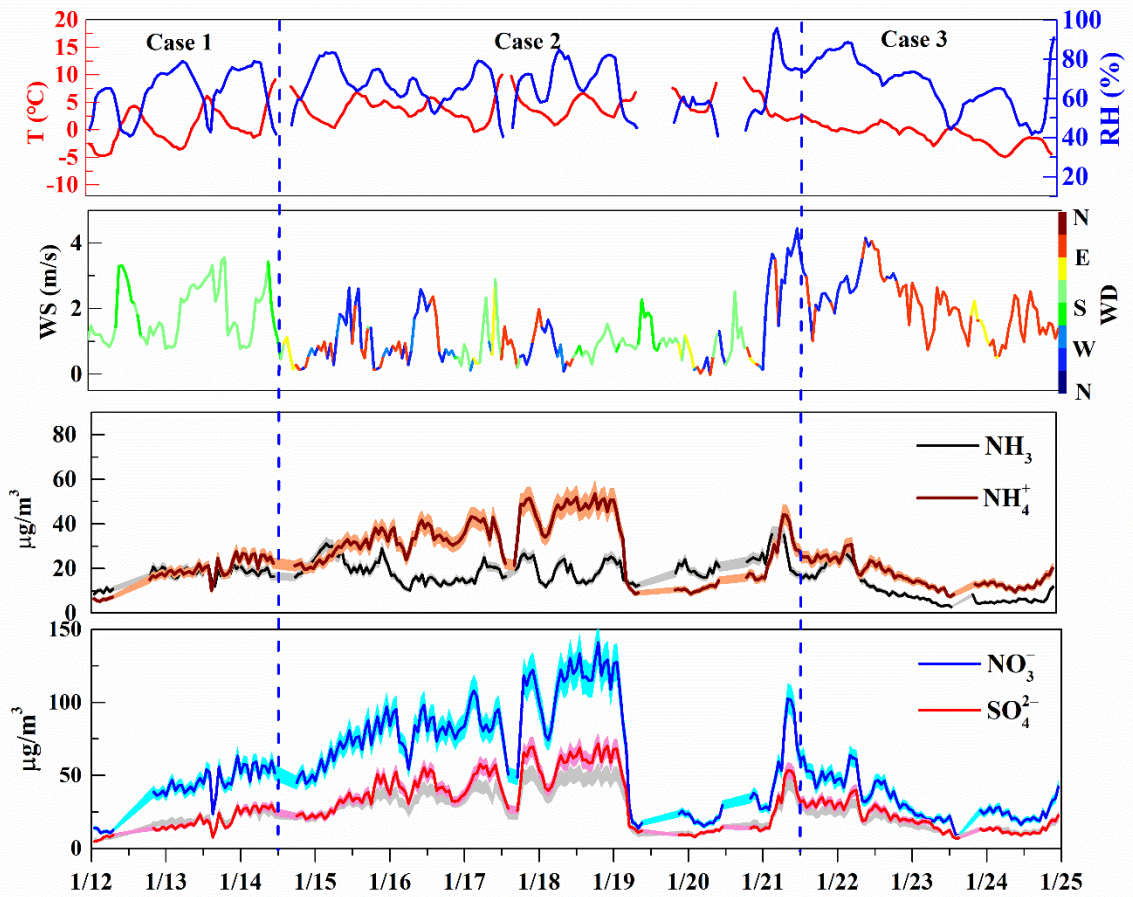
Fig. 2 Temporal variations of temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD), and concentrations of NH_3, NH_4^+, SO_4^{2-}, and NO_3^- during three cases at the Zhengzhou (U-ZZ) site. The shaded areas represent the measurement uncertainties.
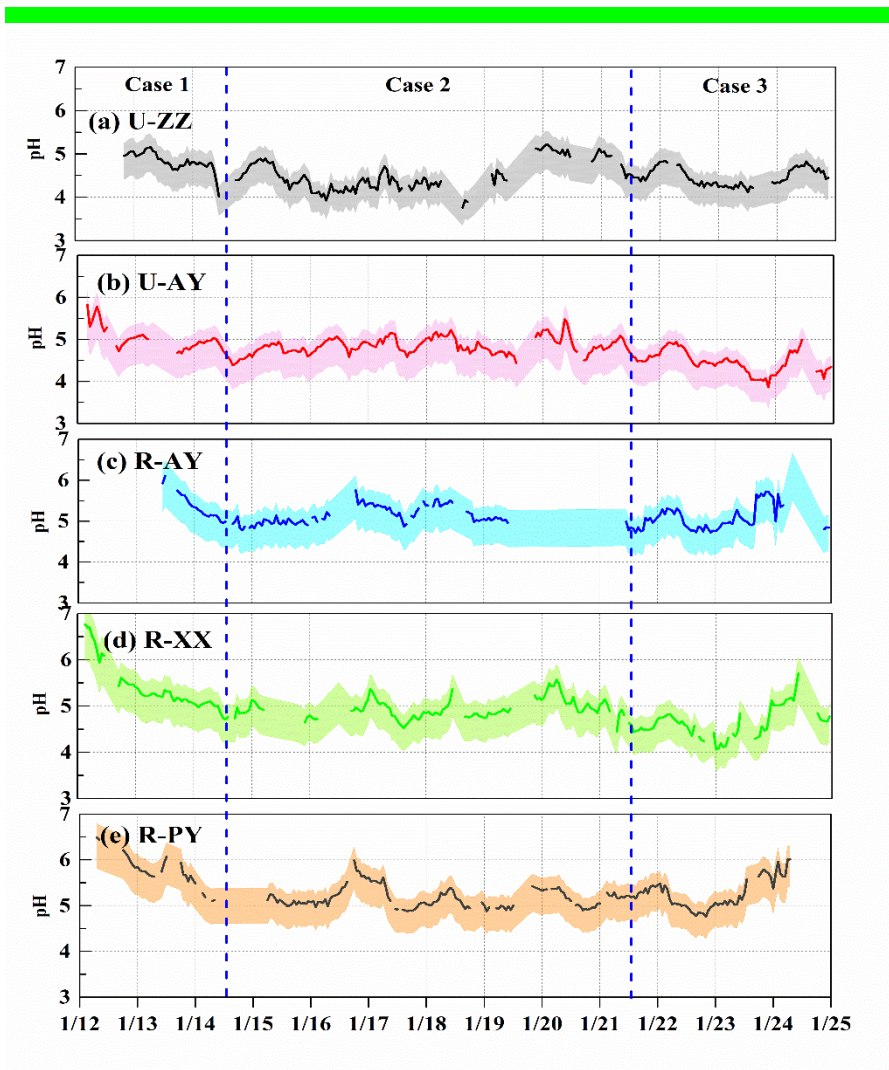
Fig. S8 Time series of predicted PM$_{2.5}$ pH at the five sites. The shaded areas show the range of uncertainty in pH for the pH$_{max}$ and pH$_{min}$ calculations.

Fig 5 This figure is very difficult to understand. What were the conditions across which modeling was conducted at each site? Did those ranges that are plotted as contour colors extend beyond the ranges plotted as a bar? More information would be required in the caption or an associated table in the SI to make this figure helpful.

Response: Sorry for the misunderstanding. We have added more information about the sensitivity tests of Fig. 5 in the caption and supplied an associated table (Table S4).
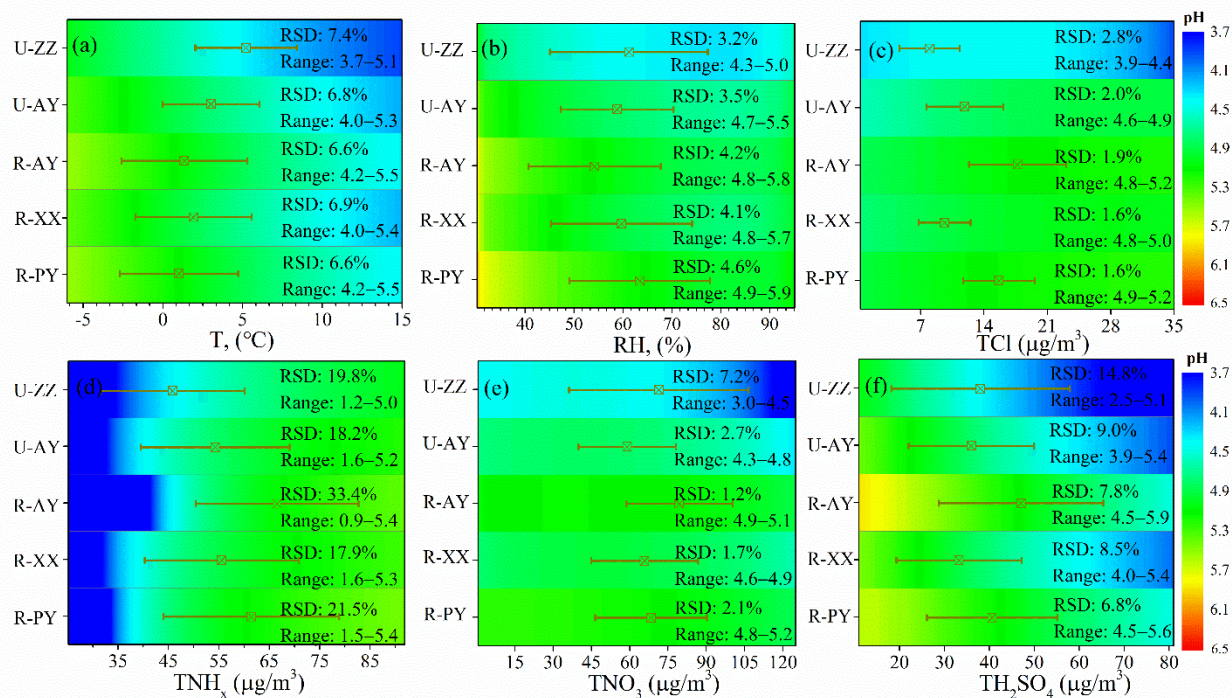
Fig. 5 Comparison of the sensitivities of PM$_{2.5}$ pH to T, RH, TCl, TNH$_x$, TNO$_3$, and TH$_2$SO$_4$ among the five sites. A given range for a variable for all sites with corresponding average values of other parameters was used as input to the ISORROPIA-II model. The range of the x-axis is close to the observed minimum and maximum values in Case 2 (Table S4). The color scale bar represents the pH values. The square plots on the graph represent the average values of each factor observed in Case 2 with standard deviation as an error bar. The relative standard deviation (RSD) and range (Range) represent the variation degree and range (min–max) of the pH values in the test.

Table S4 Variation ranges of each variable for assessing the different effects of this variable among five sites and their observed minimum and maximum values.

Species	Observation		Setting		Gradient
	Min	Max	Min	Max	
T (°C)	−5.8	14.3	−6	15	0.1
RH (%)	26.8	92.3	30	95	0.1
TNH$_x$ (μg/m^3)	21.2	96.7	25	95	0.01 μmol/m^3
TNO$_3$ (μg/m^3)	5.8	132.6	1	125	0.01 μmol/m^3
TH$_2$SO$_4$ (μg/m^3)	6.9	82.7	10	80	0.01 μmol/m^3
TCl (μg/m^3)	0.54	39.5	0.35	35	0.01 μmol/m^3
TNa (μg/m^3)	0.29	3.33	0.25	3.5	0.01 μmol/m^3
K$^+$ (μg/m^3)	0.27	7.8	0.1	7.5	0.01 μmol/m^3
Ca^{2+} (μg/m^3)	0.2	5.2	0.4	6	0.01 μmol/m^3

Mg^{2+} (µg/m^3)	0.11	3.1	0.25	3.5	0.01 µmol/m^3

Fig 6 Why is excess NHx not just NH3(g) as predicted from ISORROPIA? As calculated, excess NHx ignores non-ideality as well as bisulfate formation.

Response: This figure was used to examine the effects of major indicators of ammonia (i.e., TNH$_x$, Required-NH$_x$, and Excess-NH$_x$) on aerosol acidity and support the conclusion that the presence of Excess-NH$_x$ was likely important for the less acidic of PM$_{2.5}$ during the severe haze episodes in this region.

Aerosols in this research were expected to be ammonia-rich because almost all the mole ratios of NH$_4^+$ to SO$_4^{2-}$ were higher than 2; at this value each mole of sulfate removes 2 mol of ammonium (Squizzato et al., 2013), meaning that SO$_4^{2-}$ mainly took the form of (NH$_4$)$_2$SO$_4$. In addition, with respect to measurements of semi-volatile gases, the concentrations of NH$_3$ were extremely higher than HNO$_3$ and HCl. Therefore, similar to Blanchard et al. (2000), Song et al. (2018), and Liu et al. (2017), Required-NH$_x$ and Excess-NH$_x$ were calculated using the formulas in Text S3. Excess-NH$_x$ in this study represents a part of TNH$_x$ (gas NH$_3$ + particle NH$_4^+$), while the other NH$_x$ plus nonvolatile cations have been equivalent to all anions.

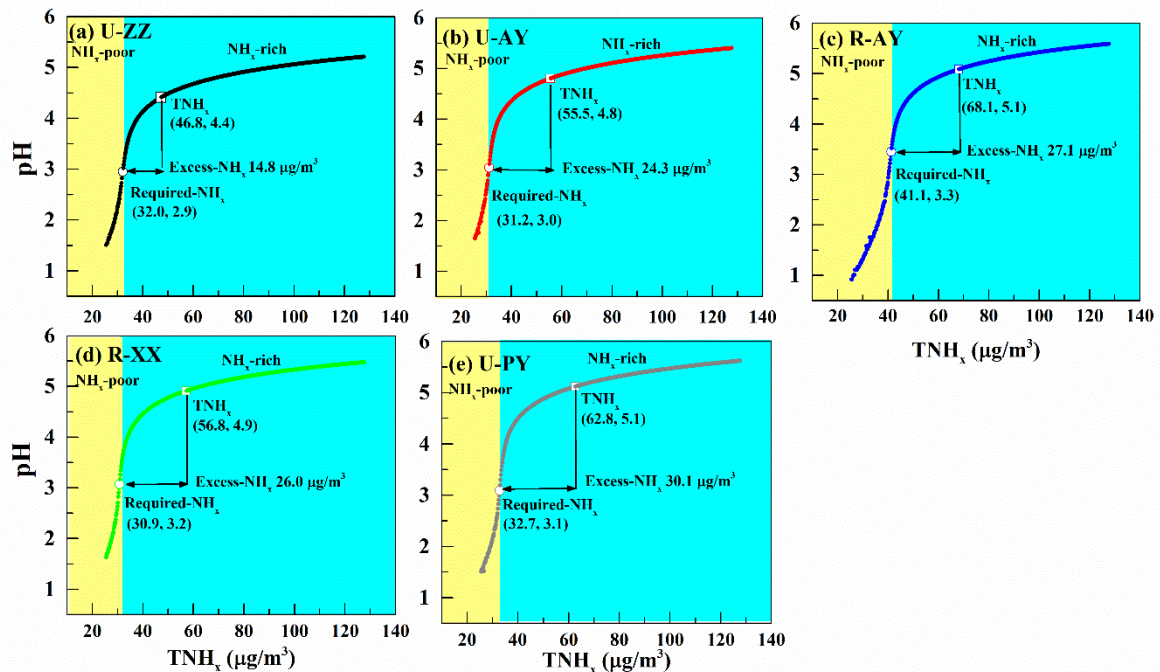Fig. 7 Sensitivity tests of PM$_{2.5}$ pH to TNH$_x$ at the five sites to examine the effects of major indicators of NH$_3$ (i.e., TNH$_x$, Required-NH$_x$, and Excess-NH$_x$) on aerosol acidity. Particle pH was calculated by using a wide range of TNH$_x$ (25–130 µg/m^3) and average values of other parameters during Case 2 of each site. The concentrations of TNH$_x$, Required-NH$_x$, and Excess-NH$_x$ with corresponding pH values are marked

References:

Blanchard, C. L., P. M. Roth, S. J. Tanenbaum, S. D. Ziman, and J. H. Seinfeld: The use of ambient measurements to identify which precursor species limit aerosol nitrate formation, J. Air Waste Manage. Assoc., 50, 2073–2084, 2000.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., Zhu, T.: Fine particle pH during severe haze episodes in northern China. Geophys. Res. Lett., 44, 5213−5221, 2017.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., Mcelroy, M. B.: Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models. Atmos. Chem. Phy., 18, 7423−7438, 2018.

Squizzato, S., Masiol, M., Brunelli, A., Pistollato, S., Tarabotti, E., Rampazzo, G., Pavoni, B.: Factors determining the formation of secondary inorganic aerosol: a case study in the Po Valley (Italy). Atmos. Chem. Phys. 13, 1927–1939, 2013.

Fig 7 How was SO4(aq)2- specified when running ISORROPIA? If the authors mean total sulfate, please correct the figure caption and axis label. Although all of the sulfate remains in the aerosol phase in ISORROPIA, it does not all become SO4(aq)2- necessarily

Response: Sorry for the misunderstanding. We have modified the descriptions of the input data of ISORROPIA: "Input data, including RH, T, concentrations of K$^+$, Ca^{2+}, and Mg^{2+}, and total (i.e., gas + aerosol) concentrations of TNH$_x$, H$_2$SO$_4$ (TH$_2$SO$_4$, replaced by observed SO$_4^{2-}$), Na (TNa, replaced by observed Na$^+$), TCl, and TNO$_3$, were used to calculate the…". Moreover, all figures have been modified. We hope it has been improved in the revised version.
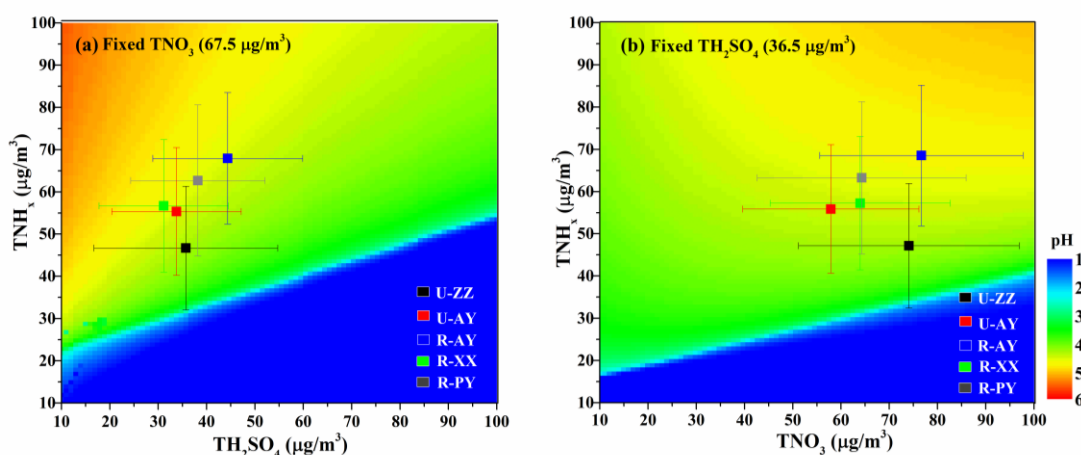

Fig. 6 pH calculated with fixed meteorological parameters (T = 275.5 K and RH = 60 %) under different combinations of TNH$_x$ and (a) TH$_2$SO$_4$ (Fixed TNO$_3$ = 67.5 μg/m^3) and (b) TNO$_3$ (Fixed TH$_2$SO$_4$ = 36.5 μg/m^3). The color scale bar represents the pH values. The markers on the graph represent the average concentrations of TNH$_x$, TH$_2$SO$_4$, and TNO$_3$ at the five sites during Case 2 with standard deviation as error bar.