

Responses to the reviewers

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

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 a unit-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.

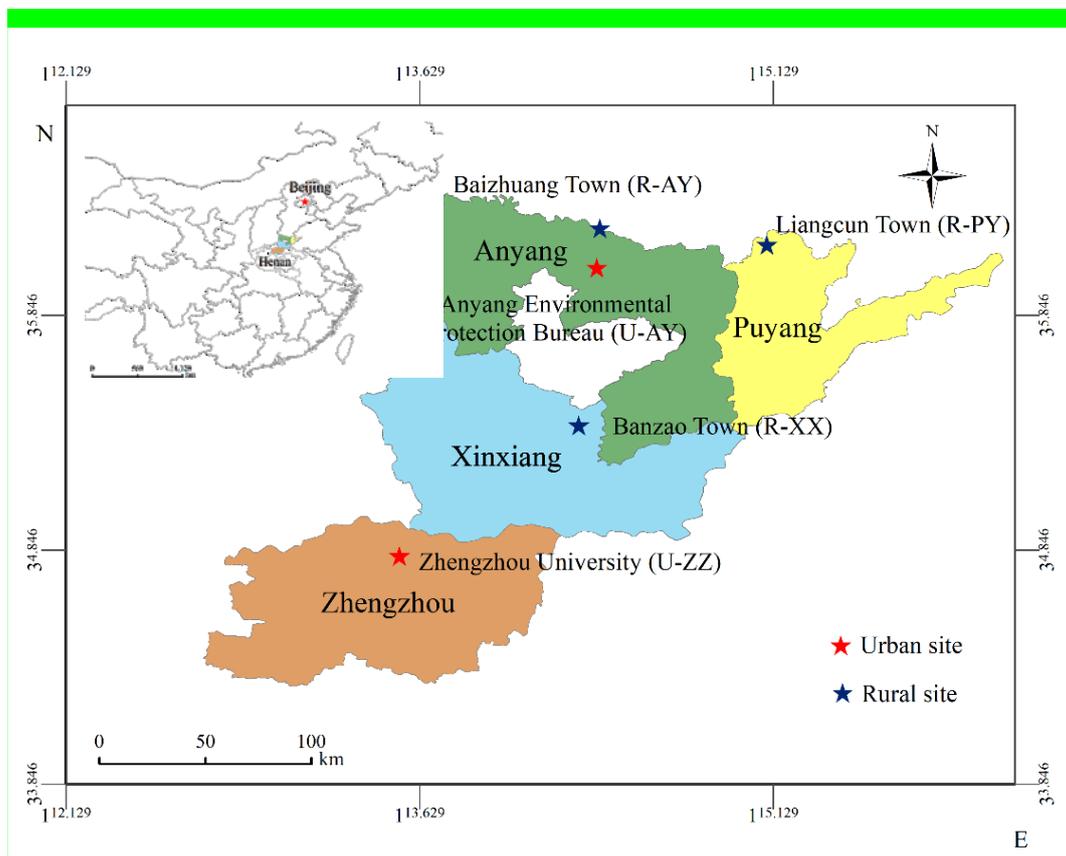


Fig. S1 Locations of the five monitoring stations in Henan Province, China (i.e., urban sites at Zhengzhou (U-ZZ) and Anyang (U-AY), rural sites at Anyang (R-AY), Xinxiang (R-XX), and Puyang (R-PY)). © 2019 National Geomatics Center of China. All rights reserved.

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).

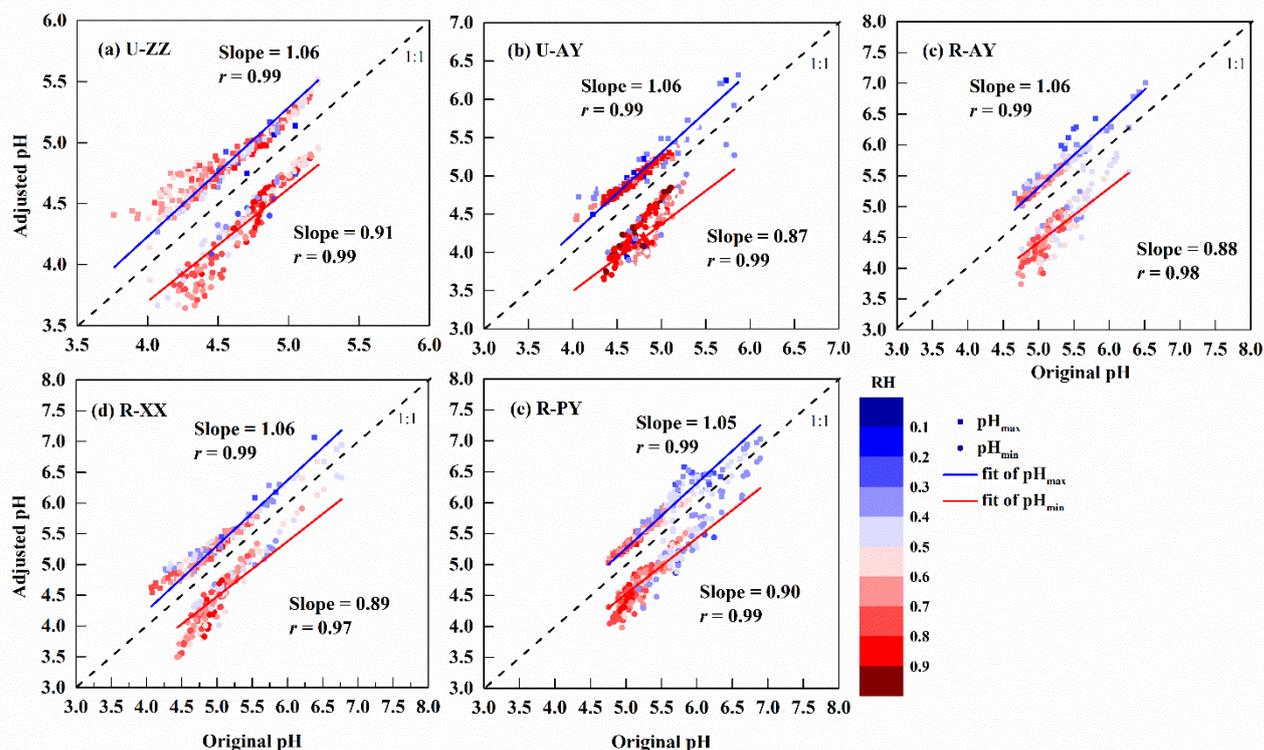


Fig. 1 pH uncertainties of the five sites based on two extreme scenarios of measurement uncertainty. Cations and organic carbon concentrations (OC) were adjusted up to within their maximum positive uncertainties, anions, relative humidity (RH) and temperature (T) were adjusted down within their maximum 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. The color scale bar represents adjusted RH.

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 $\text{PM}_{2.5}$ 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 recalculated 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 Typically, 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.

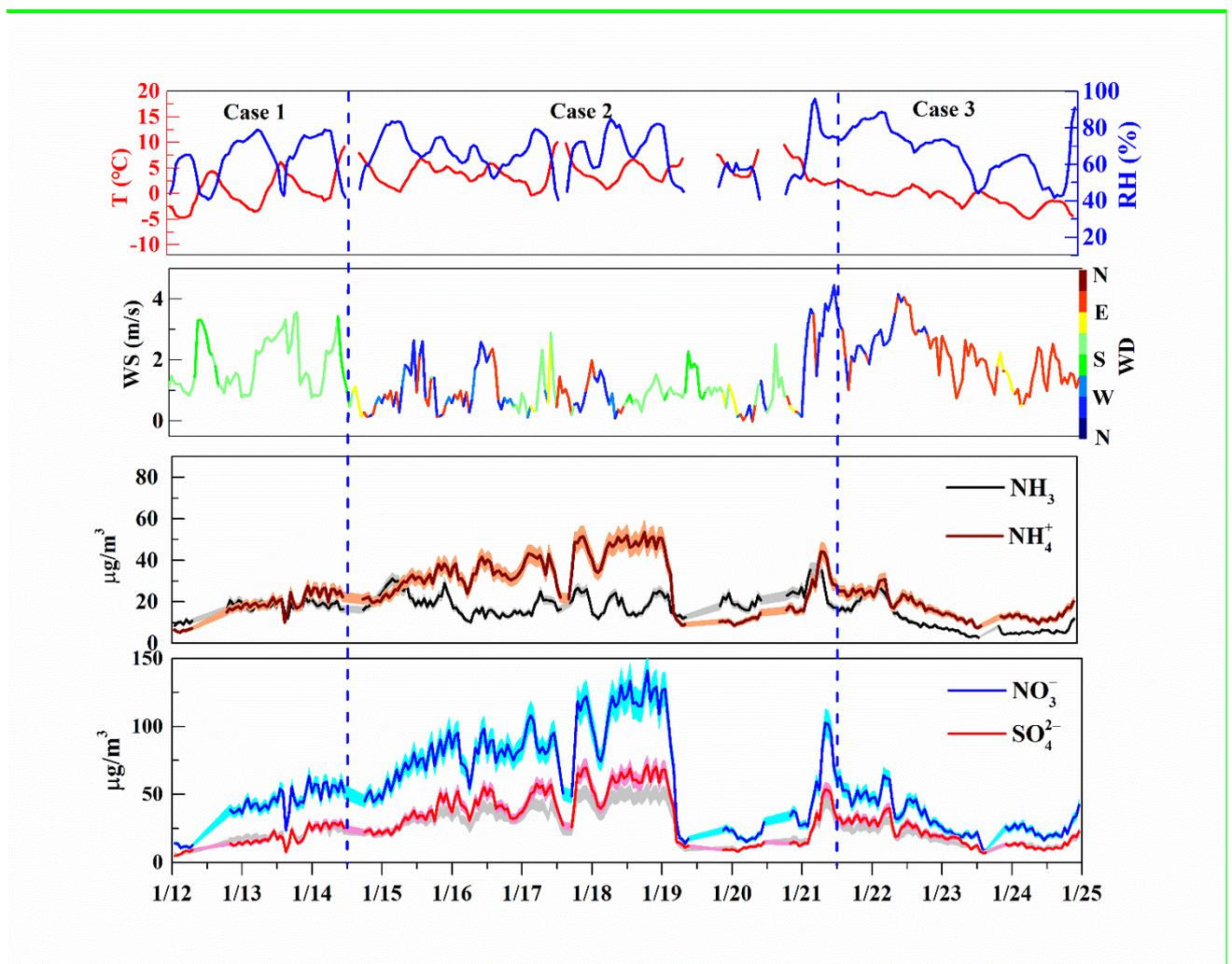


Fig. 2 Temporal variations of T, RH, wind speed (WS), wind direction (WD), and concentrations of NH_3 , NH_4^+ , SO_4^{2-} , and NO_3^- during three cases at the Zhengzhou (U-ZZ) site. The shaded areas represent the measurement uncertainties.

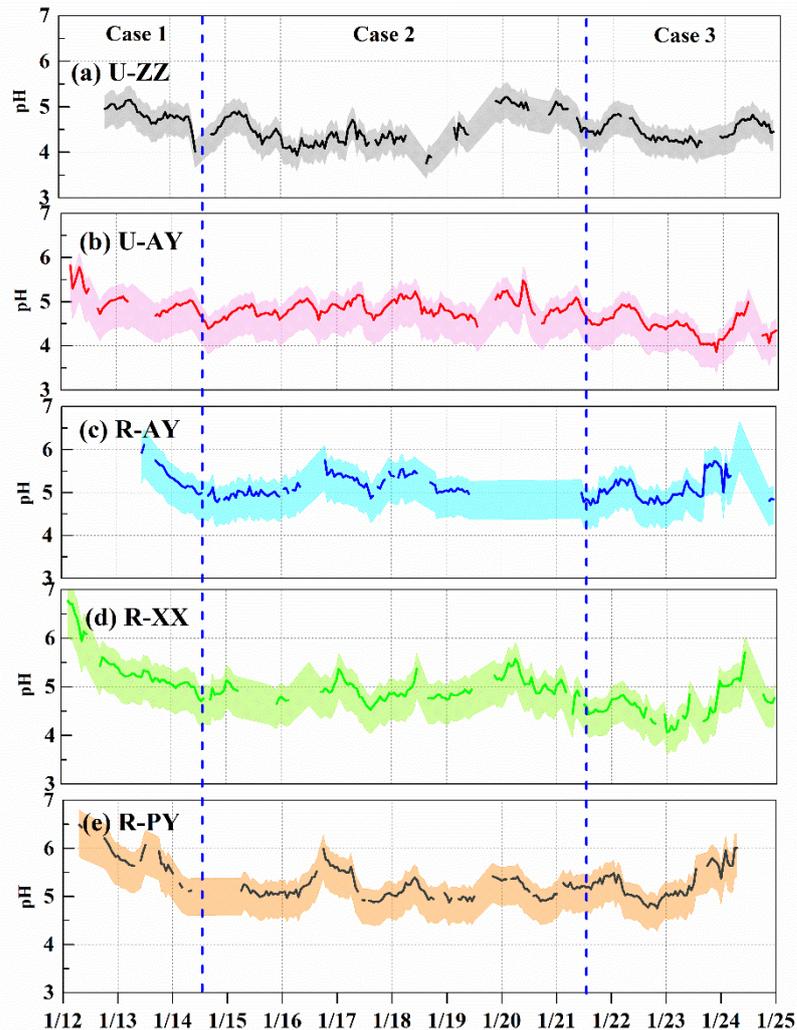


Fig. S8 Time series of predicted $\text{PM}_{2.5}$ pH at the five sites. The shaded areas show the range of uncertainty in pH for the pH_{max} and pH_{min} calculations.

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).

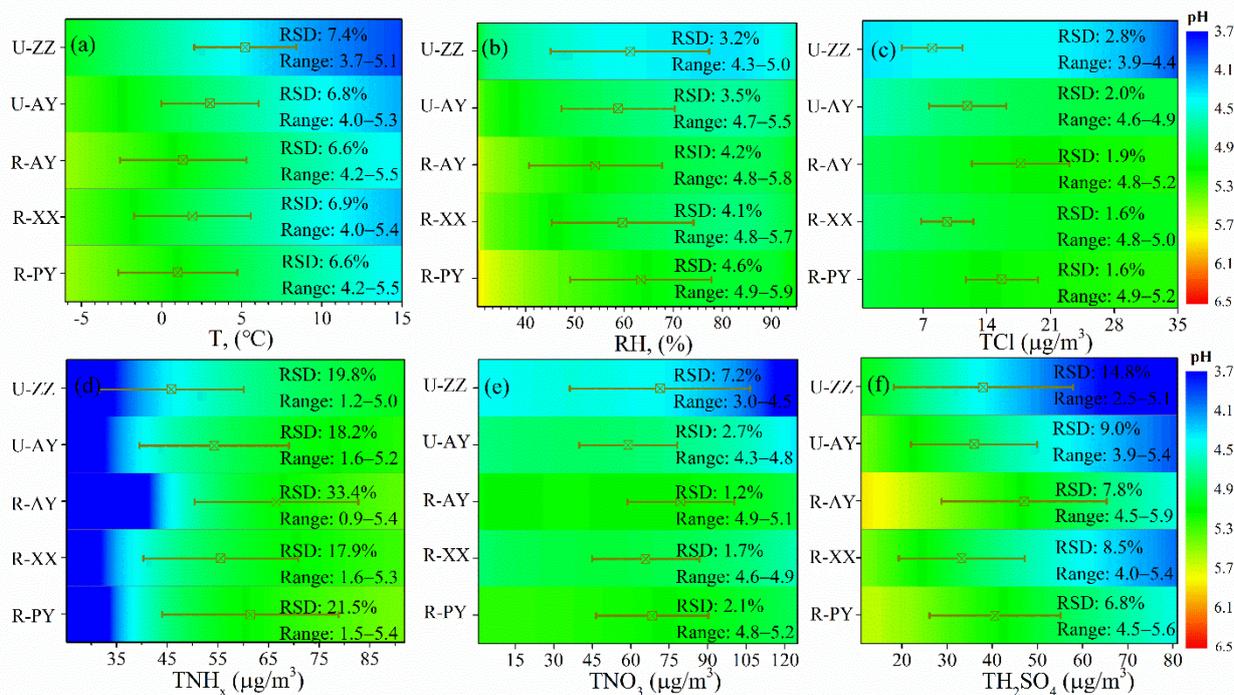


Fig. 5 Comparison of the sensitivities of PM_{2.5} pH to T, RH, TCl (HCl_(g) + Cl_(aq)⁻), TNH_x (NH_{3(g)} + NH_{4(aq)}⁺), TNO₃ (HNO_{3(g)} + NO_{3(aq)}⁻), and TH₂SO₄ (replaced by observed SO₄²⁻) among the five sites. A given range for a variable for all sites with corresponding average values of other 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 relative standard deviation (RSD) and range (Range) represent the sensitivity degree of pH to this variable and range (min–max) of the re-predicted pH value in the test, respectively. The square plots on the graph represent the average values of each variable observed in Case 2 with standard deviation as an error bar.

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 ($\mu\text{g}/\text{m}^3$)	0.54	39.5	0.35	35	0.01 $\mu\text{mol}/\text{m}^3$
TNa ($\mu\text{g}/\text{m}^3$)	0.29	3.33	0.25	3.5	0.01 $\mu\text{mol}/\text{m}^3$
K ⁺ ($\mu\text{g}/\text{m}^3$)	0.27	7.8	0.1	7.5	0.01 $\mu\text{mol}/\text{m}^3$
Ca ²⁺ ($\mu\text{g}/\text{m}^3$)	0.2	5.2	0.4	6	0.01 $\mu\text{mol}/\text{m}^3$
Mg ²⁺ ($\mu\text{g}/\text{m}^3$)	0.11	3.1	0.25	3.5	0.01 $\mu\text{mol}/\text{m}^3$

Fig 6 Why is excess NH_x not just NH₃(g) as predicted from ISORROPIA? As calculated, excess NH_x 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 NH₄⁺ to SO₄²⁻ were higher than 2; at this value each mole of sulfate removes 2 mol of ammonium (Squizzato et al., 2013), meaning that SO₄²⁻ mainly took the form of (NH₄)₂SO₄. In addition, with respect to measurements of semi-volatile gases, the concentrations of NH₃ were extremely higher than HNO₃ 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 NH₃ + particle NH₄⁺), while the other NH_x plus nonvolatile cations have been equivalent to all anions.

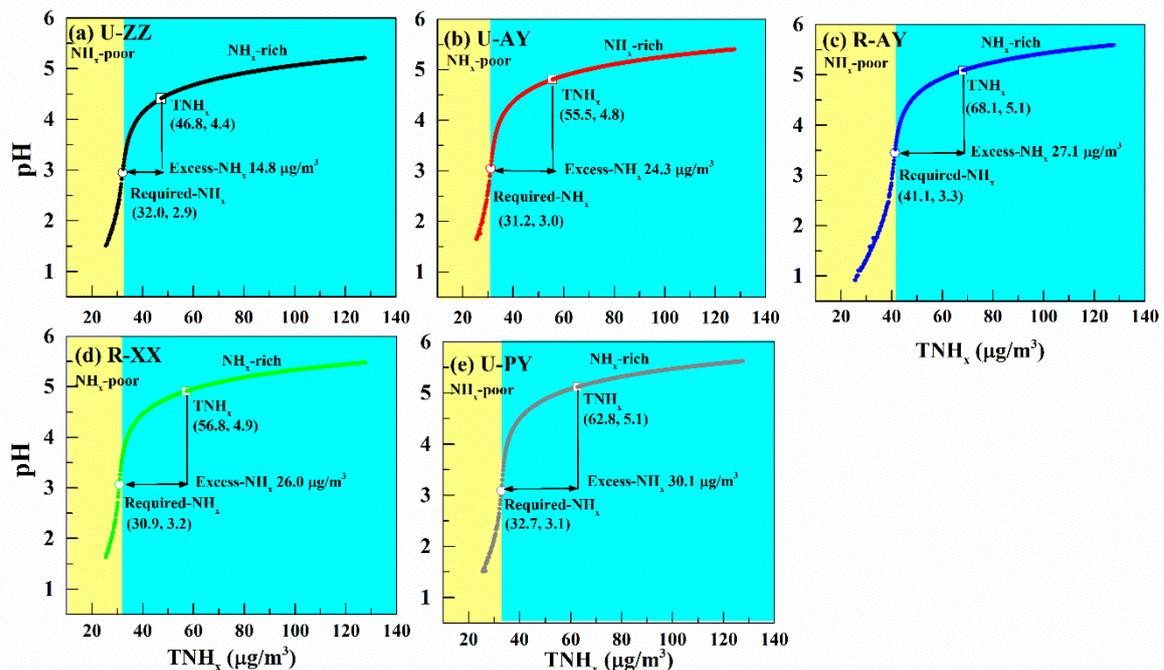


Fig. 7 Particle pH corresponds to increasing TNH_x at the five sites to examine the effects of major

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 ($25\text{--}130\ \mu\text{g}/\text{m}^3$) 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 by a hollow box, hollow circle, and arrow respectively. The yellow and blue background colors correspond to the NH_x -poor and NH_x -rich, respectively.

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. Phys.*, 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 $\text{SO}_4(\text{aq})_2^-$ 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 $\text{SO}_4(\text{aq})_2^-$ 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_2SO_4 (TH_2SO_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.

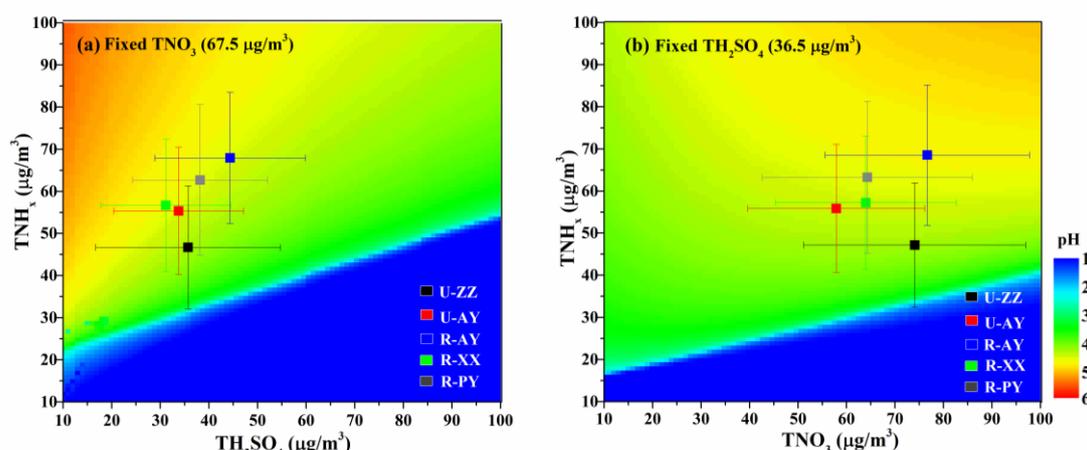


Fig. 6 Particle pH calculated with fixed meteorological parameters ($T = 275.5\ \text{K}$ and $\text{RH} = 60\ \%$) under different combinations of TNH_x and (a) TH_2SO_4 (Fixed $\text{TNO}_3 = 67.5\ \mu\text{g}/\text{m}^3$) and (b) TNO_3 (Fixed TH_2SO_4

= 36.5 $\mu\text{g}/\text{m}^3$). The color scale bar represents the pH values. The markers on the graph represent the average concentrations of TNH_x , TH_2SO_4 , and TNO_3 at the five sites during Case 2 with standard deviation as error bar.



1 **Role of ammonia on fine-particle pH in agricultural regions of China:**
2 **Comparison between urban and rural sites**

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22 **Abstract:** Particle acidity is a fundamental property that affects atmospheric particulate chemistry.
23 Synchronous online monitoring was performed in two urban sites (e.g., Zhengzhou (U-ZZ) and
24 Anyang (U-AY)) and three rural sites (e.g., Anyang (R-AY), Xinxiang (R-XX), and Puyang (R-PY))
25 in Henan Province during a haze episode to investigate the pH value and its driving factors in the
26 agricultural regions of China. The pH values of particles calculated by ISORROPIA-II model at rural
27 sites were slightly higher than those at urban sites, with the median (min–max) values of 5.2 (4.8–6.9,
28 R-PY), 5.1 (4.7–6.5, R-AY), 4.9 (4.1–6.8, R-XX), 4.8 (3.9–5.9, U-AY), and 4.5 (3.8–5.2, U-ZZ).
29 Sensitivity tests show that TNH_x (total ammonium (gas + aerosol)), followed by total sulfate, were the
30 important factors that influenced the predicted pH. Generally, particle pH increased with the cation
31 increasing and the decrease in the anion, temperature, and relative humidity. Similar pH values (~3.0)
32 at the required NH_x concentrations for the five sites indicated that the presence of excess NH_x was
33 likely important for the less acidic of $\text{PM}_{2.5}$ during the severe haze episodes in this region. Moreover,
34 the concentrations of excess NH_x may drive the higher pH values at rural sites, because of the higher
35 excess NH_x concentrations at rural sites than those at urban sites. The underlying influence of regional
36 transport on local particle pH cannot be neglected by differing the chemical components of $\text{PM}_{2.5}$ and
37 meteorological conditions. Air masses transported from rural and agricultural regions may enhance the
38 particle pH value in urban aerosols given the high pH of particles and high ammonia levels. These
39 results suggest that ammonia is urgently needed to be involved in the regional strategy for the
40 improvement of air quality in China.
41 **Keywords:** ISORROPIA-II model, Particle acidity, Ammonia, Sensitivity test, Regional transport.

42 1 Introduction

43 High concentrations of acids and bases contained in the aqueous phase define the acidity of
44 aerosols (Spurny, 1990). Particle acidity or pH value is an important parameter for atmospheric
45 particulate chemistry, such as the gas-particle partitioning of semi-volatile and volatile species (e.g.,
46 $\text{NH}_3(\text{g})/\text{NH}_4(\text{aq})^+$, $\text{HCl}(\text{g})/\text{Cl}(\text{aq})^-$, and $\text{HNO}_3(\text{g})/\text{NO}_3(\text{aq})^-$), the formation of secondary inorganic and organic
47 aerosols, and the dissolution of metallic elements (Bougiatioti et al., 2016; Meskhidze et al., 2003;
48 Seinfeld and Pandis, 2006; Shi et al., 2019; Shi et al., 2010; Surratt et al., 2010; Wang et al., 2018b).
49 Particle acidity can affect the ecosystem through its influence on wet/dry deposition, atmospheric
50 visibility, and radiative balance (Boucher and Anderson, 1995; Larssen et al., 2006; Pye et al., 2019;
51 Watson, 2002). In addition, high particle acidity has an adverse impact on public health, especially for
52 the cardiopulmonary and respiration system of humans (Dockery et al., 1996; Ostro et al., 1991).

53 Direct measurements on particle pH are challenging because of the small size and nonideality of
54 chemical species in solvated aerosols. Therefore, thermodynamic models, such as E-AIM
55 (<http://www.aim.env.uea.ac.uk/aim/aim.php>) and ISORROPIA-II (<http://isorro피아.eas.gatech.edu>)
56 (Clegg et al., 1998; Nenes et al., 1998), which rely on the measurements of particulate and gaseous
57 species, are widely used in estimating particle pH. Generally, the global distribution of fine particulate
58 matter ($\text{PM}_{2.5}$, aerodynamic diameter $\leq 2.5 \mu\text{m}$) pH is bimodal with a population of particles having a
59 mean pH of 1–3 and another population having an average pH closer to 4–5 (Pye et al., 2019). Table
60 1 shows that $\text{PM}_{2.5}$ in mainland China were moderately acidic with pH values that ranged from 3.4–
61 5.7 (Ding et al., 2019; Guo et al., 2017; Liu et al., 2017; Shi et al., 2017, 2019; Song et al., 2018; Wang
62 et al., 2019a), which were 3–5 units higher than those reported in other regions, such as Hong Kong,

63 Singapore, USA, and Greece (Behera et al., 2013; Bougiatioti et al., 2016; Guo et al., 2016; Guo et al.,
64 2014; Pathak et al., 2004).

65 High atmospheric ammonia (TNH_x, gas NH₃ plus particle NH₄⁺) is a dominant factor that drives
66 the high PM_{2.5} pH in megacities of China because it suppresses the production of particle hydronium
67 (Cheng et al., 2016; Wang et al., 2016). Liu et al. (2017) argued that excess NH₃ and elevated aerosol
68 water content (AWC) were responsible for the high pH in Beijing. Nevertheless, Guo et al. (2017) and
69 Song et al. (2018) demonstrated that high levels of ammonia did not increase the PM_{2.5} pH into a fully
70 neutralized condition in Beijing and Xi'an, China. Weber et al. (2016) calculated that only large
71 increases in NH₃ together with sulfate reductions can lead to an increase in pH. Correspondingly,
72 higher pH by about 1 unit than urban aerosols was observed in locations of intensive agriculture with
73 high NH₃ concentrations in the southeastern US (Nah et al., 2018). The primary sources for ammonia
74 include agricultural emissions, such as livestock waste, N-fertilizer application, and biomass burning,
75 as well as traffic and industrial emissions (Huang et al., 2012; Shen et al., 2011; Wang et al., 2018a).
76 Field studies have reported that elevated NH₃ and NH₄⁺ concentrations were recorded at rural sites in
77 the North China Plain (Meng et al., 2011; Meng et al., 2017; Shen et al., 2011; Wen et al., 2015).
78 Therefore, studying in an agriculturally developed region is needed to obtain insight into the role of
79 ammonia in particle pH. Unfortunately, previous studies mainly concentrated on calculating the
80 particle pH in the megacity of China, and few studies focused on the agricultural regions of China. In
81 addition to ammonia, particle pH can also be influenced by other chemical compositions and
82 meteorological conditions, such as sulfate, AWC, temperature (T), and relative humidity (RH). Sulfate
83 is often the main acid component of aerosols, and largely determines the acidity of PM_{2.5} (Weber et al.,

84 2016). Sensitivity tests in Beijing suggested that sulfate, TNH_x , and T were the common driving factors,
85 and Ca^{2+} and RH were the unique factors in special seasons (Ding et al., 2019). The pH sensitivity
86 based on the 10-year record in Canada showed that chemical compositions had various effects on
87 particle pH under different meteorological conditions; moreover, careful examination for any
88 particular region is needed (Tao and Murphy, 2019).

89 Henan Province is situated in Central China; it has a dense rural population and is a top-ranking
90 province in China in terms of agricultural production and chemical fertilizer consumption (NBS, 2016).
91 NH_3 emission inventory for Henan Province reported that approximately 1031.6 Gg NH_3 was released
92 in Henan in 2015, thereby contributing to approximately 10 % of China's total emissions
93 (approximately 10 Tg) (Huang et al., 2012; Wang et al., 2018a). Livestock waste and N-fertilizer
94 application were major sources for ammonia emissions, which may increase TNH_x concentrations at
95 rural sites than in urban sites. Furthermore, Henan Province is a severely $\text{PM}_{2.5}$ -polluted region in
96 China. In January 2018, a large-scale and long-lasting haze episode that caused $\text{PM}_{2.5}$ concentration to
97 reach $400 \mu\text{g}/\text{m}^3$ occurred in this region (Wang et al., 2019c). An experiment was performed in two
98 urban and three rural sites in Henan Province to investigate the particle acidity and its driving factor.
99 ISORROPIA-II model was utilized to estimate $\text{PM}_{2.5}$ pH using a high-time-resolution dataset. The
100 novelty of the work addressed in the present study is that this study is the first on $\text{PM}_{2.5}$ acidity by
101 comparing urban and rural sites in the agricultural regions of China. The specific objectives of the
102 study were presented as follows: (1) Estimation and comparison of the $\text{PM}_{2.5}$ pH at the five monitoring
103 sites, (2) identification of the factors that determine the pH, and (3) discussion of the role of ammonia
104 on pH. Our results are helpful to understand the factors that determine particle acidity better.

105 **2 Experiment and methods**

106 **2.1 Site descriptions**

107 Field sampling was synchronously conducted from January 12 to 24, 2018 at five sites (i.e., two
108 urban sites located in the center of Zhengzhou (U-ZZ) and Anyang (U-AY), and three sites located in
109 the rural areas of Anyang (R-AY), Xinxiang (R-XX), and Puyang (R-PY)). Locations of the five sites
110 (Fig. S1) with brief descriptions are listed in Table 2. U-ZZ site is surrounded by busy roads, and two
111 freeways are located 3 km to the south and 7 km to the east. Moreover, this site is near a coal-fired
112 power plant; a gas-fired power plant; and several small-scale industries, such as pharmaceutical
113 companies, **electronic factories**, and equipment manufacturing. U-AY site is surrounded by busy roads,
114 and Anyang steelwork is located 8 km to the west. R-AY site is surrounded by farmland and is 1 km
115 west of the Jing-Gang-Ao freeway and 1 km north of a belt freeway. R-XX and R-PY sites are
116 surrounded by farmland without other prominent anthropogenic emission sources.

117 **2.2 Instrumentations**

118 The hourly mass concentrations of water-soluble inorganic ions (WSIIs) in PM_{2.5}, such as NH₄⁺,
119 SO₄²⁻, NO₃⁻, Cl⁻, Na⁺, Mg²⁺, Ca²⁺, and K⁺ and their gaseous precursors (i.e., NH₃, HNO₃, and HCl)
120 were measured using an ambient ion monitor (URG-9000D, Thermal Fisher Scientific, USA) in U-ZZ
121 site and the monitor for aerosols and gases (MARGA, Metrohm, Switzerland) in other sites. Both
122 instruments have been successfully deployed in several other field experiments (Li et al., 2017; Shi et
123 al., 2017; Wang 2019b), and detailed information is available elsewhere (Markovic et al., 2012;
124 Rumsey et al., 2014). As a brief summary, ambient air is drawn into the systems at a flow rate of 16.7
125 L/min. Subsequently, particles and gases are collected by two aerosol sample collectors through a wet

126 parallel plate or wet rotating denuder. Aqueous solution samples are quantified by using two ion
127 chromatography analyzers. Detection limits for all species during the sampling periods were less than
128 $0.1 \mu\text{g}/\text{m}^3$. Measurement uncertainties were assumed to 10 % for URG-9000D here by reference to
129 10 % of Markovic et al. (2012) and 12 % in Hu et al. (2014). For the MARGA instrument, Song et al.
130 (2018) took 20 % as overall relative uncertainties for major species, and Rumsey et al. (2014) reported
131 that the analytical biases were lower than 10 % for SO_4^{2-} , NO_3^- , and HNO_3 , but higher than 15 % for
132 NH_3 and NH_4^+ . Therefore, overall uncertainties were estimated to be 20 % for NH_3 and NH_4^+ and 10 %
133 for other species. The combined uncertainties for TNH_x were calculated to be 14 % and 23 % for U-
134 ZZ and other sites, respectively, and 14 % uncertainties of TNO_3 ($\text{NO}_{3(\text{aq})}^- + \text{HNO}_{3(\text{g})}$) and TCl ($\text{Cl}_{(\text{aq})}^-$
135 $+ \text{HCl}_{(\text{g})}$) for all sites. Because of the complex interference during sampling periods at the five sites,
136 such as the slope from the internal calibration, the solution volume, temperature, pressure, and airflow
137 rate, the actual uncertainties might be different from the estimated value. Hourly elemental carbon (EC)
138 and organic carbon (OC) concentrations in $\text{PM}_{2.5}$ were simultaneously obtained by the semi-
139 continuous carbon analyzers (Model 4, Sunset Laboratory Inc, USA) in the same place, except for the
140 U-ZZ site, of which data were provided by the Department of Environmental Protection of Henan
141 Province. Detailed information on this instrument can be found in Panteliadis et al. (2014). Briefly,
142 $\text{PM}_{2.5}$ collected by the device was oxidized to carbon dioxide and analyzed by a nondispersive infrared
143 detector. The relative measurement uncertainty for this instrument was estimated to be 20 % (Liu et
144 al., 2013; Healy et al., 2013). Meteorological parameters, including T, RH, wind direction, and wind
145 speed, were recorded by smart weather sensor (LUFFT-WS500, Sutron Corporation, Germany), with
146 the accuracies of $\pm 0.2 \text{ }^\circ\text{C}$, $\pm 2 \%$, $< 3 \text{ }^\circ$, and 0.1 m/s , respectively.

147 2.3 pH prediction

148 Particle pH was estimated using the ISORROPIA-II thermodynamic model. Input data, including
149 RH, T, concentrations of K^+ , Ca^{2+} , Mg^{2+} , TNH_x , total sulfate (TH_2SO_4 , replaced by observed SO_4^{2-}),
150 total sodium (TNa, replaced by observed Na^+), TCl, and TNO_3 , were used to calculate the particle
151 hydronium ion concentration per volume of air (H^+_{air}) and particle water associated with inorganics
152 (AWC_{inorg}) by computing the equilibrium composition for the $Na^+-K^+-Ca^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-}-NO_3^-$ -
153 Cl^- - H_2O aerosol system. Considering that forward mode is less sensitive to measurement error than
154 the reverse mode and high RH levels were recorded in sampling periods, ISORROPIA-II was run in
155 the forward model for the aerosol system in the metastable condition (Ding et al, 2019; Guo et al.,
156 2015; Hennigan et al., 2015). Moreover, we excluded data with $RH < 30\%$, a condition where
157 predicted to observed partitioning of nitrate between the gas and particle phase are in weak correlation,
158 and thus uncertainties in the pH prediction are expected to be high (Ding et al., 2019; Guo et al., 2016).

159 Aerosol pH was calculated according to the formula (Bougiatioti et al., 2016):

$$160 \text{pH} = -\log_{10} H_{aq}^+ = -\log_{10} \frac{1000H_{air}^+}{AWC_{inorg} + AWC_{org}}, \quad (1)$$

161 where the modeled concentrations for AWC_{inorg} and H^+_{air} are $\mu\text{g}/\text{m}^3$, and AWC_{org} is the particle water
162 associated with the organics predicted using the method:

$$163 AWC_{org} = \frac{m_s}{\rho_s} \frac{k_{org}}{\left(\frac{1}{RH} - 1\right)}, \quad (2)$$

164 where m_s is the mass concentrations of organic matter ($OC \times 1.6$), ρ_s is the organic density ($1.35 \text{ g}/\text{cm}^3$),
165 and k_{org} is the organic hygroscopicity parameter (0.06) (Liu et al., 2017).

166 2.4 pH uncertainty

167 Two extreme scenarios were evaluated to estimate the pH uncertainty based on the measurement

168 uncertainties of input data (Murphy et al., 2017). Sensitivity tests of pH to input data (see Section 3.3)
169 suggest that simulated pH increase with the cation concentrations (i.e., TNH_x , TNa , K^+ , Ca^{2+} , and Mg^{2+})
170 increasing as well as the anion concentrations (i.e., TH_2SO_4 , TNO_3 , and TCl), T and RH decreasing.
171 Moreover, the pH value has a positive correlation with OC concentrations via Eqs. (1 and 2). Therefore,
172 cation and OC concentrations were adjusted up to within their maximum positive uncertainties, and
173 anions, RH and T were adjusted down within their maximum negative uncertainties, which represented
174 the pH_{max} case; for pH_{min} case, cations and OC concentrations were adjusted down, and anions, RH
175 and T were adjusted up. Figure 1 suggests that pH_{max} cases lead to 6 % (slope = 1) errors for all sites,
176 and pH_{min} cases can result in approximately 10 % deviations. Thus, pH uncertainties were set to be
177 -9-6 %, -13-6 %, -12-6 %, -11-6 %, and -10-5 % for U-ZZ, U-AY, R-AY, R-XX, and R-PY sites,
178 respectively.

179 2.5 Model validation

180 The reliability of pH estimation using the ISORROPIA-II thermodynamic model depends on
181 several assumptions, such as the equilibrated gas and particle phases (Pye et al., 2019). Thus, the
182 predicted and observed semi-volatile species (e.g., $\text{NH}_3(\text{g})/\text{NH}_4(\text{aq})^+$, $\text{HCl}(\text{g})/\text{Cl}(\text{aq})^-$, and $\text{HNO}_3(\text{g})/\text{NO}_3(\text{aq})^-$)
183 are compared in Fig. S2. Observed and predicted NH_4^+ , Cl^- , and NO_3^- exhibit significant correlations,
184 have correlation coefficients (r) above 0.95 and slopes near 1 at the five sites. In addition, NH_3
185 concentrations are in good agreement ($r > 0.95$) with slopes between 0.89 (U-ZZ) and 1.13 (R-PY).
186 These results suggest the excellent performance of ISORROPIA-II for modeling these species. The
187 differences in the slopes of NH_4^+ (Fig. S2b) and NH_3 (Fig. S2e) between U-ZZ and R-PY sites were
188 probably attributed to the unbalanced charge of input WSIs (see Text S1 for more details of calculation)

189 with average equivalent ratios (Fig. S3) of 0.99 ± 0.13 (U-ZZ) and 1.20 ± 0.12 (R-PY). However, Song
190 et al. (2018) argued that ion balance was not a key factor for pH calculation in the forward mode,
191 because the forward mode calculations account for additional constraints imposed by the partitioning
192 of semi-volatile species. To verify this, we adjusted the measured NH_4^+ concentration, which was most
193 sensitive to pH modeling (see Section 3.3), to fit the ion balance, and reran the pH calculation. As
194 shown in Fig. S4, re-predicted NH_4^+ and NH_3 concentrations have better performance ($r = 0.99, 0.94$
195 $< \text{slopes} < 1.06$) with input concentrations at two sites than before. However, re-calculated pH values
196 change slightly, and these deviations are included in the range of pH uncertainty discussed in Section
197 2.4. Therefore, the little differences in NH_x partitioning between the model and measurement among
198 the five sites were acceptable for pH calculation.

199 Correlations between the predicted and measured HNO_3 and HCl are weak. Similar problems
200 were found in the northeast U.S. and Beijing. These discrepancies were potentially due to measurement
201 uncertainties brought about by low gas concentrations, the interference of coarse-mode particles, non-
202 volatile cation measurement artifacts, uncertainties in the thermodynamic constants, and kinetic
203 limitations to mass transfer (Ding et al., 2019, Haskins et al., 2018; Pye et al., 2019; Liu et al., 2017).
204 Pye et al. (2019) suggested that ISORROPIA-II yields a mean activity coefficient of (H^+ , Cl^-) that may
205 result in the higher predicted HCl concentration. HNO_3 can be partitioned to both fine and coarse modes,
206 thereby affecting predicted fine-mode nitrate concentrations (Nah et al., 2018). The best semi-volatile
207 species for evaluation of pH modeling depend on the fraction of the gas phase. In this work, most of
208 HNO_3 and HCl concentrated in the particle phase, and thus they are not suited to test the model (Guo
209 et al., 2016).

210 The PM_{2.5} pH was also calculated by the E-AIM (Version IV) model to evaluate the performance
211 of ISORROPIA-II using the observed data (RH > 60 %) of the U-ZZ site as an example. Close
212 correlation ($r = 0.89$) is found between two models with a slope of 0.95 (Fig. S5). The pH values in
213 ISORROPIA-II are 0.46 ± 0.15 units higher than those in E-AIM. These values are comparable to the
214 founding by Liu et al. (2017) and Song et al. (2018), **which is possibly due to the differences of activity**
215 **coefficient values between the ISORROPIA-II and E-AIM models (Pye et al., 2019)**. Overall, the
216 predicted pH values using ISORROPIA-II are effective in this work.

217 **3 Results and discussion**

218 **3.1 Haze episodes**

219 During the sampling periods, five monitoring sites simultaneously experienced a long-lasting and
220 large-scale haze episode. Time series of the concentrations of major species (i.e., NH₃, NH₄⁺, SO₄²⁻,
221 and NO₃⁻) and meteorological parameters at the U-ZZ site as an example are presented in Fig. 2, and
222 other sites are integrated into Fig S6 with the mean values listed in Table 3. Three study cases were
223 classified on the basis of similar meteorological conditions and WSIs levels at the five sites. The
224 WSIs concentration, T, and RH gradually increased in the southern wind during Case 1 (January
225 12–14). Case 3 (January 21–25) was characterized by decreased WSII concentrations, T, and RH with
226 the northeastern wind. Even though the total WSIs (TWSIs) concentrations were comparable, the
227 chemical components of WSIs were various between Cases 1 and 3 (Table 3). In particular, NO₃⁻,
228 NH₄⁺, and NH₃ concentrations in Case 1 were higher than those in Case 3 at all sites. Conversely,
229 SO₄²⁻ concentrations in Case 1 were lower than those in Case 3. Wang et al. (2018a) reported that the
230 southern cities of Henan Province (e.g., Nanyang, Shangqiu, Zhoukou, and Zhumadian) had relatively

231 higher ammonia emissions than the cities involved in this study. Moreover, the northeastern air masses
232 from the Jing–Jin–Ji regions were easily enriched with sulfate (Wang et al., 2019b; Wang et al., 2018c).
233 Evidently, back trajectory frequency analysis (see Text S2 for more details of the discussion) confirmed
234 that sampling sites during Cases 1 and 3 (Figs. S7a and c) were predominantly influenced by the
235 southern and northeastern air masses, respectively.

236 Elevated WSIs concentrations during Case 2 (January 14–21) were under high T and RH
237 conditions with variable wind directions. In this case, local emissions played a key role in WSIs (Fig.
238 S7b) with average NH_4^+ , SO_4^{2-} , and NO_3^- concentrations that ranged from $31.9 \pm 12.5 \mu\text{g}/\text{m}^3$ (U-ZZ)
239 to $47.6 \pm 13.1 \mu\text{g}/\text{m}^3$ (R-AY), $32.9 \pm 12.5 \mu\text{g}/\text{m}^3$ (R-XX) to $46.8 \pm 16.9 \mu\text{g}/\text{m}^3$ (R-AY), and 58.0 ± 18.3
240 $\mu\text{g}/\text{m}^3$ (U-AY) to $76.8 \pm 21.1 \mu\text{g}/\text{m}^3$ (R-AY), respectively. Note that higher concentrations of NH_4^+ ,
241 NH_3 , and TNH_x during Case 2 were recorded at rural sites than those at urban sites. Moreover, NH_3
242 levels in this work were higher than those in other studies summarized in Table S1. Agricultural
243 emissions, including livestock waste, N-fertilizer application, and humans, were the top three ammonia
244 contributors in Henan Province (Wang et al., 2018a), which may result in elevated ammonia
245 concentrations at rural sites.

246 3.2 pH of $\text{PM}_{2.5}$ at the urban and rural sites

247 Figure 3 exhibits the predicted $\text{PM}_{2.5}$ pH values, H^+_{air} , and AWC at the five sites, pH uncertainties
248 based on the pH_{max} and pH_{min} calculations are presented in Fig. S8. $\text{PM}_{2.5}$ have consistent moderate
249 acidity during this haze episode, with median (min–max) pH values of 4.5 (3.8–5.2), 4.8 (3.9–5.8), 4.9
250 (4.1–6.2), 5.1 (4.7–6.3), and 5.2 (4.8–6.5,) at U-ZZ, U-AY, R-XX, R-AY, and R-PY, respectively. As
251 summarized in Table 1, $\text{PM}_{2.5}$ pH values were close to the results of other cities in China (e.g., Beijing,

252 Xi'an, and Tianjin), but higher than other countries (e.g., Singapore, USA, and Greece). Compared to
253 the rural sites in the USA, pH values were roughly 3 units higher at the R-AY, R-XX, and R-PY sites.
254 Moreover, statistical values of pH (Table S2) during three cases show higher pH values at rural sites
255 than those at urban sites, especially for the U-ZZ and R-PY sites during Case 1 despite their pH
256 uncertainties (Section 2.4).

257 The pH values (Table S2) of the five sites during Cases 2 and 3 were comparable but slightly
258 lower than those during Case 1. As shown in Fig. S9, predicted pH values present better correlations
259 with H^+_{air} concentrations rather than AWC. Particle hydronium ion aqueous concentration depends on
260 both the presence of ions and the amount of particle AWC (Guo et al., 2015). Moreover, H^+_{air} was
261 closely associated with the NH_3 mixing ratios, and higher NH_3 always corresponded to lower H^+_{air} (Liu
262 et al., 2017). High correlations ($r > 0.5$) between H^+_{air} and TWSIIs (Table S3) imply that local pH was
263 significantly affected by the TWSIIs levels, and probably resulting in the high acidity during Case 2.
264 H^+_{air} was also correlated with individual chemical species (e.g., TNH_x , TH_2SO_4 , TNO_3 , and TCl).
265 Therefore, the diversity of pH in Cases 1 and 3 may be partly owing to the different proportions of
266 particle- and gas-phase constituents that will be discussed in detail below. In addition, high correlations
267 between RH and H^+_{air} (Table S3) suggest the major role of meteorological conditions in particle pH.
268 Given the Case 2 was less affected by regional transport, the diurnal patterns of median pH values of
269 the five sites (Fig. 4) indicate that pH values during nighttime were 0.3 (R-PY)–0.5 (U-ZZ) units higher
270 than those during the daytime. Similar results were also found in other cities (e.g., Beijing, Tianjin,
271 southern Canada, and the USA) (Battaglia et al., 2017; Ding et al., 2019; Guo et al., 2015; Murphy et
272 al., 2017; Shi et al., 2019), resulting from the diurnal trends of T and RH (Fig. 4f). After sunrise, high

273 T facilitated the dissociation of particle-phase ammonium (e.g., NH_4NO_3) and led to a rapid loss of
274 AWC (Guo et al., 2015; Saraswati et al., 2019).

275 3.3 Sensitivity tests of pH

276 To explore the dominant factors that determine the local particle pH level and resulting in the high
277 pH at rural sites, sensitivity tests of pH to chemical species (i.e., TNH_x , TH_2SO_4 , TNO_3 , TCl , TNa , K^+ ,
278 Ca^{2+} , and Mg^{2+}) and meteorological parameters (i.e., T and RH) were performed. Firstly, the real-time
279 measured values of a variable (e.g., TNH_x) and average values of other parameters (i.e., TH_2SO_4 , TNO_3 ,
280 TCl , TNa , K^+ , Ca^{2+} , Mg^{2+} , T and RH) during Case 2 were input into ISORROPIA-II to investigate the
281 sensitivity of local pH to this variable (i.e., TNH_x) (Ding et al., 2019), and results are listed in Table 4
282 and Fig. S10. In addition, a given range for a variable for all sites with corresponding average values
283 of other parameters was simulated to compare its effects on pH among five sites (Figs. 5 and S11). The
284 chosen variation range for each variable was close to the observed minimum and maximum values
285 (Table S4), which aims to better reflect the actual observation conditions. The degree of sensitivity
286 was represented as the relative standard deviation (%RSD) of the re-calculated pH values. RSD
287 calculates the absolute value of the coefficient of variation, which helps us to determine how small or
288 large is the standard deviation when compared to the mean of the re-calculated pH data set. Therefore,
289 when the re-calculated pH data set has a higher RSD value, this variable can change the pH easier and
290 is more important for local pH.

291 As shown in Table 4, the most important factor that influenced particle pH during Case 2 was
292 TNH_x , followed by TH_2SO_4 at the five sites, and the U-ZZ site was also affected by TNO_3 . The acidity
293 of $\text{PM}_{2.5}$ is governed by the phase partitioning of semi-volatile gases such as NH_3 , HNO_3 , and HCl

294 (Pye et al., 2019). $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and NH_4NO_3 , which are mainly formed through
295 neutralization reactions between NH_3 with SO_4^{2-} and HNO_3 orderly according to the regime of local
296 ammonia, are the most abundant components of $\text{PM}_{2.5}$ in winter haze in this region (Wang et al., 2019c;
297 Pathak et al., 2008). Therefore, particle pH was driven by TNH_x , TH_2SO_4 , and TNO_3 . TNa , TCl , and
298 crustal ions (i.e., K^+ , Ca^{2+} , and Mg^{2+}) have less influence on the predicted pH values, because these
299 species were at low concentrations, together accounting for lower than 10 % of TWSIIs. However,
300 since the low volatility of these cations allows them to preferentially neutralize sulfates over NH_3 , the
301 role of crustal dust and sea spray in particle pH cannot be ignored when the mass fraction of these ions
302 are high in typical pollution events (e.g., sandstorm) or areas (e.g., coastland) (Allen et al., 2015; Guo
303 et al., 2018; Vasilakos et al., 2018). In addition to chemical species, T was more sensitive to local pH
304 than RH at the five sites, which is similar to the finding in Beijing and Canada (Ding et al., 2019; Tao
305 and Murphy, 2019). This result can be explained by the remarkable influence of T on the solubility and
306 dissociation constants of the partitioning of $\text{NH}_{3(\text{g})}/\text{NH}_{4(\text{aq})}^+$ (Hennigan et al., 2015).

307 Figures 5 and S11 compare the sensitive degrees of pH to input data among different sites. Except
308 for TNH_x , the sensitivities of pH to TH_2SO_4 , TNO_3 , and other ions at urban sites were more significant
309 than those at rural sites, particularly at U-ZZ sites of 7.2 % and 14.8 % of RSD to TH_2SO_4 and TNO_3 ,
310 respectively. To gain insight into the differences of pH sensitivity among the five sites, sensitivity tests
311 of pH to TH_2SO_4 , TNO_3 , and TNH_x were calculated using the fixed TNO_3 ($67.5 \mu\text{g}/\text{m}^3$) and TH_2SO_4
312 ($36.5 \mu\text{g}/\text{m}^3$) concentrations under the average meteorological conditions of five sites (i.e., $T = 2.5 \text{ }^\circ\text{C}$
313 and $\text{RH} = 60 \%$). These chosen values were close to the average values of the five sites during Case 2
314 (i.e., $36.4 \pm 15.4 \mu\text{g}/\text{m}^3$ for SO_4^{2-} , $67.5 \pm 23.5 \mu\text{g}/\text{m}^3$ for TNO_3 , $2.5 \pm 1.5 \text{ }^\circ\text{C}$ for T, and $59.3 \pm 14.0 \%$

315 for RH), and other chemical species were set to be zero. As shown in Fig. 6, sensitivities of pH to
316 TH₂SO₄ and TNO₃ increase with the decrease in TNH_x concentration, particularly when the TNH_x
317 concentrations are lower than 60 µg/m³ and 40 µg/m³, respectively. Therefore, the pH changes tended
318 to become more sensitive to TH₂SO₄ and TNO₃ at the U-ZZ site (Fig. 5e, f) with the lowest TNH_x
319 concentrations (46.8 ± 14.7 µg/m³). All these results may be explained by the presence of excess
320 ammonia that will be discussed below.

321 Sensitivity tests suggest (Fig. 5, S10, and S11) that particle pH gradually grows with increased
322 cation and decreased anion concentrations. Specifically, the TNH_x concentration that increased from
323 25 µg/m³ to 90 µg/m³ can promote particle pH by 3.5 (U-ZZ)–4.5 (R-AY) units. The crustal cations
324 and sea spray have limited effects on pH, but a 10-fold increase in these species still can increase
325 predicted pH values by about 0.1 units. TH₂SO₄, and TNO₃ that increased from 10 µg/m³ to 80 µg/m³,
326 and 1 µg/m³ to 125 µg/m³ can reduce the pH values by 1.5 (R-PY)–4.0 (U-ZZ), and 0.2 (R-AY)–1.4
327 (U-ZZ) units, respectively. In addition, a 20 °C (–5 °C to 15 °C) and 65 % (30 % to 95 %) increase
328 drops the pH by approximately 1.3 and 2.7 units at the five sites, respectively. Corresponding to the
329 observed data during Case 2 (Table 3), lower TNH_x concentrations and higher T values were probably
330 responsible for the higher acidity at urban sites than those at rural sites. Moreover, Figure 6 shows that
331 particle pH increase with decreasing TH₂SO₄ (Fig. 6a) or increasing TNO₃ (Fig. 6b), particularly when
332 the TNH_x is at high concentration. These results indicate that predicted pH will be enhanced by
333 increasing the TNO₃/TH₂SO₄ ratio, which is consistent with the observation in Beijing (Xie et al.,
334 2019). All these may be due to the elevated ammonia partitioning with nitrate fraction increase, and
335 nitrate-rich particles would absorb more water compared to the sulfate-rich particles (Xie et al., 2019).

336 Based on the above, higher TNH_x (Table 3) and $\text{TNO}_3/\text{TH}_2\text{SO}_4$ ratios (2.9 ± 0.6 and 1.7 ± 0.6 for Cases
337 1 and 3 respectively) during Case 1 may lead to the higher pH values than those during Case 3, even
338 though the TWSIIs levels were comparable. In the long run, the decreasing sulfate concentration in
339 $\text{PM}_{2.5}$ accompanied with increasing nitrate concentration has been recorded during haze episodes in
340 China, because strong actions were taken to reduce the coal consumption in recent years (Tian et al.,
341 2017; Wang et al., 2017). Considering the ammonia in the atmosphere of North China might still be
342 increasing (Liu et al., 2018), future acidity of $\text{PM}_{2.5}$ during winter haze episodes is expected to become
343 increasingly less acidic in this area. A more careful analysis is needed to test this inference, however,
344 because fine-mode particle remains a relatively constant pH of 0–2 despite a 70 % reduction in sulfates
345 in the USA (Vasilakos et al., 2018; Weber et al., 2016).

346 **3.4 Role of ammonia on pH**

347 It has been suggested that unusually high levels of NH_3 can increase pH, on average, a 5-fold to
348 10-fold increase in the NH_3 levels leads to a one-unit change in pH (Nah et al., 2018; Weber et al.,
349 2016; Guo et al., 2017). To examine the effects of major indicators of ammonia (i.e., TNH_x , Required-
350 NH_x , and Excess- NH_x , see Text S3 for more details of calculation) on aerosol acidity, particle pH was
351 calculated by using a wide range of TNH_x ($25\text{--}130 \mu\text{g}/\text{m}^3$) and average values of other parameters
352 during Case 2 (Table 3) of each site. Simultaneously, the concentrations of TNH_x , Required- NH_x ,
353 Excess- NH_x , and corresponding pH values are illustrated in Fig. 7. An “S-curve” growth trend of pH
354 to increasing TNH_x appears with the inflection point around the Required- NH_x concentration. In the
355 case when the input TNH_x concentration is lower than the Required- NH_x , the growth rate of pH
356 increase with TNH_x increasing, otherwise, the pH growth flattens out, which is similar to the findings

357 of Weber et al. (2016) and Bougiatioti et al. (2016). In the process of increasing NH_3 concentration,
358 NH_3 reacted with SO_4^{2-} and HNO_3 orderly, during when large amounts of H^+ were consumed and pH
359 values rapidly increased. Theoretically, the Required- NH_x plus nonvolatile cations can neutralize all
360 anions regardless of the phase partitioning and bisulfate formation, and thus changes in TNH_x around
361 the Required- NH_x concentrations have a significant impact on particle pH. Subsequently, dissolving
362 Excess- NH_x into the particles became difficult, and pH values increased slowly (Ding et al., 2019;
363 Seinfeld and Pandis, 2016). Therefore, the underlying reason why TNH_x concentrations lower than 60
364 $\mu\text{g}/\text{m}^3$ and 40 $\mu\text{g}/\text{m}^3$ elevated the pH sensitivities (Fig. 6) to TH_2SO_4 and TNO_3 is that the Excess- NH_x
365 will be exhausted under the case of TH_2SO_4 and TNO_3 that ranged from 10 $\mu\text{g}/\text{m}^3$ to 100 $\mu\text{g}/\text{m}^3$,
366 respectively. On the other hand, the pH values of the five sites at the Required- NH_x concentrations are
367 near 3.0, which is in coincidence with the pH value of Beijing in the no-excess- NH_x cases (Liu et al.,
368 2017). Therefore, the presence of Excess- NH_x in the aerosol was likely important for the less acidic of
369 $\text{PM}_{2.5}$ and can enhance the pH values by 1.5 (U-ZZ)–2 (R-PY) units. Considering that the Excess- NH_x
370 concentrations at rural sites (e.g., $30.1 \pm 6.2 \mu\text{g}/\text{m}^3$ at R-PY) were higher than those at urban sites (e.g.,
371 $14.8 \pm 4.1 \mu\text{g}/\text{m}^3$ at U-ZZ), and thus Excess- NH_x concentrations may drive the pH values of rural sites
372 higher than those of urban sites.

373 3.5 Implications of regional transport

374 From the above discussion, the differences of pH among three cases indicate that the underlying
375 influence of regional transport on local particle pH cannot be neglected by differing the chemical
376 components of $\text{PM}_{2.5}$ and meteorological conditions. In particular, the median pH values (Table S2) of
377 Case 1, during when the air masses transported from the south of sampling regions, increased by 0.2–

378 0.9 units than those during Cases 2 and 3. Aqueous formations of sulfate are strongly dependent on
379 particle pH. Chen et al. (2016) reported that the aqueous-phase sulfate production rates from NO₂ and
380 O₃ oxidation of SO₂ had a positive correlation with particle pH during the Beijing haze events. When
381 pH exceeded approximately 4.5 (higher than this value at rural sites in this work), NO₂-oxidation
382 dominated the sulfate formation, and its reaction rate increased by one order of magnitude with the
383 rise of pH by one unit. Thus, air masses transported from rural and agricultural regions may promote
384 the sulfate formation in urban aerosols. In addition to sulfate, higher aerosol pH favors partitioning of
385 TNO₃ toward aerosol NO₃ rather than gaseous HNO₃ and thus elevating the particle mass
386 concentration (Nenes et al., 2019; Weber et al., 2016). Sampling regions in this study are located in the
387 transport route for Beijing (MEP, 2017), thereby frequently affecting its local particle pH. The lifetimes
388 of NH₃ (1–5 days or less) and NH₄⁺ (1–15 days) in the atmosphere are sufficient for transporting to
389 Beijing during a haze episode (Aneja, 2000; Lefer et al., 1999; Warneck, 1988). Ding et al. (2019)
390 have also observed that PM_{2.5} pH from the southwest direction was generally higher than that from the
391 northern direction in Beijing. Therefore, the particle pH in Beijing may be enhanced when southern
392 air masses from this region accompany elevated-pH particles and high ammonia levels.

393 4 Conclusions

394 An experiment was performed using a series of high-time-resolution instruments in two urban
395 (i.e., U-ZZ and U-AY) and three rural sites (i.e., R-AY, R-XX, and R-PY) in Henan Province during a
396 large-scale and long-lasting haze episode. The ISORROPIA-II model was used to investigate the pH
397 value and its driving factors. PM_{2.5} exhibited moderate acidity with median pH values of 4.5 (3.8–5.2),
398 4.8 (3.9–5.8), 4.9 (4.1–6.2), 5.1 (4.7–6.3), and 5.2 (4.8–6.5,) at U-ZZ, U-AY, R-XX, R-AY, and R-PY,

399 respectively. The pH values at rural sites were slightly higher than those at urban sites.

400 The predicted pH values of PM_{2.5} were significantly affected by the WSIs levels, different
401 proportions of particle- and gas-phase constituents, and meteorological parameters. Sensitivity tests
402 show that TNH_x, followed by TH₂SO₄, were the important factors that influenced the predicted pH at
403 the five sites. In addition, T was more sensitive to local pH than RH. Generally, particle pH rose with
404 the increase in cation and the decrease in the anion, T, and RH. Further study suggests that predicted
405 pH will be enhanced by increasing the TNO₃/TH₂SO₄ ratio. Therefore, elevated TNH_x concentrations
406 and lower T were probably responsible for the higher pH values at rural sites than those at urban sites,
407 and higher TNH_x and TNO₃/TH₂SO₄ ratios during Case 1 may lead to the higher pH values than those
408 during Case 3.

409 An “S-curve” growth trend of pH to increasing TNH_x was found with the inflection point around
410 the Required-NH_x concentration. Moreover, the pH values of the five sites at the Required-NH_x
411 concentrations are near 3.0, and the presence of Excess-NH_x in the aerosol can enhance the pH values
412 by 1.5 (U-ZZ)–2 (R-PY) units, and thus Excess-NH_x was likely important for the less acidic of PM_{2.5}
413 during the severe haze episodes in this region. Considering that the Excess-NH_x concentrations at rural
414 sites were higher than those at urban sites, Excess-NH_x concentrations may drive the pH values of rural
415 sites higher than those of urban sites.

416 The underlying influence of regional transport on local particle pH cannot be neglected by
417 differing the chemical components of PM_{2.5} and meteorological conditions. Air masses transported
418 from rural and agricultural regions with elevated pH particles and high ammonia levels may promote
419 the secondary particle formation in urban aerosols. Therefore, ammonia should be involved in the

420 regional strategy for improving the air quality in China.

421

422 *Data availability. All data in this work are available by contacting the corresponding author Shasha*

423 *Yin (shashayin@zzu.edu.cn)*

424

425 *Author contributions. Shasha Yin and Ruiqin Zhang designed and led this study. Shasha Yin was*

426 *responsible for all observations and data collection. Lingling Wang, Yuqing Li, Chen Wang, and Weisi*

427 *Wang interpreted the data and discussed the results. Shenbo Wang wrote the paper.*

428

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

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621

622 **Figure lists:**

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

629 Fig. 2 Temporal variations of T, RH, wind speed (WS), wind direction (WD), and concentrations of
630 NH_3 , NH_4^+ , SO_4^{2-} , and NO_3^- during three cases at the Zhengzhou (U-ZZ) site. The shaded areas
631 represent the measurement uncertainties.

632 Fig. 3 Time series and box plot of predicted $\text{PM}_{2.5}$ pH, H^+_{air} , and aerosol water content (AWC) at the
633 five sites. In each box, the top, middle and bottom lines represent the 75th, 50th, and 25th percentile
634 of statistical data, respectively; the upper and lower whiskers represent the maximum and minimum
635 values, respectively.

636 Fig. 4 (a)–(e) Diurnal patterns of median pH values, (f) average RH, and T of the five sites in Case 2.
637 The upper and lower ends of the line represent the maximum and minimum values of pH,
638 respectively. The color scale bar represents AWC concentration.

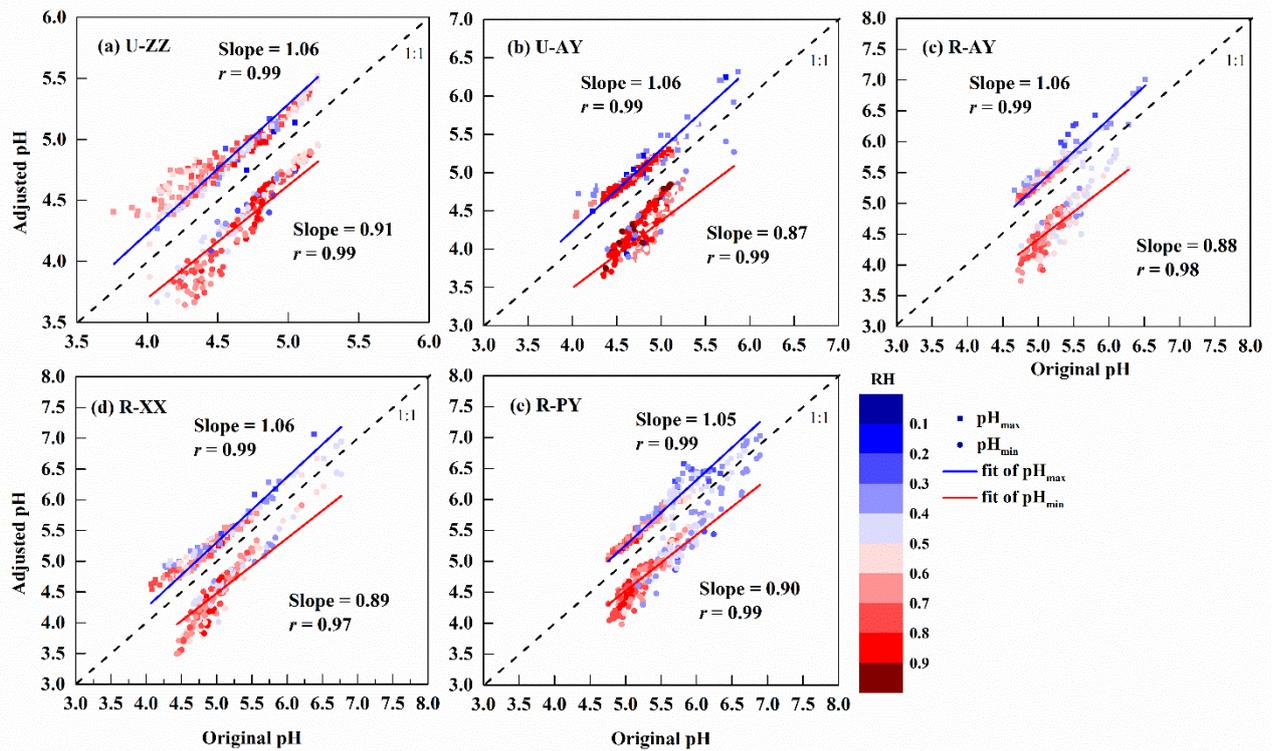
639 Fig. 5 Comparison of the sensitivities of $\text{PM}_{2.5}$ pH to T, RH, TCl ($\text{HCl}_{(\text{g})} + \text{Cl}_{(\text{aq})}^-$), TNH_x ($\text{NH}_{3(\text{g})} +$
640 $\text{NH}_{4(\text{aq})}^+$), TNO_3 ($\text{HNO}_{3(\text{g})} + \text{NO}_{3(\text{aq})}^-$), and TH_2SO_4 (replaced by observed SO_4^{2-}) among the five
641 sites. A given range for a variable for all sites with corresponding average values of other parameters
642 was used as input to the ISORROPIA-II model. The range of the x-axis is close to the observed

643 minimum and maximum values in Case 2 (Table S4). The color scale bar represents the pH values.
644 The relative standard deviation (RSD) and range (Range) represent the sensitivity degree of pH to
645 this variable and range (min–max) of the re-predicted pH value in the test, respectively. The square
646 plots on the graph represent the average values of each variable observed in Case 2 with standard
647 deviation as an error bar.

648 Fig. 6 Particle pH calculated with fixed meteorological parameters ($T = 275.5$ K and $RH = 60\%$)
649 under different combinations of TNH_x and (a) TH_2SO_4 (Fixed $TNO_3 = 67.5 \mu g/m^3$) and (b) TNO_3
650 (Fixed $TH_2SO_4 = 36.5 \mu g/m^3$). The color scale bar represents the pH values. The markers on the
651 graph represent the average concentrations of TNH_x , TH_2SO_4 , and TNO_3 at the five sites during Case
652 2 with standard deviation as error bar.

653 Fig. 7 Particle pH corresponds to increasing TNH_x at the five sites to examine the effects of major
654 indicators of NH_3 (i.e., TNH_x , Required- NH_x , and Excess- NH_x) on aerosol acidity. Particle pH was
655 calculated by using a wide range of TNH_x (25 – $130 \mu g/m^3$) and average values of other parameters
656 during Case 2 of each site. The concentrations of TNH_x , Required- NH_x , and Excess- NH_x with
657 corresponding pH values are marked by a hollow box, hollow circle, and arrow respectively. The
658 yellow and blue background colors correspond to the NH_x -poor and NH_x -rich, respectively.

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661 Fig. 1 pH uncertainties of the five sites based on two extreme scenarios of measurement uncertainty.

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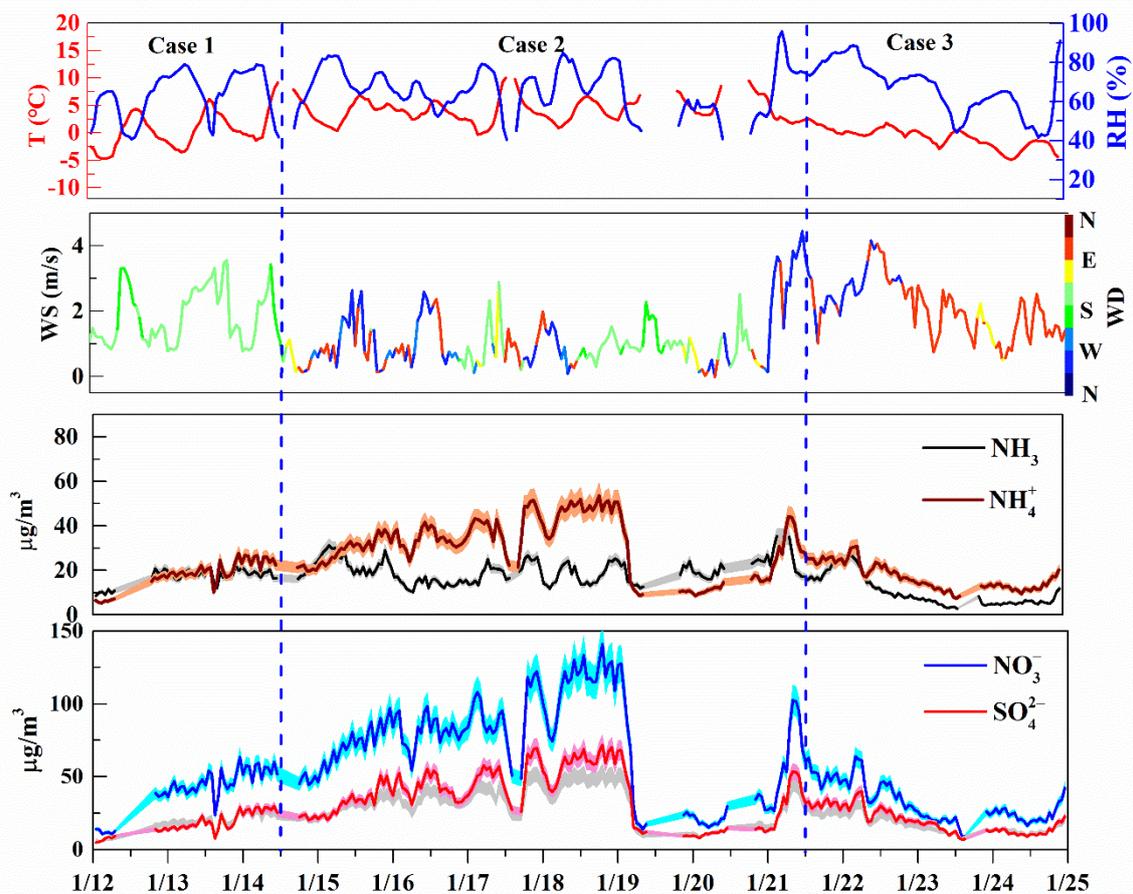
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668

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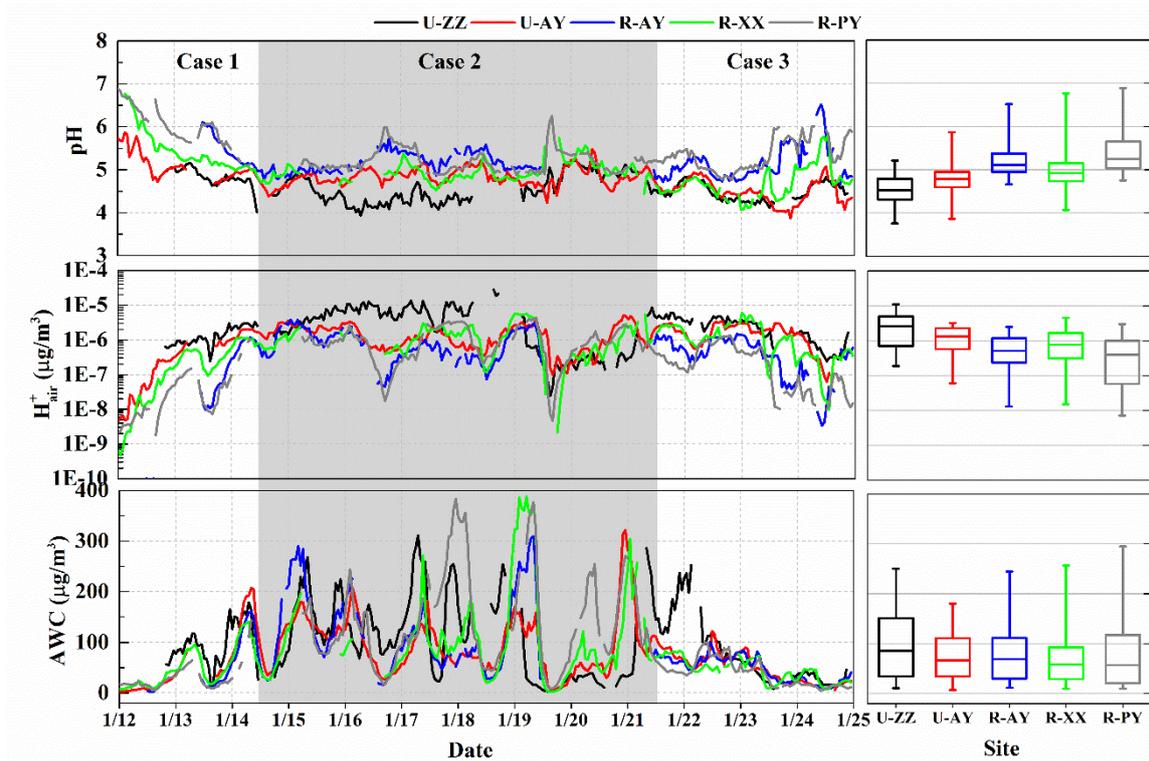
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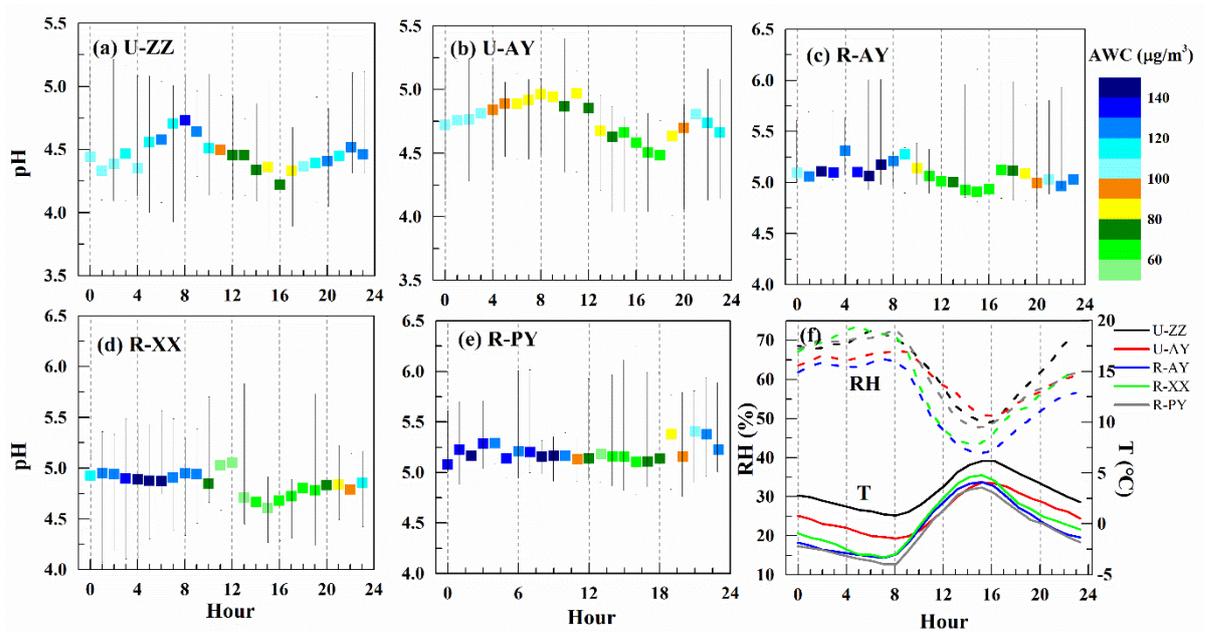


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676 Fig. 3 Time series and box plot of predicted $\text{PM}_{2.5}$ pH, H^+_{air} , and aerosol water content (AWC) at the
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 679 values, respectively.

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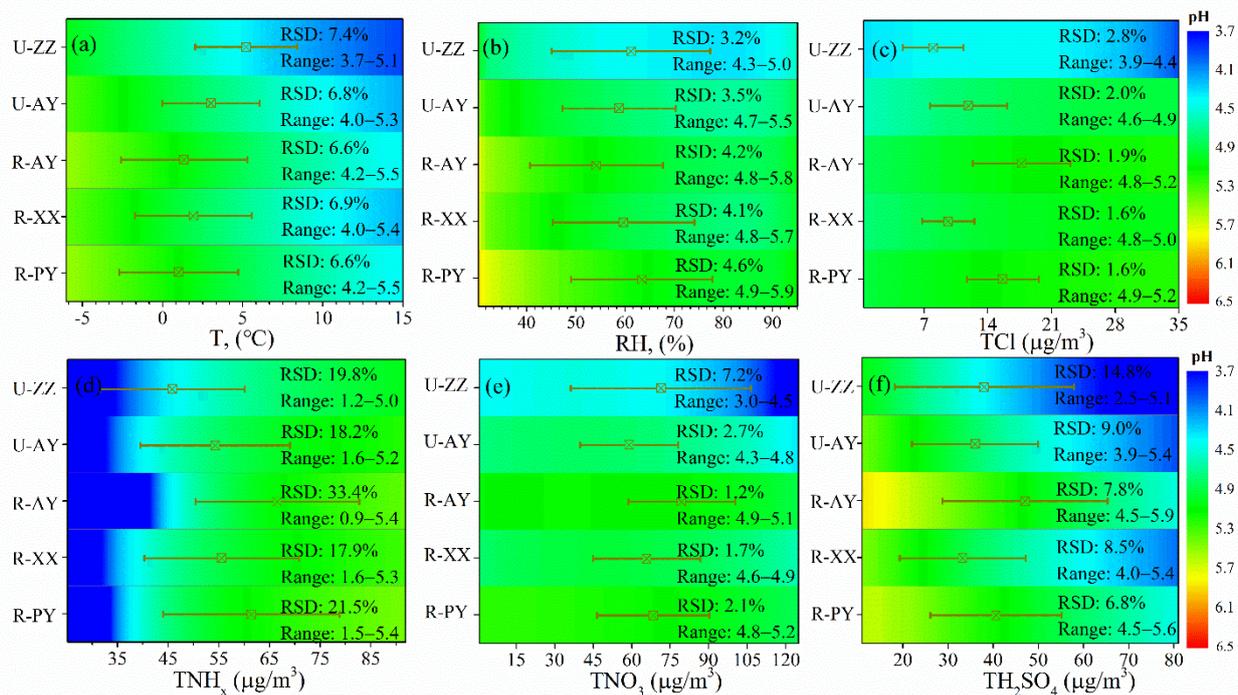
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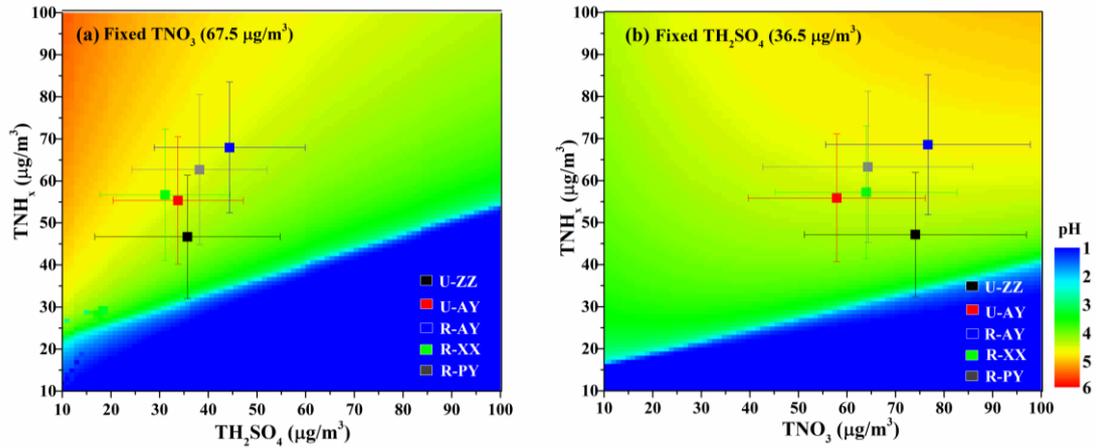
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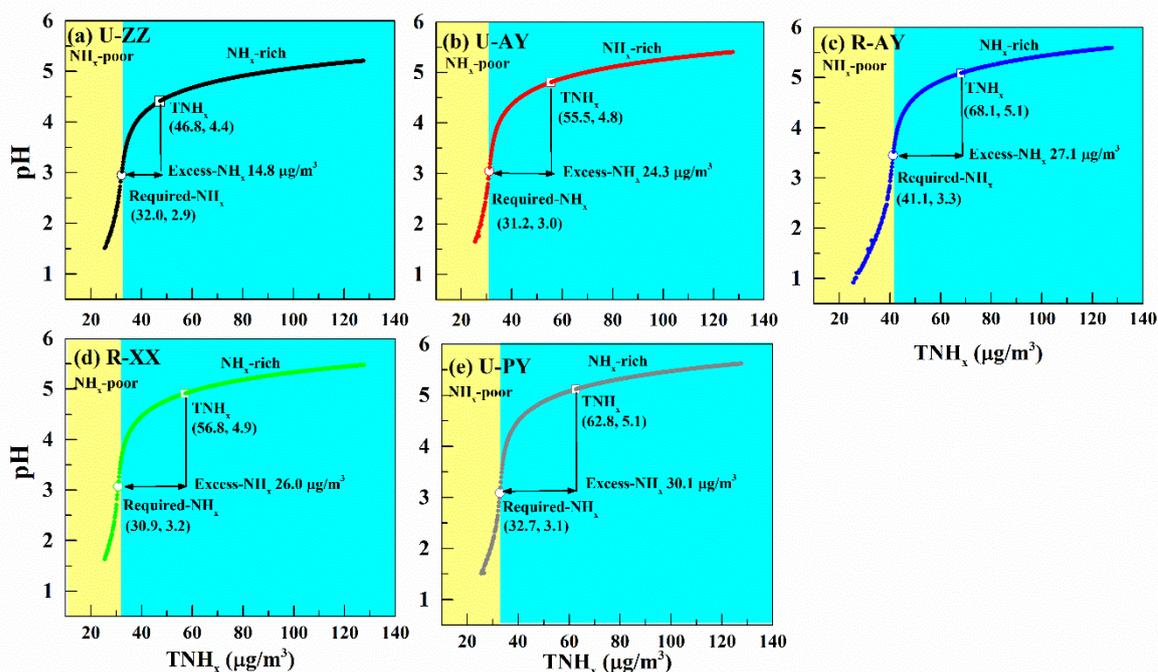
706 Fig. 6 Particle pH calculated with fixed meteorological parameters ($T = 275.5 \text{ K}$ and $\text{RH} = 60 \%$)

707 under different combinations of TNH_x and (a) TH_2SO_4 (Fixed $\text{TNO}_3 = 67.5 \mu\text{g}/\text{m}^3$) and (b) TNO_3

708 (Fixed $\text{TH}_2\text{SO}_4 = 36.5 \mu\text{g}/\text{m}^3$). The color scale bar represents the pH values. The markers on the

709 graph represent the average concentrations of TNH_x , TH_2SO_4 , and TNO_3 at the five sites during Case

710 2 with standard deviation as error bar.



711

712 Fig. 7 Particle pH corresponds to increasing TNH_x at the five sites to examine the effects of major

713 indicators of NH₃ (i.e., TNH_x, Required-NH_x, and Excess-NH_x) on aerosol acidity. Particle pH was

714 calculated by using a wide range of TNH_x (25–130 µg/m³) and average values of other parameters

715 during Case 2 of each site. The concentrations of TNH_x, Required-NH_x, and Excess-NH_x with

716 corresponding pH values are marked by a hollow box, hollow circle, and arrow respectively. The

717 yellow and blue background colors correspond to the NH_x-poor and NH_x-rich, respectively.

718

719

Table lists:

Table 1 Comparison of the particle pH values in this study (median, min–max) and other sites (mean \pm standard deviation).

Table 2 Descriptions of the five sampling sites.

Table 3 Summary (mean \pm standard deviation) of gaseous precursors ($\mu\text{g}/\text{m}^3$), water-soluble inorganic ions ($\mu\text{g}/\text{m}^3$), T ($^{\circ}\text{C}$), and RH (%) during three cases of haze periods at five monitoring sites.

Table 4 Sensitivity of pH to input data. The real-time measured values of a variable and the average values of other parameters during Case 2 were input into the ISORROPIA II. The degree of sensitivity was represented as the relative standard deviation (%RSD) of the re-calculated pH values, higher RSD implied higher sensitivity of this factor to pH and thus is more important for local pH.

Table 1 Comparison of the particle pH values in this study (median, min–max) and other sites (mean \pm standard deviation).

	Observation site	Period	pH	Model	Reference
This study	Zhengzhou, China (Urban)	Jan 2018	4.5 (3.8–5.2)		
	Anyang, China (Urban)	Jan 2018	4.8 (3.9–5.8)		
	Anyang, China (Rural)	Jan 2018	4.9 (4.1–6.2)	ISORROPIA-II	
	Xinxiang, China (Rural)	Jan 2018	5.1 (4.7–6.3)		
	Puyang, China (Rural)	Jan 2018	5.2 (4.8–6.5)		
China	Beijing, China (Urban)	Feb 2017	4.5 \pm 0.7	ISORROPIA-II	Ding et al., 2019
	Beijing, China (Urban)	Dec 2016	4.3 \pm 0.4	ISORROPIA-II	Liu et al., 2017
	Beijing, China (Urban)	Jan–Feb 2015	4.5	ISORROPIA-II	Guo et al., 2017
	Xi'an, China (Urban)	Nove–Dec 2012	5.0	ISORROPIA-II	Guo et al., 2017
	Tianjin, China (Urban)	Dec–Jun 2015	4.9 \pm 1.4	ISORROPIA-II	Shi et al., 2017
	Tianjin, China (Urban)	Aug 2015	3.4 \pm 0.5	ISORROPIA-II	Shi et al., 2019
	Hohhot, China	Winter 2015	5.7	ISORROPIA-II	Wang et al., 2019
	PRD, China (Rural)	Fall-winter season 2012	0.81 \pm 0.24	AIM-II model	Fu et al., 2015
	Hong Kong, China (Urban)	2001	0.25	AIM-II model	Pathak et al., 2004
Other countries	Singapore (Urban)	Sep–Nov 2011	0.60	AIM-IV model	Sailesh et al., 2013
	Northeastern US (Urban)	Feb–Mar 2015	0.07 \pm 0.96	ISORROPIA-II	Guo et al., 2016
	Alabama, USA (Rural)	Jun–Jul 2013	1.94 \pm 0.59	ISORROPIA-II	Guo et al., 2015
	Georgia, USA (Rural)	Aug–Oct 2016	2.2 \pm 0.6	ISORROPIA-II	Nah et al., 2018
	Crete, Greece (Background)	Aug–Nov 2012	1.25 \pm 1.14	ISORROPIA-II	Boucher et al., 2016

Table 2 Descriptions of the five sampling sites.

City	Classification	Site	Coordinate	Location	Surrounding environment	Emission (Gg)		
						NH ₃ [*]	SO ₂ ^{**}	NO _x ^{**}
Zhengzhou	Urban	U-ZZ	34.82° N 113.54° E	West to the Zhengzhou downtown (Zhengzhou University)	Densely occupied residences, light industry, freeways and roads	39.2	36.7	31.8
Anyang	Urban	U-AY	36.09° N 114.41° E	East to the Anyang downtown (Anyang Environmental Protection Bureau)	Occupied residences, heavy industry and traffic roads	57.8	46.9	37.1
	Rural	R-AY	36.22° N 114.39° E	15 km north of Anyang city (Baizhuang town)	High ways, small villages, and cropland			
Xinxiang	Rural	R-XX	35.38° N 114.30° E	35 km northeast of Xinxiang city (Banzao town)	Small villages and cropland	72.1	8.9	19.6
Puyang	Rural	R-PY	36.15° N 115.10° E	44 km north of Puyang city (Liangcun town)	Small villages and cropland	39.6	3.4	3.2

* Data from a 2015-based NH₃ emission inventory (Wang et al., 2018a).

** Data from Henan Statistical Yearbook of 2018 (BSH, 2018).

Table 3 Summary (mean \pm standard deviation) of gaseous precursors ($\mu\text{g}/\text{m}^3$), water-soluble inorganic ions ($\mu\text{g}/\text{m}^3$), T ($^{\circ}\text{C}$), and RH (%) during three cases of haze periods at five sites.

	Case 1 (January 12–14)					Case 2 (January 14–21)					Case 3 (January 21–25)				
	U-ZZ	U-AY	R-AY	R-XX	R-PY	U-ZZ	U-AY	R-AY	R-XX	R-PY	U-ZZ	U-AY	R-AY	R-XX	R-PY
HNO ₃	0.9 \pm 0.2	0.7 \pm 0.2	3.1 \pm 0.2	3.0 \pm 0.1	3.9 \pm 0.1	1.3 \pm 0.3	1.1 \pm 0.3	3.7 \pm 0.4	3.7 \pm 0.5	4.2 \pm 0.2	0.9 \pm 0.3	0.7 \pm 0.2	4.9 \pm 1.0	3.3 \pm 0.2	3.3 \pm 0.2
NH ₃	17.0 \pm 3.7	19.6 \pm 8.0	22.9 \pm 6.3	21.6 \pm 4.1	17.8 \pm 3.7	19.5 \pm 5.2	23.6 \pm 6.5	25.2 \pm 6.5	24.7 \pm 9.9	26.5 \pm 6.7	10.5 \pm 6.9	8.8 \pm 4.7	10.6 \pm 4.7	8.4 \pm 3.5	12.1 \pm 3.5
HCl	0.1 \pm 0.0	0.7 \pm 0.6	0.5 \pm 0.1	0.6 \pm 0.1	1.8 \pm 0.1	0.1 \pm 0.1	0.4 \pm 0.1	0.6 \pm 0.2	0.6 \pm 0.1	2.0 \pm 0.1	0.1 \pm 0.1	0.5 \pm 0.1	1.7 \pm 0.1	1.0 \pm 0.4	1.5 \pm 0.4
NO ₃ ⁻	41.5 \pm 14.6	28.0 \pm 14.6	43.0 \pm 12.5	32.8 \pm 12.9	25.2 \pm 9.1	74.2 \pm 32.9	58.0 \pm 18.3	76.8 \pm 21.1	64.1 \pm 18.7	64.4 \pm 21.7	32.4 \pm 13.5	18.9 \pm 5.4	26.0 \pm 5.8	25.1 \pm 6.7	18.8 \pm 4.3
NH ₄ ⁺	18.6 \pm 6.2	15.9 \pm 8.3	21.8 \pm 8.0	14.9 \pm 6.2	12.8 \pm 4.5	31.9 \pm 12.5	35.2 \pm 12.0	47.6 \pm 13.1	35.6 \pm 10.4	39.9 \pm 14.9	17.4 \pm 6.0	11.6 \pm 4.4	14.3 \pm 4.4	12.9 \pm 4.0	10.1 \pm 2.9
SO ₄ ²⁻	17.8 \pm 7.2	14.4 \pm 9.0	13.7 \pm 10.0	10.0 \pm 5.5	8.6 \pm 2.3	38.3 \pm 18.0	34.5 \pm 13.0	46.8 \pm 16.9	32.9 \pm 12.5	39.2 \pm 13.6	19.8 \pm 8.6	15.1 \pm 6.1	15.1 \pm 7.3	14.4 \pm 4.8	13.3 \pm 4.0
Ca ²⁺	0.7 \pm 0.5	0.5 \pm 0.3	5.0 \pm 2.2	0.8 \pm 0.2	3.4 \pm 0.3	0.5 \pm 0.4	0.4 \pm 0.4	2.2 \pm 1.2	1.0 \pm 0.3	3.3 \pm 0.6	0.1 \pm 0.1	0.2 \pm 0.2	1.8 \pm 0.7	0.5 \pm 0.1	2.4 \pm 0.5
Na ⁺	1.5 \pm 0.2	1.0 \pm 0.0	1.4 \pm 0.4	0.7 \pm 0.1	2.2 \pm 0.1	1.6 \pm 0.2	1.0 \pm 0.1	1.4 \pm 0.4	0.8 \pm 0.1	2.2 \pm 0.0	1.1 \pm 0.2	1.0 \pm 0.2	2.2 \pm 0.4	1.3 \pm 0.4	2.2 \pm 0.2
Cl ⁻	7.5 \pm 2.5	2.7 \pm 3.4	6.6 \pm 2.5	5.4 \pm 1.5	6.3 \pm 1.2	8.5 \pm 3.2	12.0 \pm 4.2	18.5 \pm 5.0	9.7 \pm 2.6	14.4 \pm 3.8	3.3 \pm 1.5	4.5 \pm 1.6	6.9 \pm 1.6	4.7 \pm 0.9	5.4 \pm 1.4
Mg ²⁺	0.2 \pm 0.0	0.1 \pm 0.0	0.4 \pm 0.1	0.1 \pm 0.0	0.5 \pm 0.0	0.2 \pm 0.0	0.1 \pm 0.0	0.4 \pm 0.4	0.1 \pm 0.0	0.5 \pm 0.1	0.2 \pm 0.0	0.1 \pm 0.0	0.4 \pm 0.1	0.1 \pm 0.1	0.4 \pm 0.1
K ⁺	2.9 \pm 0.7	1.4 \pm 0.5	1.6 \pm 0.6	1.6 \pm 0.4	2.5 \pm 0.6	4.4 \pm 1.7	2.4 \pm 0.7	2.9 \pm 0.7	1.9 \pm 0.6	3.7 \pm 1.1	1.9 \pm 0.7	0.9 \pm 0.3	0.8 \pm 0.3	0.8 \pm 0.2	1.2 \pm 0.4
T	0.3 \pm 3.1	-0.9 \pm 3.7	-1.8 \pm 4.4	-2.0 \pm 3.9	-1.7 \pm 4.8	4.2 \pm 2.2	2.6 \pm 2.5	0.1 \pm 2.8	1.2 \pm 2.9	0.4 \pm 3.0	-0.8 \pm 1.8	-2.7 \pm 1.8	-3.2 \pm 1.9	-2.8 \pm 2.6	-4 \pm 2.3
RH	63.7 \pm 12.1	60.3 \pm 15.4	54.0 \pm 16.0	58.5 \pm 13.5	49.7 \pm 14.5	66.0 \pm 11.4	60.1 \pm 9.9	58.6 \pm 9.9	62.7 \pm 11.6	65.8 \pm 11.7	67 \pm 13.1	63.7 \pm 13.8	55.9 \pm 13.6	59 \pm 13.7	56.8 \pm 16

Table 4 Sensitivity of pH to input data. The real-time measured values of a variable and the average values of other parameters during Case 2 were input into the ISORROPIA II. The degree of sensitivity was represented as the relative standard deviation (%RSD) of the re-calculated pH values, higher RSD implied higher sensitivity of this factor to pH and thus is more important for local pH.

	TH ₂ SO ₄	TNH _x	TNO ₃	TNa	TCl	Ca ²⁺	K ⁺	Mg ²⁺	RH	T
U-ZZ	12.1 %	12.8 %	6.1 %	0.1 %	0.3 %	3.3 %	0.3 %	0.2 %	1.3 %	2.7 %
U-AY	5.8 %	7.4 %	1.0 %	0.1 %	1.1 %	0.4 %	0.3 %	0.0 %	1.6 %	2.8 %
R-AY	6.5 %	10.9 %	1.4 %	0.1 %	0.7 %	1.2 %	0.2 %	0.3 %	1.9 %	2.7 %
R-XX	5.4 %	11.1 %	1.1 %	0.1 %	0.7 %	0.4 %	0.2 %	0.1 %	2.0 %	2.9 %
R-PY	4.7 %	9.4 %	1.5 %	0.0 %	0.7 %	0.5 %	0.4 %	0.1 %	2.3 %	3.1 %

1 Supplement materials:

2

3 **Text S1 Calculation of ions balance and equivalent ratio.**

4 **Text S2 Backward trajectory frequency analysis**

5 **Text S3 NH_x calculation**

6

7 **Text S1 Calculation of ions balance and equivalent ratio.**

8 The ions balance and equivalent ratio are calculated using the following formulas:

9
$$[\text{cations}] = \frac{[\text{NH}_4^+]}{18} + \frac{[\text{Na}^+]}{23} + \frac{[\text{K}^+]}{39} + \frac{[\text{Ca}^{2+}]}{20} + \frac{[\text{Mg}^{2+}]}{12} \quad (1)$$

10
$$[\text{anions}] = \frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{Cl}^-]}{35.5} \quad (2)$$

11
$$\text{ion balance} = [\text{cations}] - [\text{anions}] \quad (3)$$

12
$$\text{equivalent ratio} = [\text{cations}]/[\text{anions}] \quad (4)$$

13 where [Na⁺], [K⁺], [Ca²⁺], [Mg²⁺], [NH₄⁺], [SO₄²⁻], [NO₃⁻], and [Cl⁻] are the measured concentrations

14 (μg/m³) in the atmosphere. In addition to the measurement uncertainties, equivalent ratios lower than

15 1 might be attributed to the loss of cations from the volatilization of ammonium and unmeasured

16 hydrogen ions (Meng et al., 2016). Equivalent ratios higher than 1 were most likely caused by water-

17 soluble organic anions, CO₃²⁻ and HCO₃⁻ contents that were not detected in chemical analysis (Tian et

18 al., 2018).

19

20 **Text S2 Backward trajectory frequency analysis**

21 The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Web version of the

22 National Oceanic and Atmospheric Administration Air Resources Laboratory (Stein et al., 2015) was
23 used to calculate backward trajectories from gridded meteorological data (at 500 m above ground level)
24 at regular time intervals (12 h). For modeling the trajectory frequency, the system will start a trajectory
25 from a single location and height every 6 hours and then sum the frequency that the trajectory passed
26 over a grid cell and then normalize by either the total number of trajectories or endpoints. The grid
27 resolution was selected as 1° according to the scale of the desired result. The frequency distribution
28 maps (Fig. S7) of the five sampling sites recorded during the three cases support our findings: the
29 southern regions of Henan Province (e.g., Xuchang and Zhumadian cities) were a high probability (>
30 20 %) source for the five sites during Case 1 (Fig. S7a); the trajectory frequency during Case 2 (Fig.
31 S7b) uniformly distributed around the receptor sites is most probably connected to local emissions;
32 and the five sites during Case 3 (Fig. S7c) were affected by the air masses from northeastern areas
33 (e.g., Dezhou and Liaocheng cities) with the frequencies higher than 20 %.

34

35 Text S3 NH_x calculation

36 With respect to measurements of semi-volatile gases, the concentrations of NH₃ were extremely
37 higher than HNO₃ and HCl, consistent with the Song et al. (2018) and Liu et al. (2017). TNH_x, required
38 NH_x (Required-NH_x), and excess NH_x (Excess-NH_x) concentrations were calculated using the
39 following formulas:

$$40 \text{ Total NH}_x = 17 \times \left(\frac{[\text{NH}_4^+]}{18} + \frac{[\text{NH}_3]}{17} \right), \quad (5)$$

$$\text{Required NH}_x = 17 \times \left(\frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{63} + \frac{[\text{Cl}^-]}{35.5} + \frac{[\text{HNO}_3]}{64} + \frac{[\text{HCl}]}{36.5} \right) - 17 \times \left(\frac{[\text{Na}^+]}{23} + \frac{[\text{K}^+]}{39} + \frac{[\text{Ca}^{2+}]}{20} + \frac{[\text{Mg}^{2+}]}{12} \right), \quad (6)$$

$$\text{Excess NH}_x = \text{total NH}_x - \text{required NH}_x, \quad (7)$$

where $[\text{Na}^+]$, $[\text{K}^+]$, $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{NH}_4^+]$, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{Cl}^-]$, $[\text{NH}_3]$, $[\text{HNO}_3]$, and $[\text{HCl}]$ are the measured mass concentrations ($\mu\text{g}/\text{m}^3$) of these species. 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 (Blanchard et al., 2000). If Excess- NH_x is above 0, then the system is considered NH_x -

rich. Otherwise, the system is under the NH_x -poor condition.

Figure lists:

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.

Fig. S2 Comparison between the predicted and measured NH_4^+ , NO_3^- , Cl^- , NH_3 , HNO_3 and HCl at the five sites.

Fig. S3 Ion balance of water-soluble inorganic ions at the five sites.

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.

Fig. S5 Comparison of predicted pH by ISORROPIA-II with E-AIM IV at the U-ZZ site.

Fig. S6 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 U-AY (a), R-

62 AY (b), R-XX (c), and R-PY (d) sites. The shaded areas represent the measurement uncertainties.

63 Fig. S7 Trajectory frequencies of typical periods at the five sites during Cases 1(a), 2(b), and 3(c).

64 The color scale bar represents the percentage of trajectories passing through each grid to total

65 trajectories.

66 Fig. S8 Time series of predicted $PM_{2.5}$ pH at the five sites. The shaded areas show the range of

67 uncertainty in pH for the pH_{max} and pH_{min} calculations.

68 Fig. S9 Correlations between pH and H^+_{air} during sampling periods at the five sites. The color scale

69 bar represents the aerosol water content (AWC) concentration.

70 Fig. S10 Sensitivity tests of $PM_{2.5}$ pH to input data. The real-time measured values of a variable and

71 the average values of other parameters during Case 2 were input into the ISORROPIA II model.

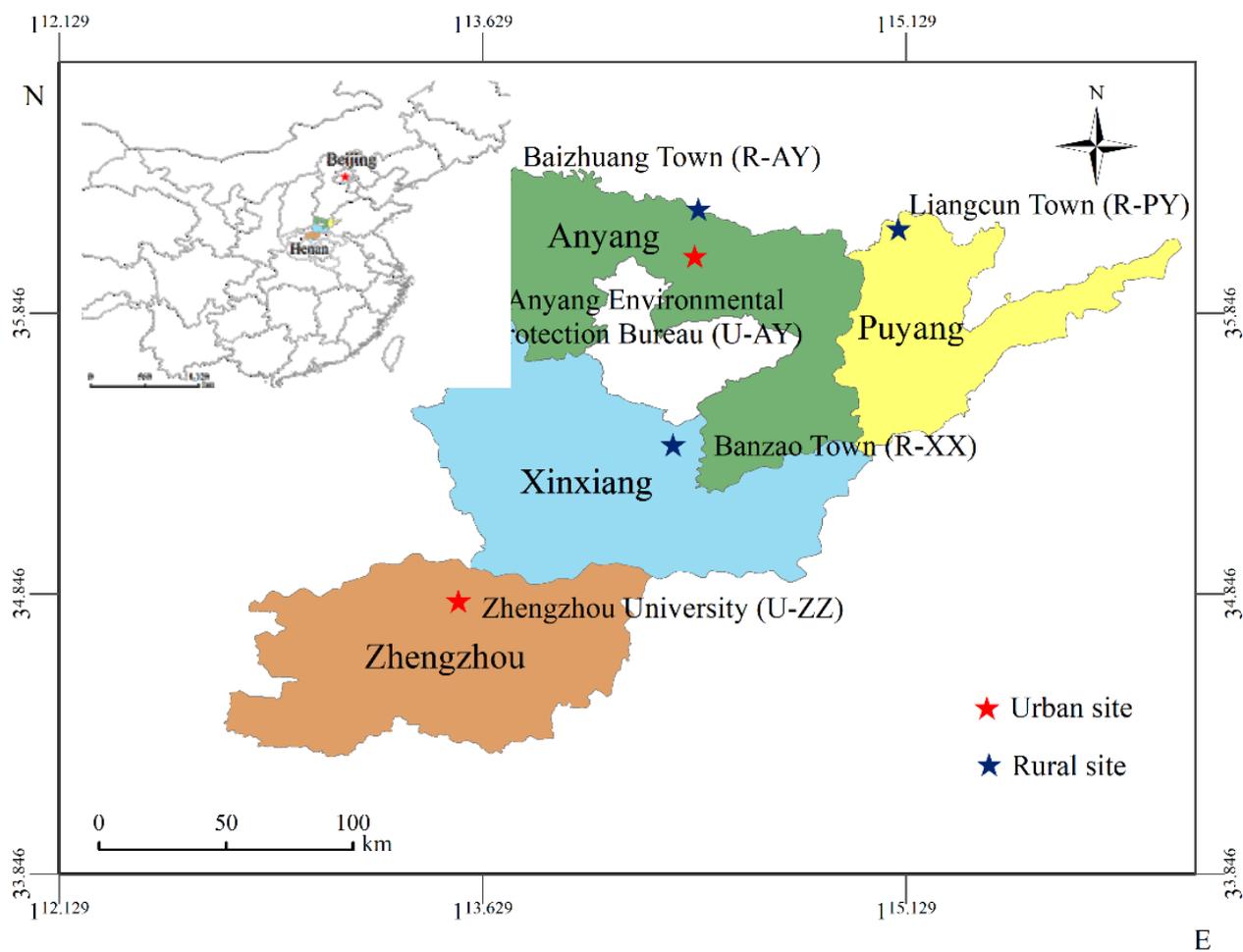
72 Fig. S11 Comparisons of the sensitivities of $PM_{2.5}$ pH to TNa, K^+ , Ca^{2+} , and Mg^{2+} among the five sites.

73 The color scale bar represents the pH values. The relative standard deviation (RSD) and range (Range)

74 represent the sensitivity degree of pH to this variable and range (min–max) of the re-predicted pH

75 value in the test, respectively.

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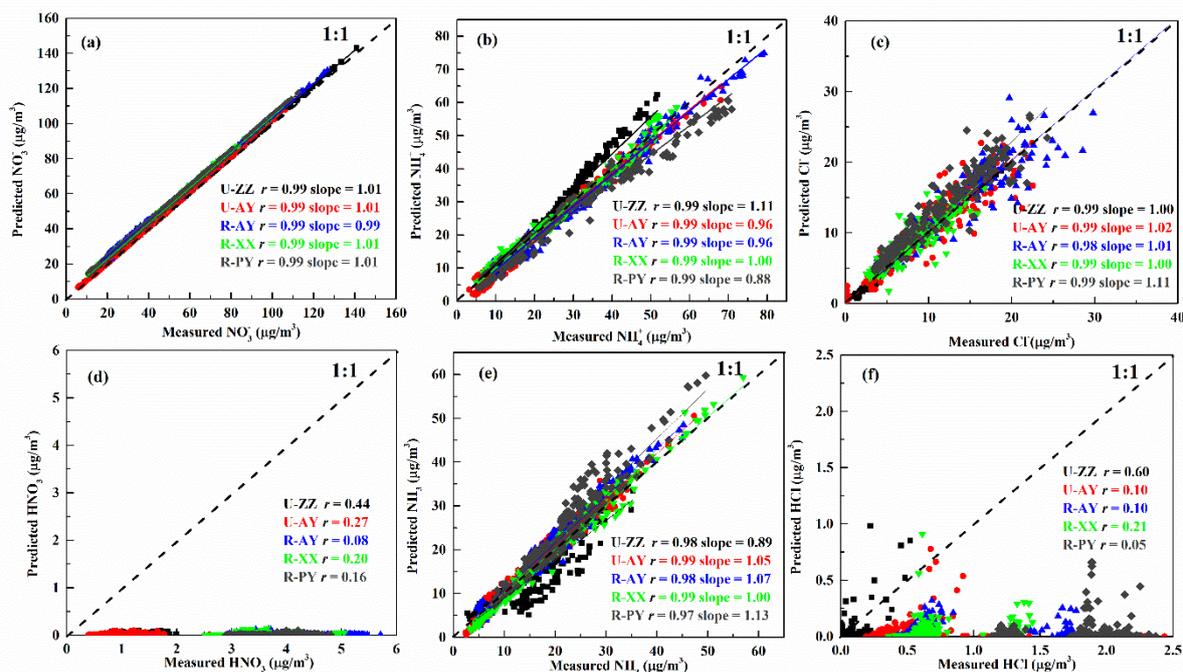
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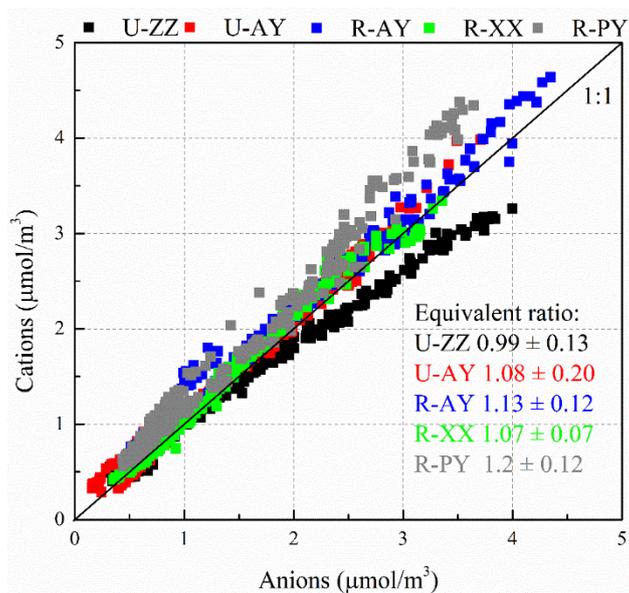


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85 Fig. S2 Comparison between the predicted and measured NH_4^+ , NO_3^- , Cl^- , NH_3 , HNO_3 and HCl at the

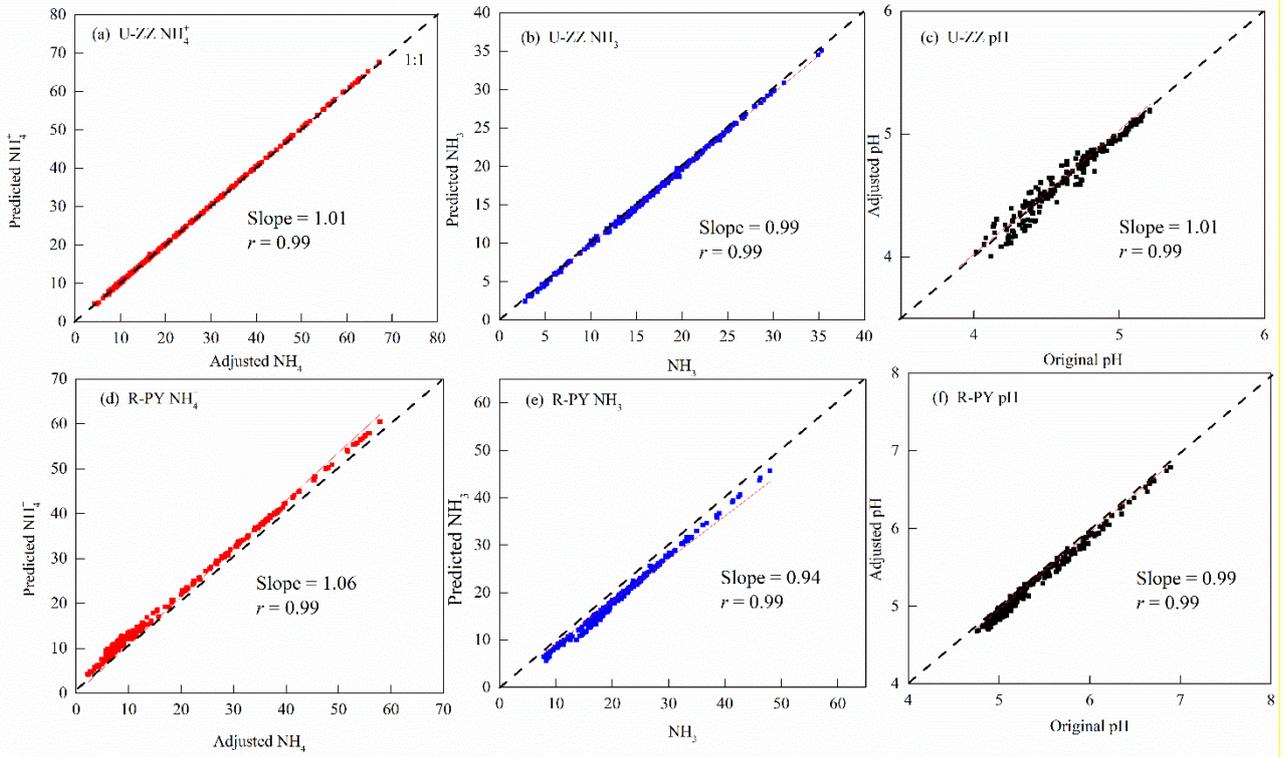
86 five sites.

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89 Fig. S3 Ion balance of water-soluble inorganic ions at the five sites.



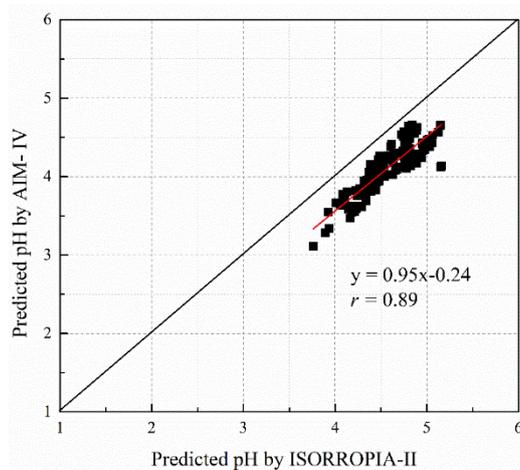
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91 Fig. S4 Comparison between the predicted and input NH_4^+ (a, d) and NH_3 (b, c) concentrations, the

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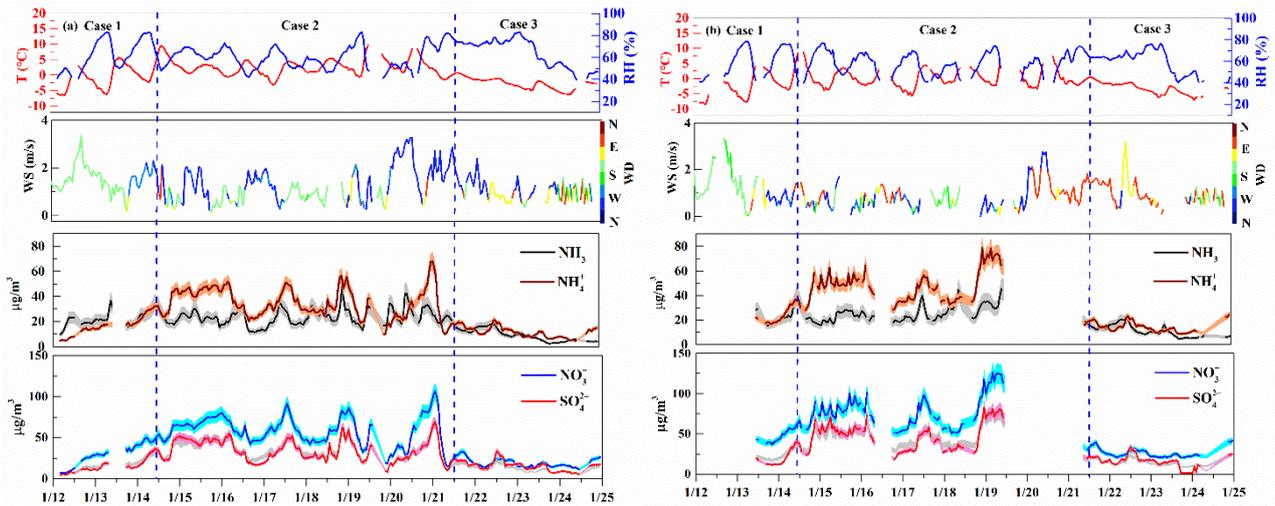
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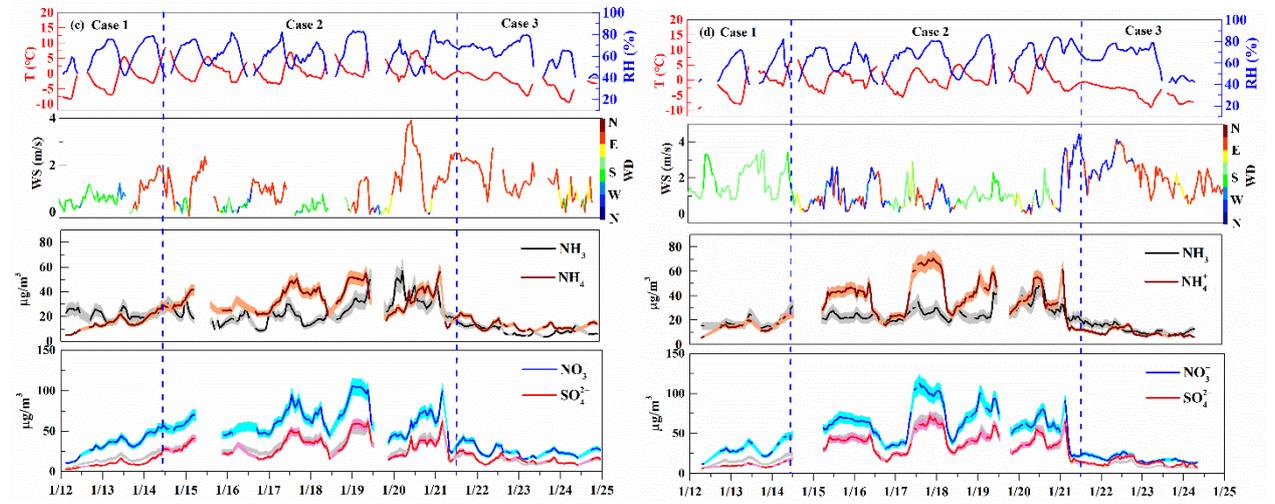
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96 Fig. S5 Comparison of predicted pH by ISORROPIA-II with E-AIM IV at the U-ZZ site.

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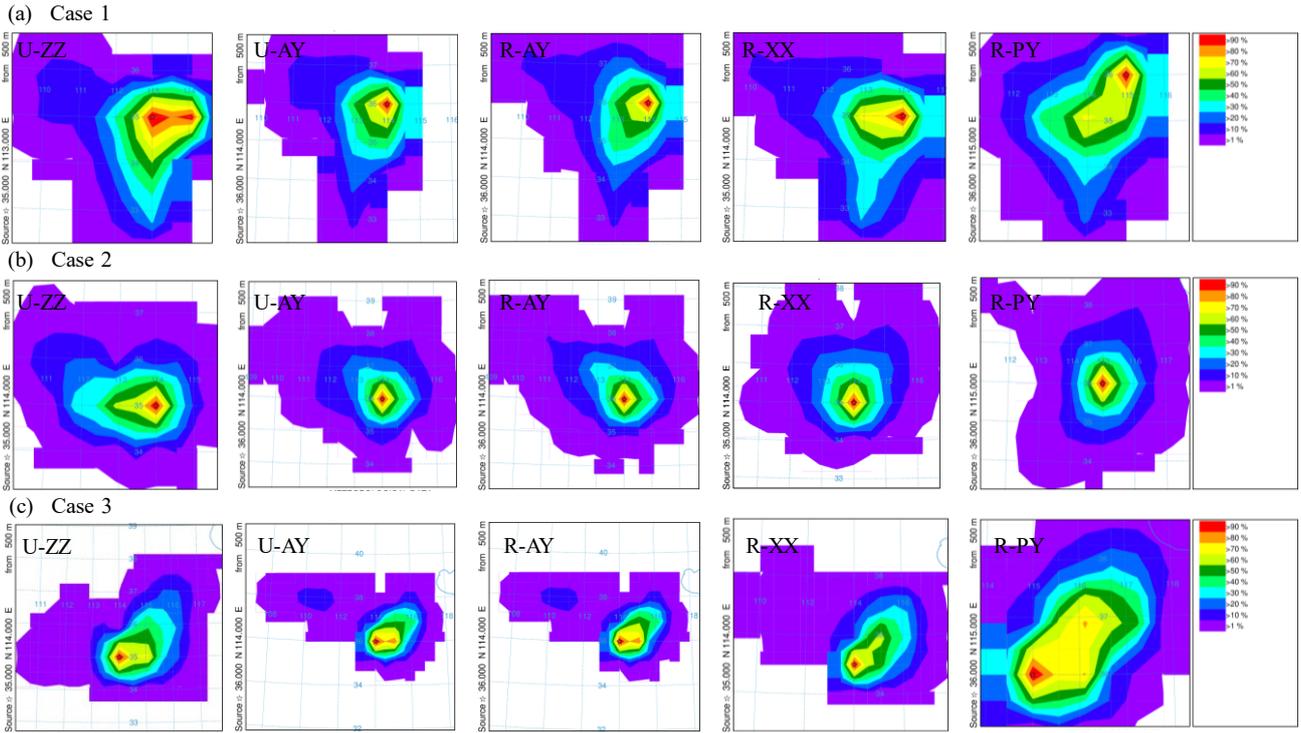
Fig. S6 Temporal variations of temperature (T), relative humidity (RH), wind speed (WS), wind

100

direction (WD), and concentrations of NH_3 , NH_4^+ , SO_4^{2-} , and NO_3^- during three cases at U-AY (a), R-

101

AY (b), R-XX (c), and R-PY (d) sites. The shaded areas represent the measurement uncertainties.

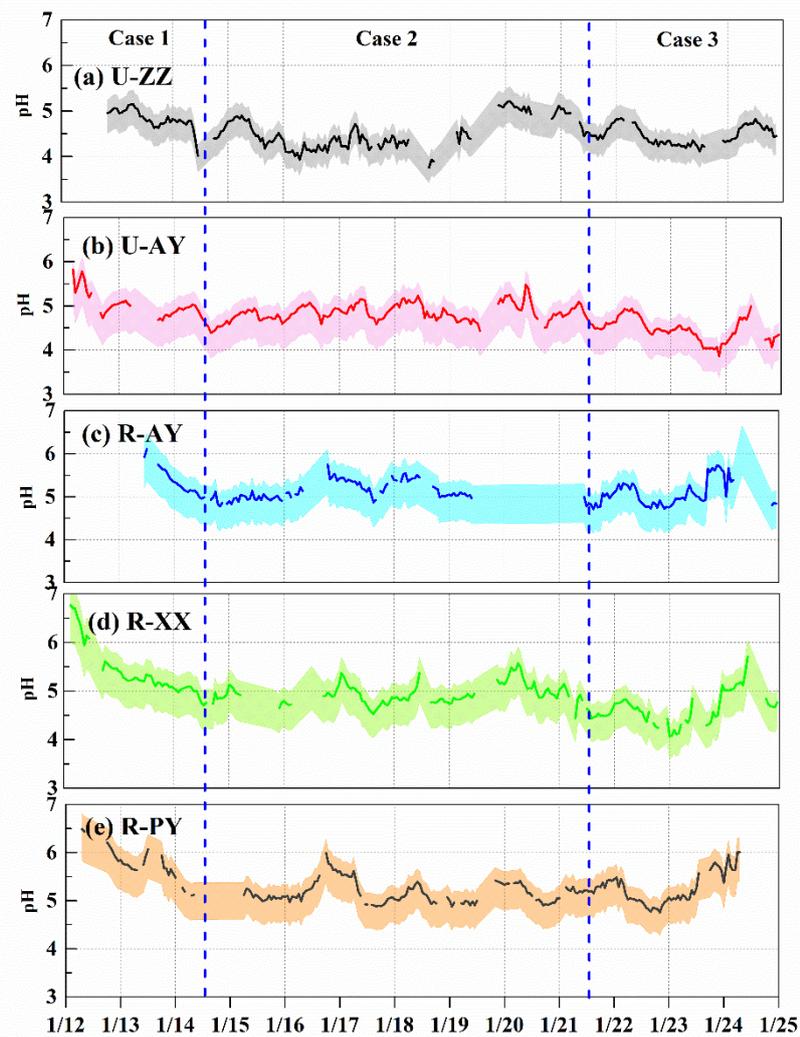


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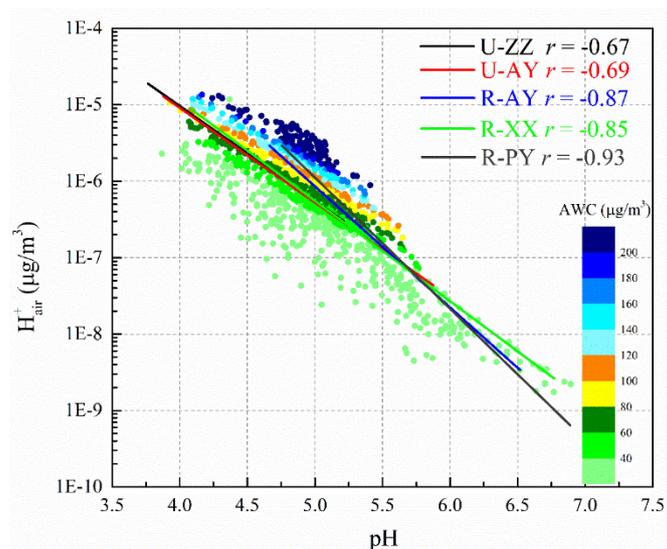


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107 Fig. S8 Time series of predicted PM_{2.5} pH at the five sites. The shaded areas show the range of

108 uncertainty in pH for the pH_{max} and pH_{min} calculations.

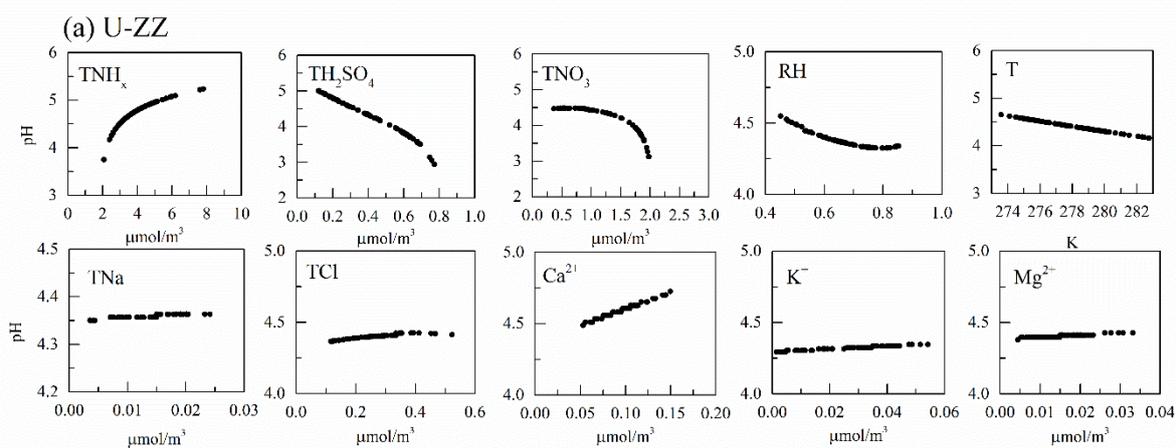
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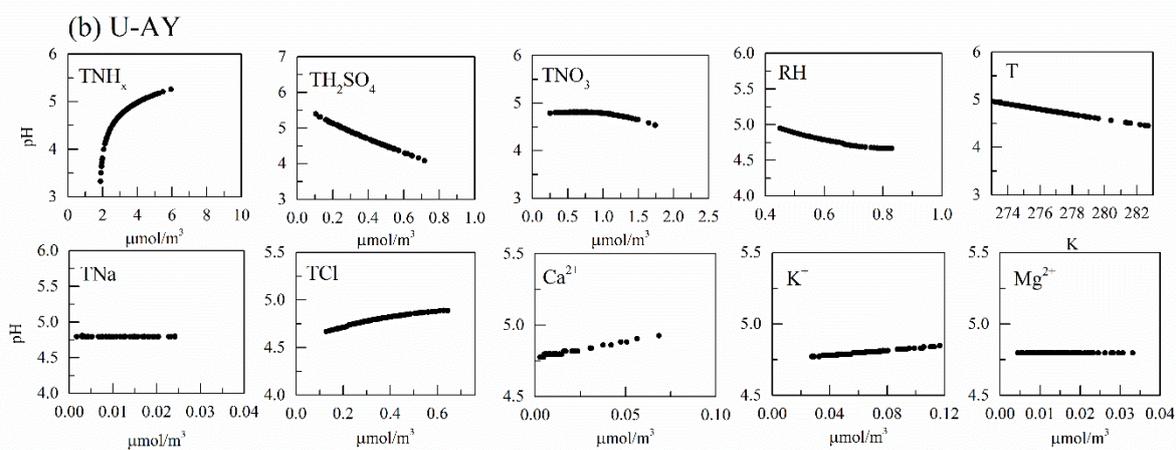
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111 Fig. S9 Correlations between pH and H^+_{air} during sampling periods at the five sites. The color scale

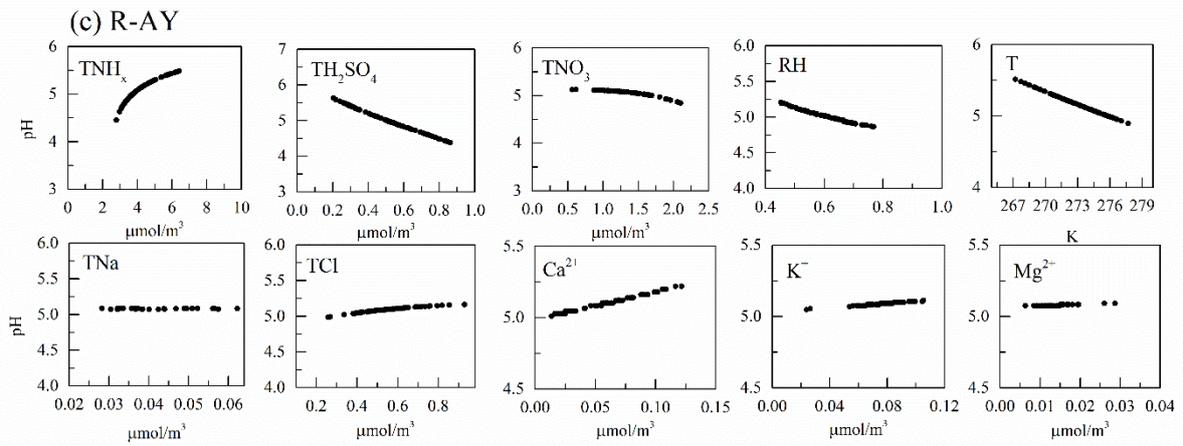
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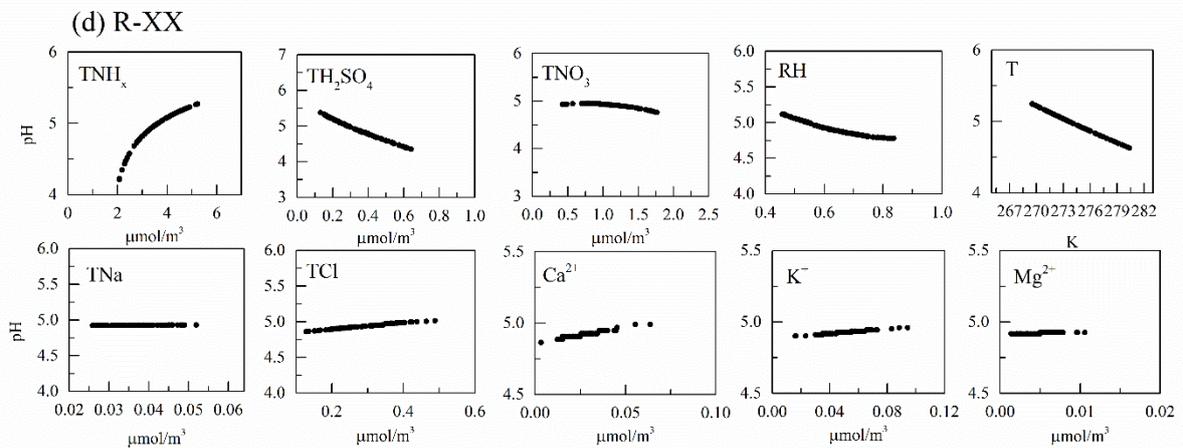
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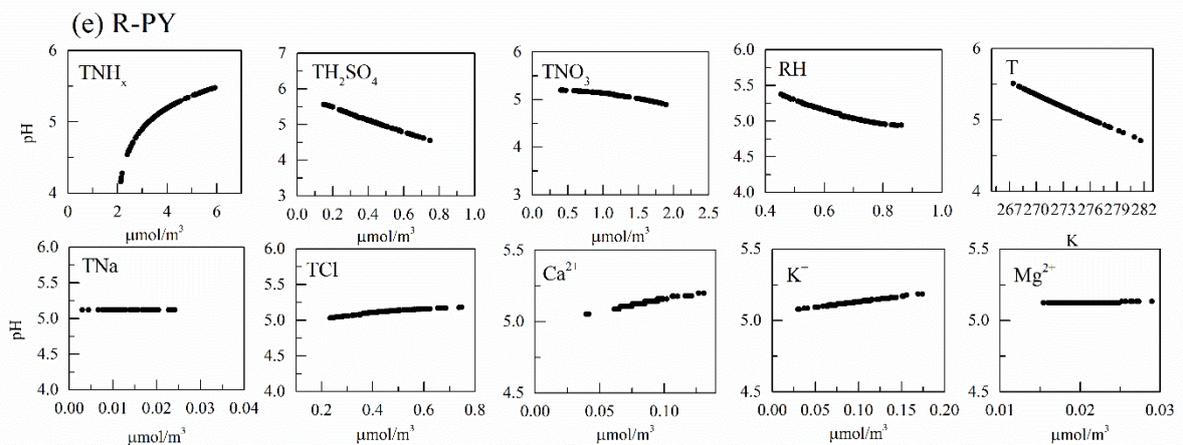
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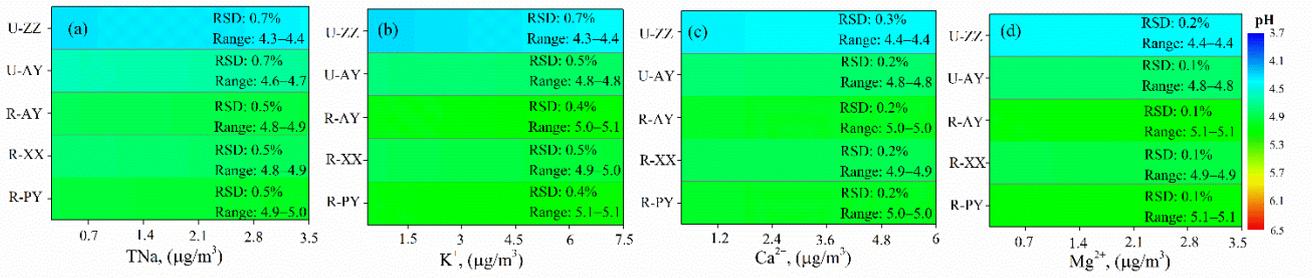
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118 Fig. S10 Sensitivity tests of PM_{2.5} pH to input data. The real-time measured values of a variable and
 119 the average values of other parameters during Case 2 were input into the ISORROPIA II model.

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122 Fig. S11 Comparisons of the sensitivities of PM_{2.5} pH to TNa (replaced by observed Na⁺), K⁺, Ca²⁺,
 123 and Mg²⁺ among the five sites. The color scale bar represents the pH values. The relative standard
 124 deviation (RSD) and range (Range) represent the sensitivity degree of pH to this variable and range
 125 (min–max) of the re-predicted pH value in the test, respectively.

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132 **Table lists:**

133 Table S1 Summarized NH₃ concentrations (µg/m³) in this study and other sites.

134 Table S2 Statistical values of pH during three cases.

135 Table S3 Pearson’s correlation coefficients (*r*) between H⁺_{air} with observed data at the five sites.

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

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142 Table S1 Summarized NH₃ concentrations (μg/m³) in this study and other sites.

Cities	Period	NH ₃	References	143
Zhengzhou, China	2018.01	22.0 ± 8.9	This study	
Anyang, China	2018.01	25.3 ± 10.5	This study	
Anyang, China	2018.01	25.8 ± 12.0	This study	
Xinxiang, China	2018.01	26.1 ± 14.0	This study	
Puyang, China	2018.01	27.1 ± 17.3	This study	
Zhengzhou, China	2017.03–2018.04	11.7	Wang et al., 2018	
Beijing, China	2015.01–03	7.3	Zhang et al., 2018	
Beijing, China	2008.02–2010.07	22.8 ± 16.3	Wang et al., 2018	
Beijing, China	2007.01–2010.07	10.2 ± 10.8	Wang et al., 2018	
Beijing, China	2001.07–2001.08	16.8–42.2	Wang et al., 2018	
North China Plain, China	2006.08–2009.09	11.7–31.9	Shen et al., 2011	
Xi'an, China	2006.04–2007.04	18.6	Wang et al., 2018	
Xi'an, China	2006.04–2007.04	20.3	Wang et al., 2018	
Chengdu, China	2014.07–2015.04	10.5 ± 4.8	Wang et al., 2016	
Wanzhou, China	2014.07–2015.04	8.3 ± 4.7	Wang et al., 2016	
shanghai, China	2014.05–2015.06	7.8	Chang et al., 2019	
Hangzhou, China	2012.04–05	12.8	Jansen et al., 2014	
Dalian, China	2010.09–2012.04	1.5	Luo et al., 2014	
Fenghua, China	2010.08–2012.05	3.7	Luo et al., 2014	
Fujian, China	2015.06–2016.05	21.0 ± 7.9	Wang et al., 2018	
Fujian, China	2015.06–2017.03	10.5–13.5	Wu et al., 2018	
Hong Kong, China	2003.10–2006.05	10.2	Tanner, 2009	
Carolina, USA	2000.01–12	0.4–3.4	Walker et al., 2004	
Delhi, India	2013.01–2015.12	25.3 ± 4.6	Saraswati et al., 2019	

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Table S2 Statistical values of pH during three cases.

	Case 1				Case 2				Case 3			
	25th percentile	Median	75th percentile	Average	25th percentile	Median	75th percentile	Average	25th percentile	Median	75th percentile	Average
U-ZZ	4.7	4.8	5.0	4.8	4.3	4.5	4.8	4.5	4.3	4.5	4.7	4.5
U-AY	4.8	5.0	5.2	5.1	4.7	4.8	5.0	4.8	4.4	4.5	4.8	4.5
R-AY	5.1	5.4	5.8	5.5	5.0	5.1	5.4	5.2	4.9	5.0	5.3	5.1
R-XX	5.1	5.3	5.6	5.4	4.8	4.9	5.1	4.9	4.5	4.7	5.0	4.7
R-PY	5.7	6.0	6.3	6.0	5.0	5.1	5.4	5.2	5.0	5.2	5.4	5.3

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Table S3 Pearson's correlation coefficients (r) between H^+_{air} with observed data at the five sites.

	U-ZZ	U-AY	R-AY	R-XX	R-PY
TWSII _s	0.834**	0.521**	0.676**	0.530**	0.774**
TNH _x	0.650**	0.368**	0.544**	0.301**	0.703**
TH ₂ SO ₄	0.867**	0.625**	0.765**	0.638**	0.811**
TNO ₃	0.828**	0.458**	0.607**	0.502**	0.767**
TCl	0.430**	0.406**	0.602**	0.223**	0.419**
K ⁺	0.757**	0.388**	0.551**	0.138*	0.485**
Ca ²⁺	-0.161*	-0.234**	-0.137*	-0.248**	0.06
TNa	0.306**	-0.095	0.098	0.103	-0.138*
Mg ²⁺	-0.009	-0.027	-0.018	-0.050	0.026
AWC	0.63**	0.739**	0.903**	0.755**	0.938**
T	0.012	0.045	-0.138*	-0.023	0.146*
RH	0.337**	0.610**	0.631**	0.637**	0.658**

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

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

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