Reviewer comments:

Reviewer #2:

This study presents a one-year measurement of $PM_{2.5}$ and water-soluble inorganic ions at a semi-arid background site in northwestern China. This study aims to characterize the seasonal variability of aerosol levels and composition, aerosol acidity, and its driving factors. The dataset is potentially valuable as observation in this region are relatively less abundant compared with other more extensively studied areas in China such as North China Plain. However, the manuscript in its current form is difficult to follow and interpret. The method descriptions lack key information, making it hard to assess the robustness of the conclusions. There are also obvious errors and unclear expressions throughout the manuscript. My specific comments are listed below.

Response: We thank the reviewer's comments, which are very helpful for us to improve our work. Detailed revision and response to the comments are list below.

1. Section 3.1: The measurements show interesting features, including relatively lower $PM_{2.5}$ levels possibly due to distance from urban cores, nitrate-dominate composition compared to sulfate, and high calcium concentrations in spring. These could have important implications for aerosol acidity and may differ from conditions in other urban or sulfate-dominated regions. This aspect could be emphasized more clearly. At the same time, some analyses seem less relevant to aerosol pH and do not add much context, thus could be reduced. For example, the discussion related to the cation/anion balance and the comparison between observed and predicted NH_4^+. It is not sufficient to use ion balance alone to infer aerosol acidity, as mentioned in Lines 312–314. The imbalance is more likely influenced by unmeasured species such as CO_3^{2-}, HCO_3^-, organics, rather than H^+. The discussion related to "predicted NH_4^+"is also unclear. What is the "predicted NH_4^+" and why predicting NH_4^+? The ammonia-sulfate ratio is also only indirectly related to aerosol acidity, and this analysis does not seem to provide additional information.

Response: Thank you for this comment.

1) To better highlight the implications of the observed chemical characteristics for aerosol acidity, we have added important discussion regarding the influence of nitrate dominance and high spring calcium concentrations on aerosol acidity at lines 323-327 and lines 355-359 in the revised manuscript.

Lines 323-327:

Nitrate dominance, as opposed to sulfate-dominated conditions, indicates a stronger reliance of aerosol acid-base balance on the partitioning of semi-volatile

NH_4NO_3. This partitioning process is highly sensitive to ambient temperature, relative humidity, and ammonia concentration, which may result in greater dynamic variations in aerosol pH (Song et al., 2019; Guo et al., 2016).

Lines 355-359:

The pronounced Ca^{2+} peak in spring, originating from dust transport from the Loess Plateau, introduces substantial alkaline mineral components into the atmosphere. These components provide an additional seasonal neutralization capacity and thus exert a significant influence on aerosol acidity (Shen et al., 2024).

2) In line with your suggestion, we have reduced the discussion related to cation-anion balance, as it is less directly relevant to aerosol pH and does not add substantial context. At the same time, We have also clarified the concept of predicted NH_4^+, its analytical purpose, and its relationship with aerosol acidity, adding a detailed discussion at lines 337–353 and providing further explanation in the caption of Fig. S2.

Lines 337-353:

To further quantitatively validate this conclusion, we performed a linear fitting analysis between the predicted NH_4^+ and the observed NH_4^+, indicating that NH_4^+ remains in excess after neutralizing SO_4^{2-} and NO_3^- (Fig. S2). When assuming that NO_3^- and SO_4^{2-} exist in the forms of $(NH_4)_2SO_4$ and NH_4NO_3, the slope (k) for each season approaches 1, indicating complete conversion to $(NH_4)_2SO_4$ ($[NH_4^+] = [NO_3^-] \times 18/62 + [SO_4^{2-}] \times 36/96$, $\mu g\ m^{-3}$) rather than to acidic NH_4HSO_4 ($[NH_4^+] = [NO_3^-] \times 18/62 + [SO_4^{2-}] \times 18/96$). After SO_4^{2-} is completely neutralized, any excess NH_4^+ then reacts with NO_3^- to form NH_4NO_3. The $k < 1$ signifies the observed NH_4^+ concentration is higher than the NH_4^+ concentration predicted based on the complete neutralisation assumption,and NH_4^+ remains in excess after fully neutralising SO_4^{2-} and NO_3^-. In practice, the observed excess NH_4^+ may interact with other anions, such as Cl^- from biomass burning, potentially forming NH_4Cl (Ye et al., 2019). This demonstrates that NH_3 is sufficiently abundant in the Guanzhong Plain to fully neutralize the major inorganic acids. This provides direct chemical evidence explaining the elevated aerosol pH levels in the ammonia-rich Guanzhong Plain and establishes a foundation for the subsequent analysis of the buffering contribution of NH_x to aerosol acidity.

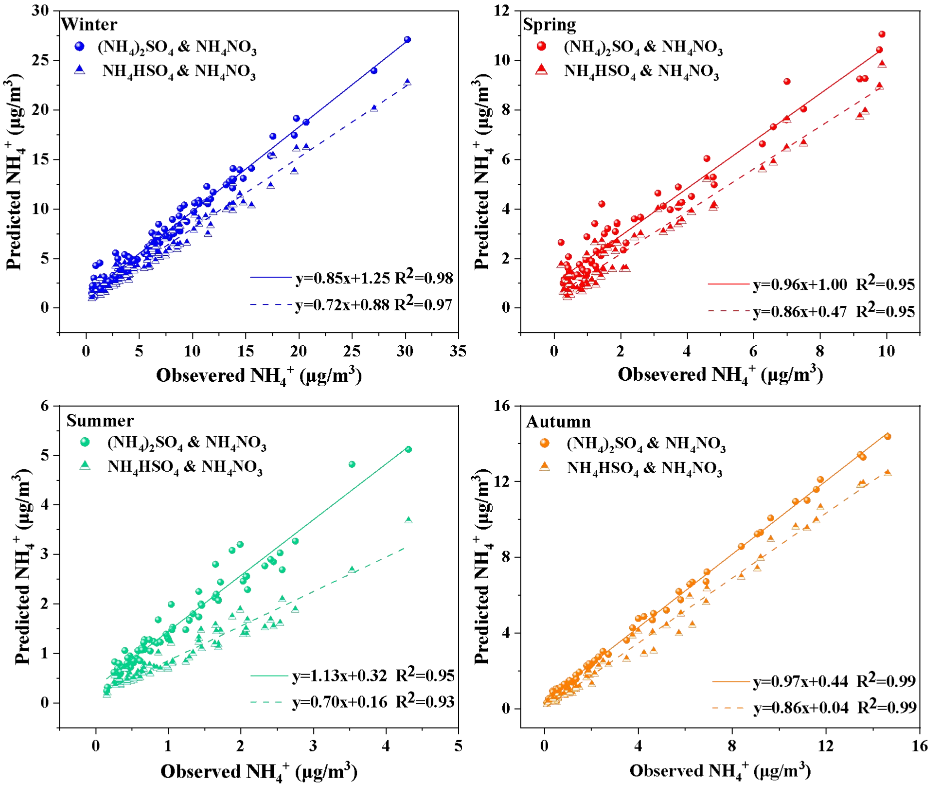

Fig. S2 Linear relationship between observed and predicted values of NH_4^+

(When NH_4^+, SO_4^{2-}, and NO_3^- exist in the atmosphere as $(NH_4)_2SO_4$ and NH_4NO_3, the predicted NH_4^+ concentration is calculated as:$[NH_4^+]=[NO_3^-]\times18/62+[SO_4^{2-}]\times36/96$; When exist as NH_4HSO_4 and NH_4NO_3, it is calculated as:$[NH_4^+]=[NO_3^-]\times18/62+[SO_4^{2-}]\times18/96$, μg m^{-3})

2. Section 2.4: The description of the multiple linear regression model lacks important details, which makes the results difficult to interpret. Even with a citation, a brief summary is needed to provide basic information, such as how the predicting variables are selected and how the significant tests are performed. Besides, the author should provide more information about the training data instead of only listing a reference. Does the training dataset represent the conditions at this site? If it is from an urban core, are the concentrations much higher than here? How long does the training dataset span? Does it sufficiently cover all seasons? How many data points are used? In Figure 4, the predicted NHR shows some bias compared with observations. How does this bias affect the pH calculation? Also, is the predicted NH_3 level within the range of the training data If not, is it valid to extrapolate to this site? In Table S2, some t values are very low (close to 0). Are these variables really useful in predicting NHR? What are the corresponding p-values? Without a clearer description of the training data and validation, the use of predicted NH_3 hence the pH estimates are not convincing. In addition, to help validate the pH results at this site, it would be helpful to compare NH_3-NH_4^+ partitioning from ISORROPIA output with that used as the input (calculated by measured NH_4^+ and estimated NH_3).

Response: We thank the reviewer for the thorough and constructive comments.

1) We have revised the manuscript to provide detailed information on the multiple linear regression model, training data, and model validation in section 2.4. We also added a supplementary table (Table S1) to compare how seasonal aerosol pH in response to changing NHR.

Lines 215-237:

Given the well-established thermodynamic and chemical relationships between NHR and factors such as NO_3^-, SO_4^{2-}, and T (C, Fountoukis et al., 2007), all parameters that serve as inputs to the thermodynamic model ISORROPIA-II, were included as candidate independent variables. Multiple linear regression (MLR) was performed using SPSS software with NHR as the dependent variable, and the model parameters were estimated using ordinary least squares.

The model was trained using a previous high-resolution (1-hour) online $PM_{2.5}$ dataset from an urban site in Xi'an during 2016-2017 (Wu et al., 2020), which included major WSIIs concentrations in $PM_{2.5}$, ammonia concentrations, and meteorological data from the same observation site. The data covered all four seasons: winter (n = 605, from 21 December 2016 to 23 January 2017), spring (n = 704, from 31 March to 30 April 2016), summer (n = 591, from 8 July to 6 August 2017), and autumn (n = 1032, from 1 October to 15 November 2017). Following model construction, its validity and accuracy were systematically assessed using the correlation coefficient, the F-test, and the t-test (Wei et al., 2023). For variables with $p > 0.05$, they were retained to preserve model integrity, as they may indirectly influence NHR and were shown to have a negligible effect on pH verified by comparison (Table S1). Despite the variations in ion concentrations between the training data and our study site, the thermodynamic mechanism that governs NHR remains consistent across different concentration levels. Furthermore, the ranges of the key input variables encompass the observed values at our site. Consequently, the model trained on urban data can be effectively utilized to predict NHR at the background site.

Table S1 Seasonal aerosol pH in response to changing NHR (training data).

	Observed NHR	Deviation +20% NHR	Deviation -20% NHR	Estimated NHR	Remove p <0.05 factors Estimated NHR
pH-Winter	4.87 ± 0.48	4.70 ± 0.49	5.03 ± 0.48	4.99 ± 0.49	4.95 ± 0.49
pH-Spring	4.26 ± 0.59	4.16 ± 0.60	4.39 ± 0.57	4.12 ± 0.61	4.09 ± 0.61
pH-Summer	3.93 ± 0.70	3.83 ± 0.71	4.03 ± 0.69	4.00 ± 0.73	4.05 ± 0.75
pH-Autumn	4.80 ± 0.64	4.69 ± 0.64	4.93 ± 0.63	4.55 ± 0.64	4.57 ± 0.64

The observed NHR denotes the measured ammonium conversion ratio. Deviation +20% NHR represents 1.2 times the observed NHR, and deviation −20% NHR represents 0.8 times the observed NHR. The estimated NHR was derived through multiple linear regression analysis, and the estimated NHR after removing factors with $p < 0.05$ was obtained through multiple linear regression analysis.

2) We have also added the corresponding p-values for each factor from the t-tests in Supplementary Table S4, along with an explanation for retaining the low t-value factors.

Lines 227-232: Following model construction, its validity and accuracy were systematically assessed using the correlation coefficient, the F-test, and the t-test (Wei et al., 2023). For variables with $p > 0.05$, they were retained to preserve model integrity, as they may indirectly influence NHR and were shown to have a negligible effect on pH verified by comparison (Table S1).

Table S4 Results of T-test and F-test

Winter Model	**T-test**			**F-test**		**Model Summary**		
	Non-standardized coefficient	**T**	**Sig.**	**F**	**Sig.**	**R**	**R^2**	**Estimated standard error**
Constant	1.204	3.029	0.003	295.93	$P < 0.01$	0.88	0.77	0.082
SO_4^{2-}	-0.003	-5.531	0.000					
NO_3^-	0.006	15.476	0.000					
K^+	0.023	4.297	0.000					
Mg^{2+}	0.328	3.134	0.002					
Ca^{2+}	-0.017	-1.578	0.115					
T	-0.004	-2.581	0.010					
RH	0.001	0.060	0.952					
Spring Model	**T-test**			**F-test**		**Model Summary**		
Constant	0.533	2.835	0.005	219.02	$P < 0.01$	0.83	0.69	0.044
SO_4^{2-}	0.006	12.774	0.000					
NO_3^-	0.005	15.513	0.000					
K^+	-0.018	-2.745	0.006					
Mg^{2+}	-0.065	-0.898	0.370					
Ca^{2+}	-0.017	-3.375	0.001					
T	-0.001	-2.018	0.044					
RH	-0.009	-0.581	0.562					
Summer Model	**T-test**			**F-test**		**Model Summary**		
Constant	-1.389	-9.369	0.000	339.18	$P < 0.01$	0.82	0.67	0.045
SO_4^{2-}	0.007	18.481	0.000					
NO_3^-	0.006	14.972	0.000					
K^+	0.010	0.864	0.388					
Mg^{2+}	0.021	1.794	0.073					
Ca^{2+}	-0.003	-1.281	0.200					
T	0.005	9.903	0.000					
RH	0.066	5.279	0.000					
Autumn Model	**T-test**			**F-test**		**Model Summary**		
Constant	0.656	4.944	0.000	537.31	$P < 0.01$	0.86	0.74	0.057
SO_4^{2-}	0.006	16.318	0.000					
NO_3^-	0.003	15.854	0.000					
K^+	-0.003	-0.637	0.524					
Mg^{2+}	-0.064	-4.426	0.000					
Ca^{2+}	-0.040	-12.934	0.000					
T	-0.001	-3.197	0.001					
RH	0.012	1.435	0.152					

3) Regarding the discrepancy between the observed and estimated NHR for the training data, we have already provided a detailed explanation in the paper. In addition, we have added the Fig.S3 to show the correlation between daily mean input and output NHR from the ISORROPIA-II.

.Lines 405-417:

This study assessed the reliability of the MLR model estimates through two validation levels. First, the NHR estimated by the MLR model for 2016–2017 was compared to the observed NHR (Fig. 4). The results revealed a significant positive correlation across all seasons (with the intercept constrained to zero, $R^2 > 0.94$, $P < 0.01$), indicating that the MLR model predicts NHR with high accuracy. Second, to further validate the pH results at our site, we compared the NHR output from the ISORROPIA-II model with the input NHR (Fig. S3). The results again demonstrated a strong linear correlation (with the intercept constrained to zero, $R^2 > 0.83$, $P < 0.01$), thereby supporting the reliability of subsequent pH simulations. However, a disparity exists between the predicted and observed NHR in Fig. 4 and S3. To evaluate its impact on aerosol pH, we calculated the pH changes associated with both positive and negative NHR deviations (Table S1). The overall pH change resulting from these deviations is less than 0.2 units, which does not affect the primary conclusions.

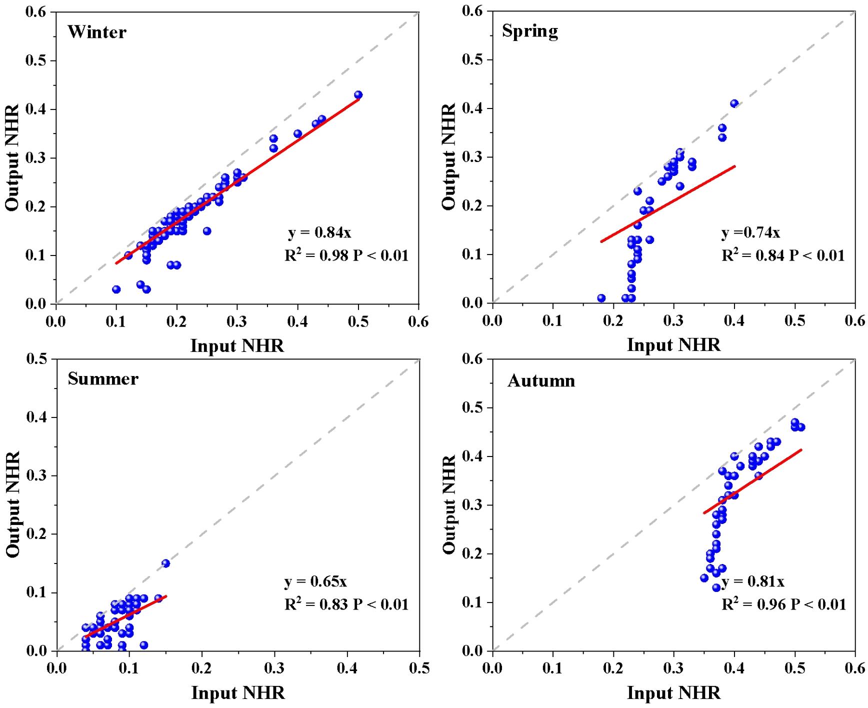

Fig. S3 Correlation between daily mean input and output NHR from the ISORROPIA-II

4) Regarding whether the NH_3 concentration falls within the training data range and its validity：

Lines 418-428:

Furthermore, the NH_3 concentrations derived from NHR at our site remain below 60 μg m^{-3}, well within the range of the training dataset from urban site. However, the seasonal NH_3 pattern at our site (2022: winter > summer > spring > autumn) differs from that in the training dataset (2016: summer > spring > autumn > winter). This discrepancy can be attributed to the significant reduction in SO_2 emissions resulting from air pollution control. In 2016, the high concentration of SO_2 emitted from coal combustion reacts rapidly with NH_3 to form $(NH_4)_2SO_4$, and this process consumes large amounts of gaseous NH_3 in winter (Wang et al., 2016; Liu et al., 2023). Due to interannual NH_3 variability, we employed the thermodynamically stable NHR for model training and validation, back-calculated NH_3 from the estimated NHR and measured NH_4^+, and then used these values in ISORROPIA-II to simulate aerosol pH.

3. Section 2.5: The sensitivity tests and quantitative analysis both lack necessary details, even though references are provided. For the sensitivity analysis, the "relative standard deviation" mentioned in the abstract and in Line 489 appears abruptly. What does it represent, and what is the purpose of this analysis? The quantitative decomposition of pH contributions seems to use a different method, but the description is unclear. The text mentions change from "scenario 1 to scenario 2," but what are these scenarios? This makes Figure 7 difficult to interpret. In spring, the sum of contributions from all components does not match the overall pH change shown by the markers, which seems inconsistent with the method description in Section 2.5. Both the sensitivity analysis and the contribution decomposition aim to explain the drivers of aerosol acidity. Why are both methods needed, and what is the connection between them? At present, they read like two separate analyses presented in parallel, with some repetition and even conflicting interpretations. For example, in the sensitivity test, higher temperature reduces ALWC and increases acidity (Lines 524–525), whereas in the quantitative analysis, temperature is said to enhance aerosol acidity in winter and spring but not in summer and autumn.

Response: Thank you for this comment.

1) We have provided a supplementary explanation of RSD in the Methods section 2.5. The RSD is derived from the coefficient of variation of pH responses in sensitivity analysis (i.e., the ratio of standard deviation to mean), indicates the relative sensitivity of aerosol pH to typical fluctuations of a given factor.

Lines 247-256:

To quantitatively evaluate the influence of each factor on aerosol pH, two complementary approaches were utilized: the relative standard deviation (RSD) method and the ΔpH contribution decomposition method. The RSD, which is derived from the coefficient of variation of pH responses in sensitivity analysis (i.e., the ratio of standard deviation to mean), indicates the relative sensitivity of aerosol pH to typical fluctuations of a given factor; a higher RSD signifies a greater potential impact. However, the RSD method provides only a relative ranking and does not directly determine the absolute contribution of each factor to the observed pH. Consequently, this study emphasizes the quantitative analysis of ΔpH contributions quantitative analysis.

2) Thank you for pointing out the lack of clarity in Figure 7. The markers correspond to the right Y-axis and indicate the seasonal mean pH values, not the total ΔpH. The bar chart in Figure 7 presents the independent contribution of each specific factor to the total ΔpH between two seasons, where $\Delta pH = pH_2 - pH_1$. Taking Spring versus Summer as an example: the measured mean pH in Spring (pH_1) is 3.64 and in Summer (pH_2) is 2.67, so the total $\Delta pH = -0.98$. For a given factor, such as temperature (T), we kept all other Spring parameters unchanged and replaced only the T value from the Spring measurement with the Summer measurement, then used the ISORROPIA-II model to compute the resulting pH change, which gave $\Delta pH_T = -0.49$. The same procedure was applied to each of the other factors (RH, SO_4^{2-}, NH_x, Ca^{2+}, etc.) to obtain their independent contributions.

As briefly noted in Section 2.5, the "others" term represents the residual change not captured by these single-factor replacements; it arises from synergistic effects and non-linear interactions among variables.Thus, the total ΔpH satisfies the equation $\sum pH_j + \Delta pH_{others} = \Delta pH_{total}$. In a stacked bar chart, positive and negative bars partially cancel each other, so the net height is smaller than the sum of absolute values, but the algebraic sum of all contributions plus the "others" term exactly equals the ΔpH_{total}.

To avoid any ambiguity, we have provided a supplementary table (Table S2) and added the definition of "others" in the caption of, listing the ΔpH_{total} for each season and the independent contributions of each factor to the ΔpH_{total}.

Table S2 Seasonal ΔpH-total and the independent contribution of each factor.

	ΔpH -total	ΔpH -T	ΔpH-RH	ΔpH-SO_4^{2-}	ΔpH-NH_x	ΔpH-NO_3^-	ΔpH-Cl^-	ΔpH-NVCs	ΔpH-others
Win-Spr	-1.17	-0.62	0.05	0.19	-0.89	-0.01	-0.06	0.02	0.14
Spr-Sumr	-0.98	-0.49	0.02	0.00	0.21	0.05	-0.02	-0.38	-0.38
Sum-Aut	0.63	0.65	0.34	-0.21	-0.22	0.28	0.01	-0.06	-0.16
Aut-Win	1.52	0.54	0.04	-0.21	0.70	-0.18	0.04	-0.06	0.64

(The ΔpH-others represents the residual change of pH not captured by these single-factor replacements)

Lines 264-270:

In this study, the aforementioned method was applied to consecutive seasonal pairs in the following order: spring values were substituted into the winter scenario, summer values into spring, autumn values into summer, and winter values into autumn (Table S2). For each pairwise substitution, Scenario 2 denotes the season being introduced, while Scenario 1 refers to the base season. Consequently, the calculated ΔpH quantifies the impact of each factor's seasonal shift on aerosol pH.

3) Regarding “the relationship between the sensitivity analysis and the contribution decomposition method, as well as potentially conflicting interpretations”, the explanation is as follows: The apparent contradiction arises from the different reference frameworks used in the sensitivity analysis and the contribution decomposition. In the sensitivity analysis, each season is treated independently: we perturb one factor while holding others at their seasonal baseline to obtain the sensitivity. This analysis consistently shows that higher temperature decreases pH regardless of season. In the contribution decomposition, however, we quantify the actual contribution of temperature by substituting the temperature of another season into the current season model. For winter, we substitute the higher spring temperature ($\Delta T > 0$), leading to a negative ΔpH (enhanced acidity). For summer, we substitute the lower autumn temperature ($\Delta T < 0$), leading to a positive ΔpH (reduced acidity). Thus, the two methods are consistent: the intrinsic effect of temperature is always acidifying, but the sign of its actual contribution depends on whether the substituted reference temperature is higher or lower than the current season temperature.

Other comments:

4. Line 22-25: Without context, it is unclear what the percentages represent.

Response: Thank for your reminder.We have clarified this in the revised manuscript

Lines 25-26:

Sensitivity tests and driver analysis revealed that atmospheric temperature (22.3%-33.8%), NH_x (gas NH_3+NH_4^+, 11.4%-44.9%), and SO_4^{2-} (8.5%-10.8%) were common key factors influencing pH across all seasons, with the percentages representing the quantitative contribution of each factor to the overall pH variation.

5. Line 28: Similarly, without any context, the mentioning of relative standard deviation is unclear.

Response: Thank for your reminder.We have clarified this in the revised manuscript

Lines 28-30:

Notably, Ca^{2+} emerged as a unique driver specific to spring, the relative standard deviation (RSD) was 8.8%, indicating a substantial impact of Ca^{2+} variability on spring aerosol pH.

6. Line 33-34: What is the link between aerosol acidity driving factors and $PM_{2.5}$ control strategies? The current discussion does not provide any context for this statement. Line 128-130: What is the connection between aerosol acidity analysis and precise ammonia reduction? The current discussion did not provide any context.

Response: Thank for your comments. We have removed these ambiguous sentences from the manuscript.

7. Line 115: The word “distinct” is vague. The two examples given here are not uncommon.

Response: Thank for your comments. We have revised this inappropriate expression in the text at lines 120-121.

8. Line 135: “Guangdong Plain” should be “Guanzhong Plain”

Response: Thank for your reminder.We have clarified this in the revised manuscript

9. Lines 195-196: The method of NH_3 estimation should be clearly described in method section instead of referring to discussion section.

Response: Thank for your comments. We have added the relevant content to the manuscript

Lines 198-201:

In this study, We modified the method of Wei et al. (2023) by shifting the prediction target from NH_3 to NHR. Based on our earlier datasets (Wu et al., 2020), we performed multiple linear regression to estimate NHR, which was subsequently used to retrieve NH_3 levels.

10. Lines 289-290: What is the “NH_4^+ vertex”? Lines 288-293: The logic here is unclear.

Response: We apologize for the unclear terminology. In Fig. S1, the ternary diagram shows the molar ratios of SO_4^{2-}, NO_3^-, and NH_4^+. The “NH_4^+ vertex” refers to the corner representing 100% NH_4^+. The intended meaning is that data points in each season are mostly clustered close to that corner, indicating a high relative abundance of NH_4^+. We have revised the text to make this clearer at lines 334-337.

Lines 334-337:

Moreover, most data points cluster near the vertex representing NH_4^+ in the ternary diagram (the corner where the molar fraction of NH_4^+ approaches 100%). This directly indicates a relative abundance of NH_4^+ during the observation period.

11. Lines 330-331: What does the “signifies NH_4^+ excess post-reaction” mean?

Response: Thank you for the question. In this study, the statement “$k < 1$ signifies NH_4^+ excess post-reaction with SO_4^{2-} and NO_3^-” means that when the fitted slope $k < 1$, the observed NH_4^+ concentration is higher than the NH_4^+ concentration predicted based on the complete neutralisation assumption, and NH_4^+ remains in excess after fully neutralising SO_4^{2-} and NO_3^-. This indicates that atmospheric NH_3 is relatively abundant, providing surplus ammonium salts, which is consistent with the ammonia-rich characteristic of the Guanzhong Plain. We have revised the text to make this clearer at lines 337-353.

Lines 337-353:

To further quantitatively validate this conclusion, we performed a linear fitting analysis between the predicted NH_4^+ and the observed NH_4^+ (Fig. S2). When assuming that NO_3^- and SO_4^{2-} exist in the forms of $(NH_4)_2SO_4$ and NH_4NO_3, the slope (k) for each season approaches 1, indicating complete conversion to $(NH_4)_2SO_4$ rather than to acidic NH_4HSO_4. After SO_4^{2-} is completely neutralized, any excess NH_4^+ then reacts with NO_3^- to form NH_4NO_3. The $k < 1$ signifies the observed NH_4^+ concentration is higher than the NH_4^+ concentration predicted based on the complete neutralisation assumption,and NH_4^+ remains in excess after fully neutralising SO_4^{2-} and NO_3^-. In practice, the observed excess NH_4^+ may interact with other anions, such as Cl^- from biomass burning, potentially forming NH_4Cl. This demonstrates that NH_3 is sufficiently abundant in the Guanzhong Plain to fully neutralize the major inorganic acids. This provides direct chemical evidence explaining the elevated aerosol pH levels in the ammonia-rich Guanzhong Plain and establishes a foundation for the subsequent analysis of the buffering contribution of NH_x to aerosol acidity.

12. Lines 334-343: This reads like background information and could be shortened.

Response: Thank you for your suggestion. We have made appropriate adjustments to the text accordingly at lines 374-377.

Lines 374-377:

As a crucial precursor of secondary particulate matter, NH_3 influences aerosol acidity through the multiphase buffering of its NH_3/NH_4^+ conjugate pair (Liu et al., 2019; Saraswati et al., 2019; Zheng et al., 2020). This buffering effect is especially pronounced in the ammonia-rich Guanzhong Plain (Zhang et al., 2021; Zheng et al., 2023).

13. Lines 346-350: What is meant by “unstable outcome”?

Response: Thank you for the question. "Unstable outcome" refers to the fact that directly regressing NH_3 against meteorological and chemical factors leads to unstable predictions across different seasons, because this approach neglects the gas-particle equilibrium between NH_3 and NH_4^+. In contrast, our method first estimates the robust equilibrium parameter NHR and then back-calculates the NH_3 concentration, thereby obtaining more stable results. We have revised the text to make this clearer.

Lines 380-386:

In this study, we adapted the methodology of Wei et al. (2023) by replacing the prediction target from NH_3 to the thermodynamic state parameter NHR, and estimated the NHR using multiple linear regression analysis based on our previous short-term scale datasets (Wu et al., 2020). This is because the direct estimation of NH_3 is prone to interference from meteorological factors and the gas-particle distribution of acidic precursors, resulting in unstable outcomes in ammonia estimation.

14. Lines 422 What are "acidic products"

Response: We apologize for the unclear term. "Acidic products" refers to the strong acids generated from the aqueous-phase or heterogeneous oxidation of SO_2 and NO_x in aerosol liquid water, specifically H_2SO_4 and HNO_3. The accumulation of these acids directly contributes to the increase in H_{air}^+ concentration. To avoid ambiguity, We have revised the text to make this clearer.

Lines 480-482:

This increase further intensifies heterogeneous reactions and concentrates secondary acidic species such as H_2SO_4 and HNO_3, leading to a concurrent rise in H_{air}^+ concentration.

15. Lines 446-447 What does "acidification processes" refer to?

Response: We apologize for the unclear term. Here, "acidification processes" specifically refer to the chemical pathway by which sulfate (from heterogeneous oxidation of SO_2) generates sulfuric acid, which dissociates to release H^+, thereby increasing H_{air}^+ concentration and decreasing pH. We have revised the text to make this clearer and added a brief explanation at lines 502-505.

Lines 506-509:

The concurrent increase in ALWC and H_{air}^+ confirms the sulfate-driven acidification mechanism: SO_2 is converted to H_2SO_4 via heterogeneous oxidation, and the dissociation of H_2SO_4 releases H^+, leading to increase H_{air}^+ and decrease pH.

16. Lines 449-451: What is "heightened hydrogen ion activity"?

Response: We apologize for the unclear term. This expression denotes an increase in H^+ in the aerosol liquid phase, equivalent to enhanced acidity. The text has been revised to eliminate redundancy.

17. Lines 470-472: Why are low NH_x cases less accurate? NH_3 is from multi linear regression, while $NH_4^+$is from measurements.

Response: Thank you for pointing out the unclear description. We would like to clarify that in this study, the NH_3 concentration was not directly predicted by multiple linear regression. Instead, the NHR was first predicted using multiple linear regression, and then the NH_3 concentration was back-calculated based on the measured NH_4^+ concentration. When total NH_x (NH_3 + NH_4^+) is low, the measured NH_4^+ concentration approaches its detection limit, and the back-calculated NH_3 becomes highly sensitive to small measurement errors in NH_4^+. Therefore, the accuracy of the estimated NH_3 decreases when NH_x is below 3 μg m^{-3}.

18. Lines 488-491 The discussion related to relative standard deviation is abrupt without any context. Lines 536-539: This seems like method description but is not clearly explained earlier.

Response: Thank for your reminder.We have revised the manuscript accordingly: a definition and calculation explanation of RSD have been added in the Section 2.5 (lines 247–256), and a brief indication has been added at lines 546–548.

Lines 247-256:

To quantitatively evaluate the influence of each factor on aerosol pH, two complementary approaches were utilized: the relative standard deviation (RSD) method and the ΔpH contribution decomposition method. The RSD, which is derived from the coefficient of variation of pH responses in sensitivity analysis (i.e., the ratio of standard deviation to mean), indicates the relative sensitivity of aerosol pH to typical fluctuations of a given factor; a higher RSD signifies a greater potential impact. However, the RSD method provides only a relative ranking and does not directly determine the absolute contribution of each factor to the observed pH. Consequently, this study emphasizes the quantitative analysis of ΔpH contributions quantitative analysis.

Lines 550-552:

The relative standard deviation (RSD) can also be used to quantify the sensitivity of aerosol pH to a specific factor, with a higher RSD indicating a greater influence.

19. Lines 540-541: Concentration of what?

Response: We apologize for the unclear wording. The “decrease in concentrations” refers to the decrease in NH_3 concentration, as indicated by the preceding sentence where the higher winter NH_x is replaced by the lower spring value. We have revised the text to eliminate ambiguity.

20. Lines 541-543: This sentence is unclear. What does “weaken basic buffer capacity” mean? How does it disrupt equilibrium?

Response: Thank you for the question. We have revised the text to provide a clear explanation.at lines 611–618.

Lines 611-618:

On one hand, lower NH_3 weakens the buffering capacity of the NH_3/NH_4^+ conjugate pair, which is the dominant alkaline buffer system for aerosol pH (Zheng et al., 2020). Less NH_3 is thus available to neutralize H^+ from SO_2 and NO_x oxidation, making the system more vulnerable to acidification. On the other hand, reduced NH_3 disturbs the gas-particle equilibrium between particulate ammonium nitrate and gaseous ammonia along with nitric acid. According to Le Chatelier’s principle, a decrease in gas-phase NH_3 drives this equilibrium toward dissociation, promoting the decomposition of particulate NH_4NO_3 and releasing additional gaseous nitric acid (Guo et al., 2018).

21. Lines 549-550. How do RH and calcium play similar roles?

Response: We apologize for the ambiguous wording. The intended meaning was that calcium is an important driver in spring, and RH is another important driver in summer. We have revised the text to make this clearer.

Lines 622-626:

These results suggest that NVCs, represented by Ca^{2+}, are rich in alkaline mineral components and can enhance acid-neutralizing capacity, making them important drivers of aerosol pH variations in spring. In summer, RH alters aerosol acidity by affecting the deliquescence of hygroscopic particles, thereby serving as a key driver of aerosol pH variations.

22. Lines 552 What are the “synergistic effects”?

Response: We thank the reviewer for this comment. “synergistic effects” refers to the portion of total ΔpH that cannot be attributed to any single independent factor in our contribution decomposition analysis, represented by the residual contribution (ΔpH_{others}). This residual includes (1) interactions among factors, such as the combined effect of T and RH on pH differs from the sum of their individual contributions; (2) nonlinear responses in the thermodynamic model, and (3) the aggregate influence of other potential factors not individually considered. We have revised the text to make this clearer and added a brief explanation at lines 623-625.

Lines 627-629:

Moreover, the combined effects of factor interactions and model nonlinearity, represented by the residual contribution (ΔpH_{others}) are also significant, particularly in autumn, where they contributed 26.6% to aerosol pH variation.

23. Figure 1: Although a colorbar is provided, the current colormap is misleading. The brown color could be interpreted as high elevation.

Response: Thank for your reminder.We have revised Figure 1.

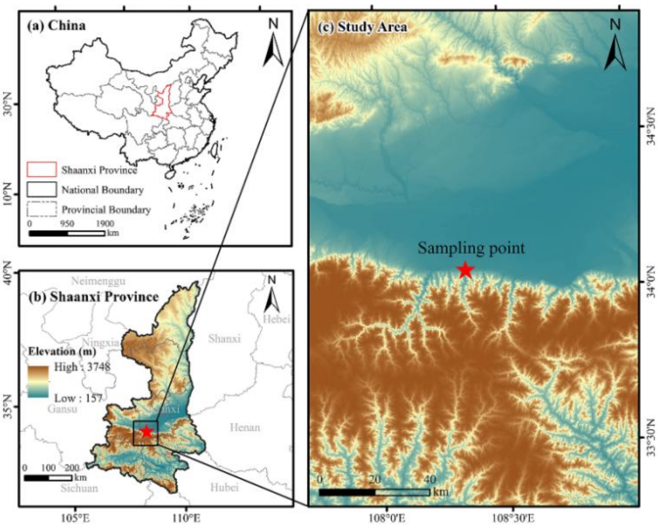

Fig.1 Locations of monitoring stations in Qinling

24. Figure 2: In the bottom panel, why are there negative $PM_{2.5}$ values? Why is the y-axis set from -200 to 300?

Response: The $PM_{2.5}$ concentrations are all positive. The negative range on the y- axis was originally used only to visually separate $PM_{2.5}$ curve from the stacked ion concentration plot below, making the trends more visible. In the revised manuscript, we have adjusted the y- axis to start from 0 to avoid any confusion.

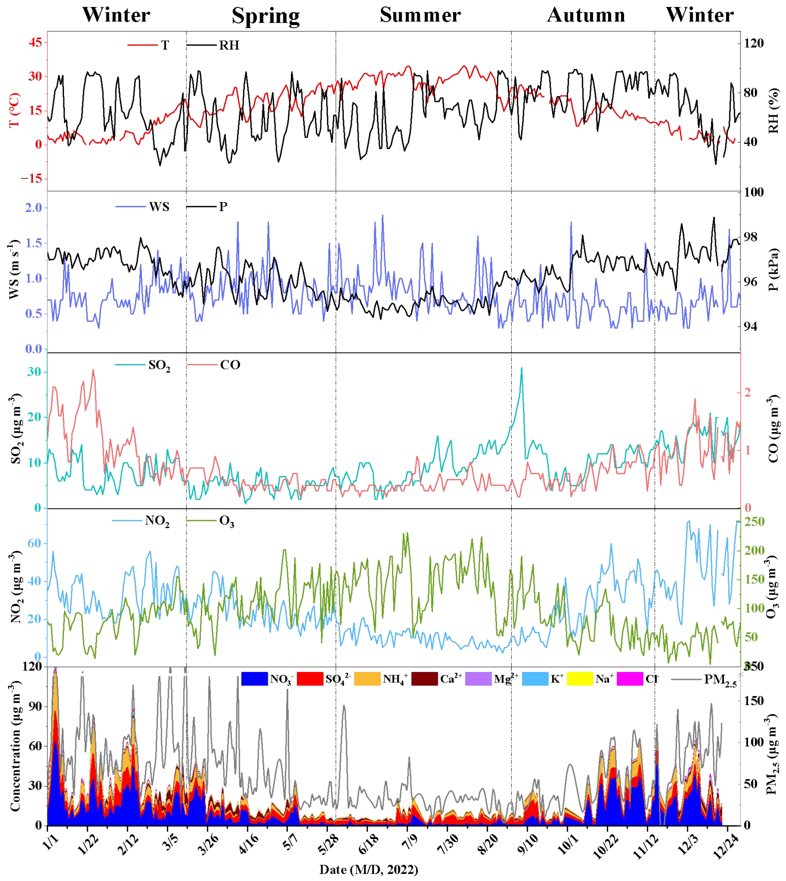

Fig. 2 The time series data for $PM_{2.5}$ mass concentrations, criteria air pollutants (SO_2, CO, NO_2, and O_3-8h), and meteorological parameters (T, RH, WS, and AP).

25. Figure 3: What do the four panels represent? Are they different seasons?

Response: Thank you for pointing this out. The four panels correspond to winter, spring, summer, and autumn. We have now labeled the panels directly in the figure and revised the caption to make the seasonal assignment explicit.

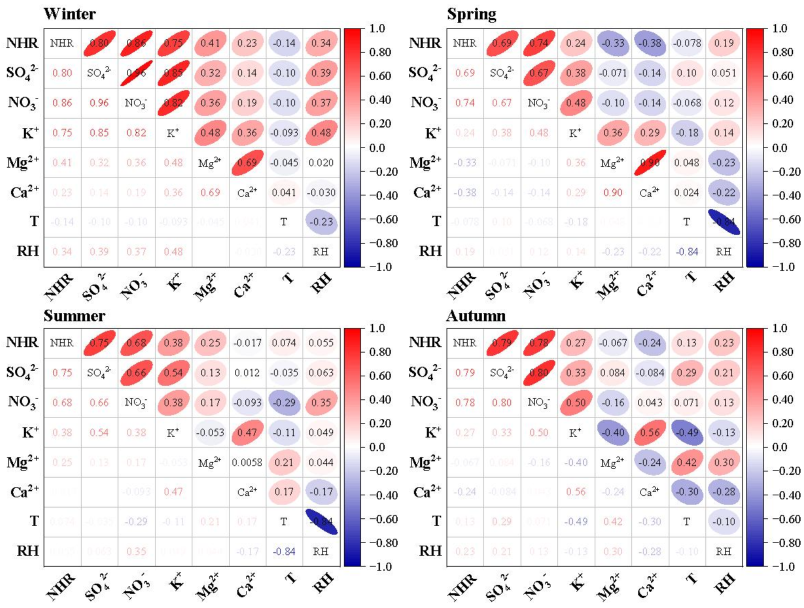

Fig. 3 Pearson correlation among various factors

26. Figure 5: Error bars should be added. It is also unclear why -200 to 200 is used as the ALWC range.

Response: We have added error bars to all series in Figure 5. We originally used a scale from -200 to 200 to separate the ALWC curve from the other variables for visual clarity, but we acknowledge that this made the interpretation ambiguous. In the revised figure, the y-axis range of ALWC has been changed accordingly to avoid any misleading negative scale.

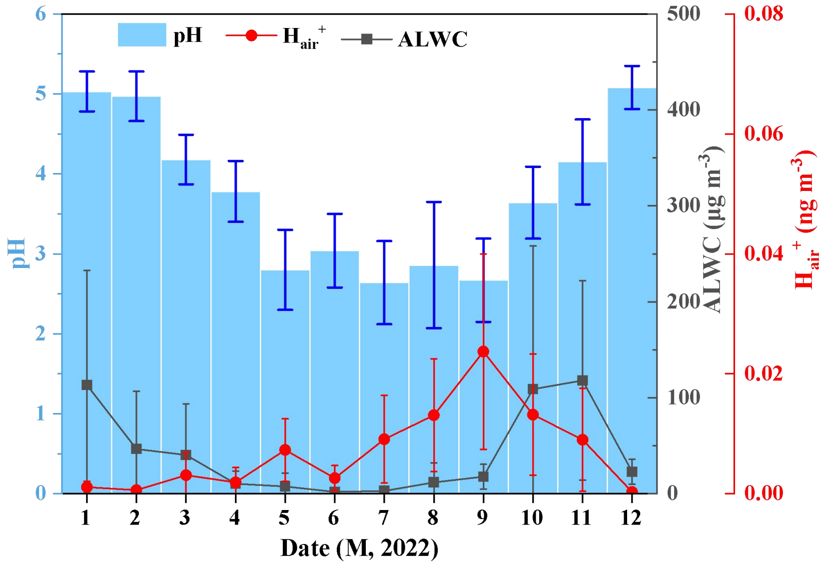

Fig.5 Monthly average aerosol pH, ALWC and H_{air}^+ changes

27. Figure 6: The line representing H^+ is thin and difficult to see.

Response: We have now adjusted the line thickness for H_{air}^+ to make it more visible.

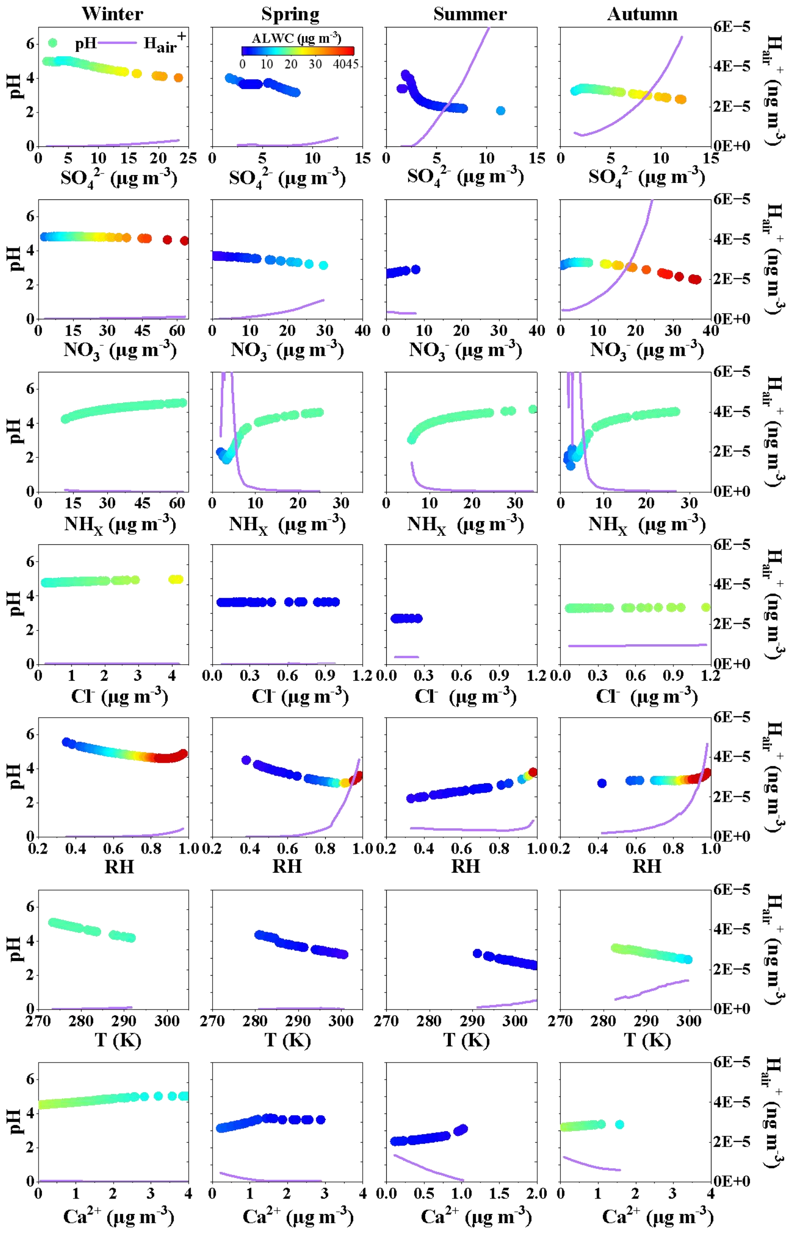

Fig. 6 Sensitivity analysis of influencing factors

28. Figure 7: The figure is difficult to interpret due to limited method description. What is included in "others"? The sum of delta pH contributions from different components does not seem to match the overall pH value, especially for Spring.

Response: We thank the reviewer for the comment. This issue has been addressed in detail in our response to the previous question regarding Section 2.5. Please see the third response above.

29. Table 1. The caption seems to be copied from Table 2. Besides, while most variables are from measurements, NHR and NH_3 seem to be derived from the multiple linear regression model. This should be clearly stated in the caption.

Response: Thank for your reminder. The caption of Table 1 has been corrected and now clearly indicates that NHR and NH_3 are calculated from the MLR model.

The caption: **Table 1 Concentrations of air pollutants, meteorological parameters, chemical components and ammonia-related species (NHR from multiple linear regression and NH_3 from back-calculates of NHR, NH_x = gas NH_3+NH_4^+) in different seasons.**

30. SI: It would be helpful to provide a separate reference list. For example, Wu et al., 2018 cited in table S4 does not match any citations in the main text.

Response: Thank for your suggestion. A separate reference list has been added at the end of the Supplementary information.

31. Table S5: There are only two polluted days in summer thus no calculation of standard deviation. This should be clearly noted in the caption. Does these two days show similar or clearly distinct results? This limited data availability should also be clearly noted in the related discussion.

Response: Thank for your reminder. We added the rigor of their analysis by using SPSS to perform an independent samples t-tests (Table S7) to compare the pH distributions between clean and polluted days across different seasons. We apologize for the miscalculation of concentrations and have recalculated the summer concentrations accordingly. We have revised in the caption, and added clearly noted in the text.

Lines 454-458:

Independent t-tests confirmed significantly higher pH on polluted days for winter, spring, and autumn ($p < 0.01$). In summer, only two polluted days were recorded, so the statistical results for summer (Table S7) should be interpreted with caution due to the very limited sample size a reliable t-test could not be performed.

Table S7 Average mass concentrations of NO_3, SO_4^{2-}, NH_4^+, $PM_{2.5}$, ALWC, H_{air}^+ and pH under clean and polluted conditions by season.The last column shows the pvalue from independent T-tests comparing pH between clean and polluted days for each season

Winter	**$PM_{2.5}$** （μg m^{-3}）	**SO_4^{2-}** （μg m^{-3}）	**NO_3^-** （μg m^{-3}）	**NH_4^+** （μg m^{-3}）	**RH** （%）	**T** （K）	**pH**	**ALWC** （μg m^{-3}）	**H_{air}^+** （μg m^{-3}）	T-test
Average	93.5 ± 40.2	7.3 ± 4.7	16.3 ± 11.9	7.3 ± 5.7	65 ± 21	278.2 ± 4.2	4.8 ± 0.5	80.4 ± 112.9	1.0E-06	$p < 0.01$
Clean	56.4 ± 10.5	5.9 ± 2.8	11.7 ± 4.9	5.6 ± 2.4	75 ± 16	278.2 ± 3.8	4.8 ± 0.4	63.3 ± 78.1	5.2E-07	
Polluted	114.9 ± 34.7	9.4 ± 5.4	23.8 ± 12.4	10.6 ± 6.1	71 ± 18	277.3 ± 4.1	5.0 ± 0.3	94.3 ± 130.6	1.0E-06	
Spring	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	61.4 ± 40.8	4.3 ± 1.7	6.4 ± 7.1	2.5 ± 2.6	62 ± 18	291.2 ± 5.8	3.6 ± 0.5	55.7 ± 132.2	6.4E-06	$p < 0.01$
Clean	42.2 ± 14.0	4.4 ± 1.6	6.8 ± 7.4	3.0 ± 2.7	70 ± 18	291.0 ± 5.8	3.3 ± 0.7	58.9 ± 140.5	6.8E-06	
Polluted	111.9 ± 35.1	7.0 ± 1.7	16.8 ± 8.1	6.0 ± 3.1	67 ± 21	288.1 ± 5.5	4.0 ± 0.3	32.5 ± 34.0	3.1E-06	
Summer	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	33.3 ± 13.7	3.5 ± 2.2	1.0 ± 1.2	1.1 ± 0.9	61 ± 16	302.0 ± 4.1	2.7 ± 0.7	10.0 ± 25.1	9.9E-06	$p > 0.01$
Clean	30.7 ± 8.3	4.2 ± 2.2	1.2 ± 1.4	1.5 ± 0.9	66 ± 16	302.2 ± 4.1	2.8 ± 0.7	10.2 ± 25.4	1.0E-05	
Polluted	92.2	4.0	1.1	1.3	57	302.2	2.7	3.8	8.9E-06	
Autumn	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	43.1 ± 25.1	4.4 ± 3.1	8.7 ± 10.8	3.8 ± 4.1	80 ± 13	290.3 ± 5.1	3.3 ± 0.7	76.2 ± 121.0	1.8E-05	$p < 0.01$
Clean	36.8 ± 15.3	4.4 ± 2.9	6.1 ± 6.3	3.1 ± 2.5	82 ± 13	290.6 ± 5.2	3.1 ± 0.7	61.9 ± 111.5	1.8E-05	
Polluted	90.9 ± 8.6	7.7 ± 1.0	29.7 ± 3.1	14 ± 1.3	86 ± 9	286.5 ± 1.3	3.9 ± 0.1	171.6 ± 149.5	1.7E-05	

*Only two polluted days in summer; so no SD calculated.

32. Figure S5. The figure shows delta ALWC, but the caption still refers to delta pH.

Response: Thank for your reminder. The Figure S4 caption has been corrected accordingly.

Fig. S5 The contribution of various influencing factors to the seasonal ALWC. The pie chart shows the relative contributions of various influencing factors to the seasonal ALWC (absolute values of ALWC was taken for pie chart).

Reference:

C. Fountoukis., and A. Nenes.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for $K^+ – Ca^{2+} – Mg^{2+} – NH_4^+ – Na^+ – SO_4^{2–} – NO_3^– – C^{l–} –H_2O$ aerosols. Atmos. Chem. Phys., 7(17), 4639–4659. https://doi.org/10.5194/acp-7-4639-2007, 2007.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern united states. J. Geophys. Res.: Atmos., 121(17), https://doi.org/10.1002/2016JD025311, 2016.

Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., and Weber, R. J.: Effectiveness of ammonia reduction on control of fine particle nitrate. Atmos. Chem. Phys., 18(16), 12241–12256, https://doi.org/10.5194/acp-18-12241-2018, 2018.

Liu, M., Huang, X., Song, Y., Tang, J., Cao, J., Zhang, X., Zhang, Q., Wang, S., Xu, T., Kang, L., Cai, X., Zhang, H., Yang, F., Wang, H., Yu, J. Z., Lau, A. K., He, L., Huang, X., Duan, L., Ding, A., Xue, L., Gao, J., Liu, B., and Zhu, T.: Ammonia emission control in China would mitigate haze pollution and nitrogen deposition, but worsen acid rain. Proc. Natl. Acad. Sci., 116(16), 7760–7765, https://doi.org/10.1073/pnas.1814880116, 2019.

Liu, P., Chen, H., Song, Y., Xue, C., Ye, C., Zhao, X., Zhang, C., Liu, J., and Mu, Y.:Atmospheric ammonia in the rural North China Plain during wintertime: Variations, sources, and implications for HONO heterogeneous formation. Sci. Total Environ., 861(25), 160768, https://doi.org/10.1016/j.scitotenv.2022.160768, 2023.

Saraswati, Sharma, S., Saxena, M., and Mandal, T.: Characteristics of gaseous and particulate ammonia and their role in the formation of secondary inorganic particulate matter at Delhi, India. Atmos. Res., 218, 34–49, https://doi.org/10.1016/j.atmosres.2018.11.010, 2019.

Shen, M., Li, J., Liu, Y., Dai, W., Wang, G., Qi, W., Chen, Y., Guo, X., Zhang, Y., Li, L., Cao, Y., Feng, Q., Su, H., and Cao, J.: Comparison of acidity and chemical composition of summertime cloud water and aerosol at an alpine site in northwest China: Implications for the neutral property of clouds in the free troposphere. Sci. Total Environ., 925, 171775, https://doi.org/10.1016/j.scitotenv.2024.171775, 2024.

Song, S., Nenes, A., Gao, M., Zhang, Y., Liu, P., Shao, J., Ye, D., Xu, W., Lei, L., Sun, Y., Liu, B., Wang, S. and McElroy, M. Thermodynamic Modeling Suggests Declines in Water Uptake and Acidity of Inorganic Aerosols in Beijing Winter Haze Events during 2014/2015−2018/2019. Environ. Sci.

Technol. Lett., 6(12), 752-760, https://doi.org/10.1021/acs.estlett.9b00621, 2019.

Wang, G., Zhang, R., Gomez, M., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P., Duce, R., Kolb, C., and Molina, M.: Persistent sulfate formation from London fog to Chinese haze. Proc. Natl. Acad. Sci., 113(48), 13630–13635, https://doi.org/10.1073/pnas.1616540113, 2016.

Wei, Y., Wang, S., Jiang, N., Zhang, R., and Hao, Q.: Comparative multi-model study of $PM_{2.5}$ acidity trend changes in ammonia-rich regions in winter: based on a new ammonia concentration assessment method. J. Hazard. Mater., 458, 131970, https://doi.org/10.1016/j.jhazmat.2023.131970, 2023.

Wu, C., Wang, G., Li, J., Li, J.J., Cao, C., Ge, S., Xie, Y., Chen, J., Li, X., Xue, G., Wang, X., Zhao, Z., and Cao, F.: The characteristics of atmospheric brown carbon in Xi'an, inland China: sources, size distributions and optical properties. Atmos. Chem. Phys., 20(4), 2017–2030, https://doi.org/10.5194/acp-20-2017-2020,2020.

Ye, X., Tao, Y., Liu, Y., Wang, R., Li, Q., Yang, X., and Chen, J.: Size-fractionated water-soluble ions during autumn and winter: Insights into volatile ammonium formation mechanisms in Shanghai, a megacity of China. Atmos. Environ.: X., 2, 100011, https://doi.org/10.1016/j.aeaoa.2019.100011, 2019.

Zhang, T., Shen, Z., Su, H., Liu, S., Zhou, J., Zhao, Z., Wang, Q., Prévôt, A. S. H., and Cao, J. J.: Effects of aerosol water content on the formation of secondary inorganic aerosol during a winter heavy $PM_{2.5}$ pollution episode in Xi'an, China. Atmos. Environ., 252, 118304, https://doi.org/10.1016/j.atmosenv.2021.118304, 2021.

Zheng, G., Su, H., Wang, S., Andreae, M., Pöschl, U., and Cheng, Y.: Multiphase buffer theory explains contrasts in atmospheric aerosol acidity. Science, 369(6509), 1374–1377, https://doi.org/10.1126/science.aba3719, 2020.

Zheng, G., Su, H., and Cheng, Y.: Role of carbon dioxide, ammonia, and organic acids in buffering atmospheric acidity: The distinct contribution in clouds and aerosols. Environ. Sci. Technol., 57(34), 12571–12582, https://doi.org/10.1021/acs.est.2c09851, 2023.

Reviewer #1:

This study conducted a year-long characteristics of water-soluble inorganic ions in $PM_{2.5}$ in the semi-arid Guanzhong region of China, and quantitatively analyzed its acidity and driving factors. The research is valuable for understanding regional aerosol chemistry, which offers a new perspective for developing $PM_{2.5}$ control strategies in the semi-arid and ammonia-rich region. While the manuscript is fundamentally sound, certain aspects require further clarification and refinement.

Response: We thank you very much for your recognition of this manuscript. We have responded to the reviewers' comment accordingly.

1. The quantitative attribution of pH drivers across seasons, particularly the identification of Ca^{2+} as a spring-specific driver and the non-linear RH effect, provides novel insights. However, the authors should more explicitly articulate how these findings advance beyond existing studies in the introduction.

Response: Thank you for this comment. We have added relevant content in the revised manuscript.

Lines 98-104:

However, existing studies have largely focused on compositional analyses in specific cities, resulting in both a lack of year-round quantitative attribution of pH drivers in semi-arid regions, insufficient comparison of chemical versus meteorological contributions, and neglect of alkaline dust, as well as an overall insufficient understanding of the trends in aerosol pH values and their primary driving factors and relative contributions.

2. Further optimization of sentence structure are needed. For instance, Line 50-54, "High aerosol acidity levels have been linked to increased risks of respiratory illnesses and specific cancers. These acidity-driven atmospheric processes collectively contribute to the generation of intricate air pollution, the deposition of pollutants through dry and wet mechanisms, and their overall effects on human health and the climate system (Mao et al., 2009; Pye et al., 2020)." The connection between the top and bottom sentences is not smooth.

Response: Thank you for this comment. We have revised the text to improve the logical flow.

Lines 51-54:

High aerosol acidity levels not only increase the risks of respiratory illnesses and specific cancers but also drive atmospheric processes that lead to complex air pollution, dry and wet deposition of pollutants, and ultimate impacts on human health and the climate system (Mao et al., 2009; Pye et al., 2020).

3. Lines 96-99: This section states that understanding of pH drivers "remains insufficient." This phrasing is vague. The authors should more precisely articulate what is missing: (1) year-round quantitative attribution in semi-arid regions? (2) comparison of chemical vs. meteorological controls? (3) integration of dust effects? Sharpening this gap will strengthen the paper's motivation.

Response: Thank you for this comment. We have revised the vague statement “understanding remains insufficient” in the original text to explicitly identify the missing aspects: quantitative attribution of annual driving factors in semi-arid regions, comparison of the contributions between chemical and meteorological factors, and integration of the influence of alkaline dust on aerosol acidity.(Lines 98-104)

4. Lines 124-130: The final paragraph of the Introduction reads as a summary of methods rather than a statement of scientific objectives. While it is useful to know what measurements and models were employed, the reader is left wondering what specific scientific questions this study aims to answer. Reformulate this paragraph to pose clear, testable research questions that emerge from the knowledge gaps identified earlier or clarify research purpose.

Response: Thank you for this comment. We have revised to clarify the study aims.

Lines 129-133:

The primary objectives of this study are: (1) to characterize the seasonal variation of aerosol acidity in the Guanzhong Plain and to examine its evolution under varying pollution levels; and (2) to identify the key driving factors influencing aerosol pH in each season and to quantify their relative contributions across different seasons.

5. Lines 101-118: This section describes the Guanzhong Plain's characteristics, but the connection to aerosol acidity could be stronger. The authors should explicitly hypothesize how each feature (e.g., semi-enclosed basin, ammonia emissions, dust transport, seasonal climate) might influence pH, setting up testable expectations for the results section.

Response: We thank the reviewer for this constructive suggestion. In the revised manuscript, we have strengthened the connection between the Guanzhong Plain’s characteristics and aerosol acidity by explicitly hypothesizing how each feature influences pH.

Lines 109-118:

The unique semi-enclosed topography, with the Loess Plateau to the north and the Qinling Mountains to the south, restricts pollutant dispersion, leading to the accumulation of various pollutants and enabling complex chemical reactions (Huang et al., 2014; Liu et al., 2025; Shen et al., 2024). This confinement likely amplifies the influence of local emissions on aerosol pH due to the accumulation of both acidic and alkaline species. The area is known for its intensive agricultural practices, contributing to high levels of ammonia emissions that influence aerosol acid-base equilibrium. The ammonia-rich condition likely neutralizes acidic components, thereby shifting aerosol pH toward a weaker acidic range (Liu et al., 2019).

6. Lines 276-278: The authors state that SNAs dominate WSIIs, but the statement remains purely descriptive, not establish a link to pH analysis later. Please state what does it mean to be SNA dominant and what is the effect on acidity.

Response: Thank you for this comment.We have revised lines 314-317 to link the SNA-dominated composition to aerosol pH.

Lines 316-319:

This SNA-dominated composition suggests that aerosol pH is regulated by the neutralization balance between NH_4^+ and the acidic anions SO_4^{2-} and NO_3^-, thereby laying a chemical foundation for the analysis of seasonal driving factors.

7. Section 3.2 presents the MLR model development in detail. However, the actual NH_3 concentrations estimated from this model (shown in Table 1) are not discussed in the text. The authors should briefly comment on the seasonal NH_3 patterns and their consistency with expectations.

Response: Thank you for this comment. In the revised manuscript, we have added a discussion of the actual NH_3 concentrations estimated.

Lines 418-428:

Furthermore, the NH_3 concentrations derived from NHR at our site remain below 60 μg m^{-3}, well within the range of the training dataset from urban site. However, the seasonal NH_3 pattern at our site (2022: winter > summer > spring > autumn) differs from that in the training dataset (2016: summer > spring > autumn > winter). This discrepancy can be attributed to the significant reduction in SO_2 emissions resulting from air pollution control. In 2016, the high concentration of SO_2 emitted from coal combustion reacts rapidly with NH_3 to form $(NH_4)_2SO_4$, and this process consumes large amounts of gaseous NH_3 in winter (Wang et al., 2016; Liu et al., 2023). Due to interannual NH_3 variability, we employed the thermodynamically stable NHR for model training and validation, back-calculated NH_3 from the estimated NHR and measured NH_4^+, and then used these values in ISORROPIA-II to simulate aerosol pH.

8. Lines 380-383: The authors report mean ALWC concentrations with large standard deviations (e.g., winter: 80.4 ± 112.9 μg m^{-3}; spring: 55.7 ± 132.2 μg m^{-3}). The fact that the standard deviation exceeds the mean in multiple seasons. Please discuss the causes of the high standard deviation of ALWC and its potential impacts on aerosol pH.

Response: Thank you for this comment. The large standard deviations reflect the strong dependence of ALWC on RH and the nonlinear hygroscopic growth of particles. We have specifically discussed this issue in the following sections of the manuscript. Please see at lines 559-595 in the revised manuscript.

9. Figure 5 shows monthly means without variability indicators. Please add error bars to convey the spread within each month.

Response: Thank you for this comment. We have added error bars to all series in Figure 5.

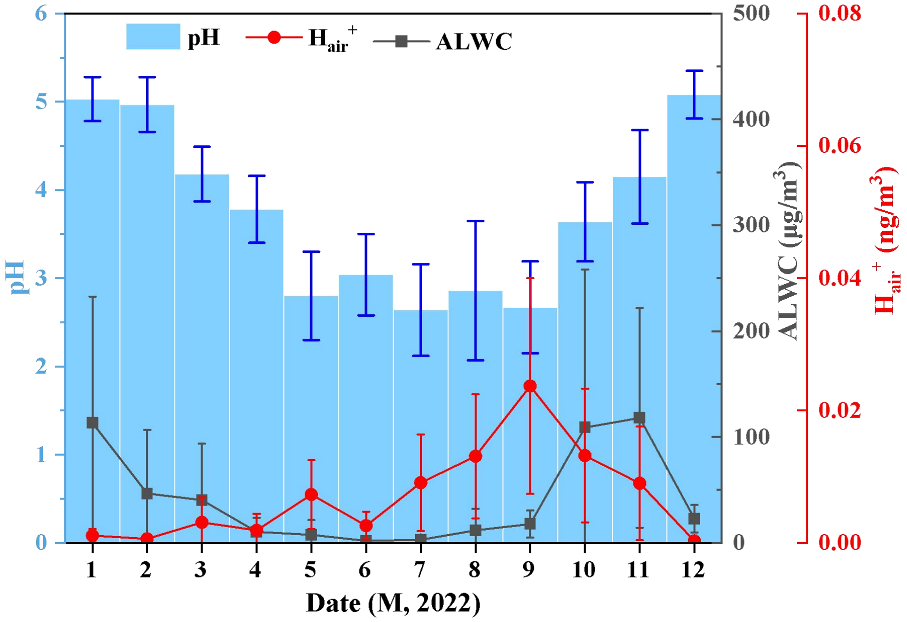

Fig.5 Monthly average aerosol pH, ALWC and H_{air}^+ changes

10. Section 3.3: The manuscript currently presents valuable data on aerosol pH under clean versus polluted conditions, but the comparison is limited to statistical summaries. To more intuitively demonstrate how aerosol chemical composition and acidity evolve with increasing pollution, I recommend adding a new figure showing the percentage change in aerosol pH and major WSIIs across different $PM_{2.5}$ concentration bins.

Response: Thank you for this suggestion. In the revised manuscript, we have added a new figure (Fig. S4) showing the percentage changes in aerosol pH and major WSIIs across different $PM_{2.5}$ concentration bins. This figure has been cited in the revised text (Section 3.3). The corresponding description has been updated accordingly.

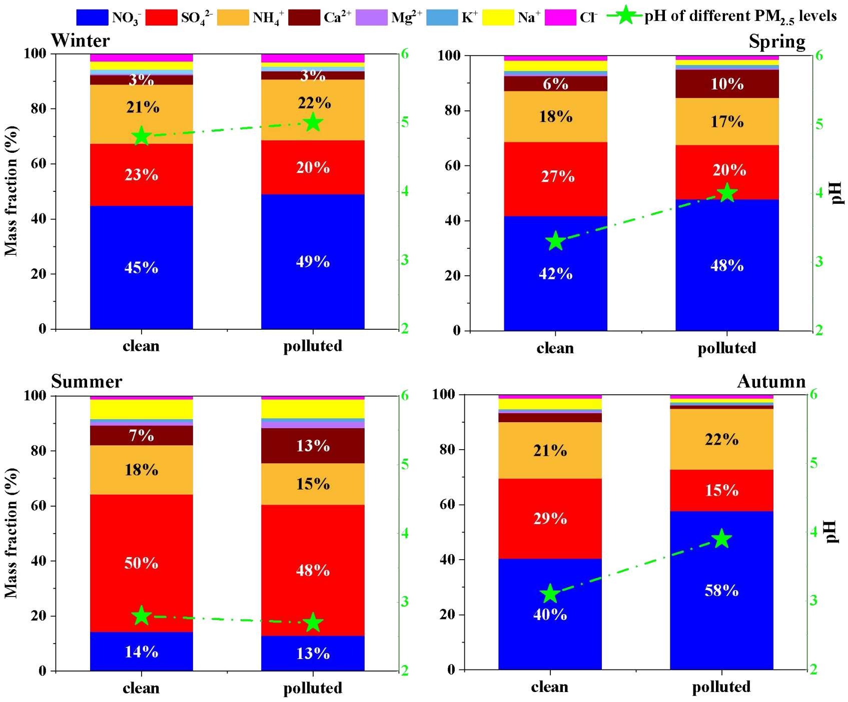

Fig. S4 Percentage change in aerosol pH and major WSIIs across different $PM_{2.5}$ concentration bins. The asterisk represents the pH

11. Lines 397-399: The finding that pH shifts from 2-5 on clean days to 3-6 on polluted days is important. The authors could enhance the rigor of their analysis by employing statistical tests (e.g., t-tests) to compare the pH distributions between clean and polluted days across different seasons.

Response: Thank you for this comment. We added the rigor of their analysis by employing statistical t-tests (Table S7) to compare the pH distributions between clean and polluted days across different seasons. We have revised in the caption, and added clearly noted in the text (lines 448-454). Furthermore, we identified an error in the calculation of the average pH and have corrected it

Lines 452-458:

Under clean conditions, aerosol pH ranged from 2 to 5, whereas under polluted and heavily polluted conditions, it was primarily concentrated between 3 and 6. Independent t-tests confirmed significantly higher pH on polluted days for winter, spring, and autumn ($p < 0.01$). In summer, only two polluted days were recorded, so the statistical results for summer (Table S7) should be interpreted with caution due to the very limited sample size a reliable t-test could not be performed.

Table S7 Average mass concentrations of NO_3, SO_4^{2-}, NH_4^+, $PM_{2.5}$, ALWC, H_{air}^+ and pH under clean and polluted conditions by season.The last column shows the pvalue from independent T-tests comparing pH between clean and polluted days for each season

Winter	**$PM_{2.5}$** （μg m^{-3}）	**SO_4^{2-}** （μg m^{-3}）	**NO_3^-** （μg m^{-3}）	**NH_4^+** （μg m^{-3}）	**RH** （%）	**T** （K）	**pH**	**ALWC** （μg m^{-3}）	**H_{air}^+** （μg m^{-3}）	T-test
Average	93.5 ± 40.2	7.3 ± 4.7	16.3 ± 11.9	7.3 ± 5.7	65 ± 21	278.2 ± 4.2	4.8 ± 0.5	80.4 ± 112.9	1.0E-06	$p < 0.01$
Clean	56.4 ± 10.5	5.9 ± 2.8	11.7 ± 4.9	5.6 ± 2.4	75 ± 16	278.2 ± 3.8	4.8 ± 0.4	63.3 ± 78.1	5.2E-07	
Polluted	114.9 ± 34.7	9.4 ± 5.4	23.8 ± 12.4	10.6 ± 6.1	71 ± 18	277.3 ± 4.1	5.0 ± 0.3	94.3 ± 130.6	1.0E-06	
Spring	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	61.4 ± 40.8	4.3 ± 1.7	6.4 ± 7.1	2.5 ± 2.6	62 ± 18	291.2 ± 5.8	3.6 ± 0.5	55.7 ± 132.2	6.4E-06	$p < 0.01$
Clean	42.2 ± 14.0	4.4 ± 1.6	6.8 ± 7.4	3.0 ± 2.7	70 ± 18	291.0 ± 5.8	3.3 ± 0.7	58.9 ± 140.5	6.8E-06	
Polluted	111.9 ± 35.1	7.0 ± 1.7	16.8 ± 8.1	6.0 ± 3.1	67 ± 21	288.1 ± 5.5	4.0 ± 0.3	32.5 ± 34.0	3.1E-06	
Summer	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	33.3 ± 13.7	3.5 ± 2.2	1.0 ± 1.2	1.1 ± 0.9	61 ± 16	302.0 ± 4.1	2.7 ± 0.7	10.0 ± 25.1	9.9E-06	$p > 0.01$
Clean	30.7 ± 8.3	4.2 ± 2.2	1.2 ± 1.4	1.5 ± 0.9	66 ± 16	302.2 ± 4.1	2.8 ± 0.7	10.2 ± 25.4	1.0E-05	
Polluted	92.2	4.0	1.1	1.3	57	302.2	2.7	3.8	8.9E-06	
Autumn	**$PM_{2.5}$**	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**RH**	**T**	**pH**	**ALWC**	**H_{air}^+**	T-test
Average	43.1 ± 25.1	4.4 ± 3.1	8.7 ± 10.8	3.8 ± 4.1	80 ± 13	290.3 ± 5.1	3.3 ± 0.7	76.2 ± 121.0	1.8E-05	$p < 0.01$
Clean	36.8 ± 15.3	4.4 ± 2.9	6.1 ± 6.3	3.1 ± 2.5	82 ± 13	290.6 ± 5.2	3.1 ± 0.7	61.9 ± 111.5	1.8E-05	
Polluted	90.9 ± 8.6	7.7 ± 1.0	29.7 ± 3.1	14 ± 1.3	86 ± 9	286.5 ± 1.3	3.9 ± 0.1	171.6 ± 149.5	1.7E-05	

*Only two polluted days in summer; so no SD calculated.

12. Lines 499-503:The inflection point at 60-85% RH and the proposed mechanism involving deliquescence of NH_4NO_3 (DRH 62%) and $(NH_4)_2SO_4$ (DRH 80%) is compelling. However, the manuscript does not address an important follow-up question: Why does the inflection point vary by season? The discussion of this seasonal variation would strengthen the mechanistic interpretation.

Response: Thank you for this comment. We have added a brief discussion immediately after the description of the deliquescence mechanism.

Lines 568-573:

Notably, the inflection point exhibits clear seasonal variations, which can be attributed to seasonal shifts in aerosol chemical composition (Table 1). Notably, the inflection point varies seasonally maybe due to the varying proportions of NO_3^- and SO_4^{2-} in SNA: high NO_3^- in autumn and winter shifts the inflection point toward lower RH (~62%), while the higher SO_4^{2-} contribution in spring shifts it toward higher RH (~80%).

13. Lines 549-551: Although pointing out the importance of NVCs in spring, do not explain their mechanism of action. The authors could integrate the discussion from Section 3.4 on Ca^{2+} to briefly elaborate on this point.

Response: Thank you for this comment. We have integrated the relevant discussion from Ca^{2+} and RH of Section 3.4 to make these points clearer.

Lines 622-626:

These results suggest that NVCs, represented by Ca^{2+}, are rich in alkaline mineral components and can enhance acid-neutralizing capacity, making them important drivers of aerosol pH variations in spring. In summer, RH alters aerosol acidity by affecting the deliquescence of hygroscopic particles, thereby serving as a key driver of aerosol pH variations.

14. Lines 556-565: The comparison with coastal cities requires additional explanation regarding the reasons for this disparity.

Response: We thank the reviewer for this suggestion. In the revised manuscript, we have added a brief explanation for the regional disparity between inland semi-arid and coastal southeastern sites.

Lines 637-643:

This difference arises from regional characteristics. In coastal areas, meteorological factors, including RH and sea-land breezes, exhibit significant variability, while the chemical composition remains relatively stable, rendering meteorological conditions predominant. Conversely, in inland semi-arid regions, chemical components such as NH_x and dust-derived Ca^{2+} exhibit pronounced seasonal fluctuations, resulting in a greater dominance of chemical factors (Jia et al., 2020; Xu et al., 2025).

15. The unit format in the full text should be unified. For instance, in Figure 6, the unit of μg/m^3 is unified as μg m^{-3}

Response: We thank the reviewer for this suggestion. The revisions have been made in figures.

16. Further refinement of language and optimization of sentence structure are needed:

1）The manuscript uses multiple terms interchangeably: "driving factors," "drivers," "influencing factors," "key factors." Please choose one primary term and use consistently throughout.

2）Lines 103-104: “Guanzhong Plain is a vital economic and agricultural center in northwestern China, the rapid industrial...”, write "where rapid" instead of "the rapid".

3）Line 106: “The mechanisms of air pollution formation and its driving factors it in the region...”, delete “it”.

4）Line 268: Write "decreased" instead of "decreasing

5）Line 282: “This might be due to driven by...”, delete “due to”.

6）Line 527: Write "enhance" instead of "enhancing".

7）Line 210: The term "multiple linear regression" appears here for the first time in the manuscript, and the abbreviation (MLR) could be added.

8）Line 368: Write "MLR" instead of "MRL".

Response: Thank you for these suggestions. We have choosen “driving factors” throughout the manuscript. Besides, we have carefully revised the corresponding sections of the manuscript to improve language clarity and optimize sentence structure.

Reference:

Cao, Y., Feng, Q., Su, H., and Cao, J.: Comparison of acidity and chemical composition of summertime cloud water and aerosol at an alpine site in northwest China: Implications for the neutral property of clouds in the free troposphere. Sci. Total Environ., 925, 171775, https://doi.org/10.1016/j.scitotenv.2024.171775, 2024.

Huang, R., Zhang, Y., Bozzetti, C., Ho, K., Cao, J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prévôt, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China. Nature, 514(7521), 218–222, https://doi.org/10.1038/nature13774, 2014.

Jia, S., Chen, W., Zhang, Q., Krishnan, P., Mao, J., Zhong, B., Huang, M., Fan, Q., Zhang, J., Chang, M., Yang, L., and Wang, X.: A quantitative analysis of the driving factors affecting seasonal variation of aerosol pH in Guangzhou, China. Sci. Total Environ., 725, 138228, https://doi.org/10.1016/j.scitotenv.2020.138228, 2020.

Liu, Y., Guo, X., Zhang, Y., Cao, Y., Jiang, Y., Qi, W., Shen, M., Li, L., Wang, Q., Dai, W., and Li, J.: Chemical characteristics of wintertime $PM_{2.5}$ in background region of northwest China during urban emission reduction. Iscience, 28(10), 113528, https://doi.org/10.1016/j.isci.2025.113528, 2025.

Liu, P., Chen, H., Song, Y., Xue, C., Ye, C., Zhao, X., Zhang, C., Liu, J., and Mu, Y.:Atmospheric ammonia in the rural North China Plain during wintertime: Variations, sources, and implications for HONO heterogeneous formation. Sci. Total Environ., 861(25), 160768, https://doi.org/10.1016/j.scitotenv.2022.160768, 2023.

Mao, I., Lin, C, Lin, C., Chen, Y., Sung, F., and Chen, M.: Exposure of acid aerosol for schoolchildren in metropolitan Taipei. Atmos. Environ., 43(35), 5622–5629, https://doi.org/10.1016/j.atmosenv.2009.07.054, 2009.

Pye, H., Nenes, A., Alexander, B., Ault, A., Barth, M., Clegg, S., Collett Jr., J. L., Fahey, K., Hennigan, C., Herrmann, H., Kanakidou, M., Kelly, J., Ku, I., McNeill, V., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J., Wang, T., Weber, R., Xing, J., Zaveri, R., and Zuend, A.: The acidity of atmospheric particles and clouds. Atmos. Chem. Phys., 20(8), 4809–4888, https://doi.org/10.5194/acp-20-4809-2020, 2020.

Shen, M., Li, J., Liu, Y., Dai, W., Wang, G., Qi, W., Chen, Y., Guo, X., Zhang, Y., Li, L., Liu, M., Huang, X., Song, Y., Tang, J., Cao, J., Zhang, X., Zhang, Q., Wang, S., Xu, T., Kang, L., Cai, X., Zhang, H., Yang, F., Wang, H., Yu, J. Z., Lau, A. K., He, L., Huang, X., Duan, L., Ding, A., Xue, L., Gao, J., Liu, B., and Zhu, T.: Ammonia emission control in China would mitigate haze pollution and nitrogen deposition, but worsen acid rain. Proc. Natl. Acad. Sci., 116(16), 7760–7765, https://doi.org/10.1073/pnas.1814880116, 2019.

Wang, G., Zhang, R., Gomez, M., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P., Duce, R., Kolb, C., and Molina, M.: Persistent sulfate formation from London fog to Chinese haze. Proc. Natl. Acad. Sci., 113(48), 13630–13635, https://doi.org/10.1073/pnas.1616540113, 2016.

Xu, K., Yin, L., Chen, Q., Liao, D., Ji, X., Zhang, K., Wu, Y., Xu, L., Li, M., Fan, X., Zhang, F., Huang, Z., Chen, J., and Hong, Y.: Quantitative analysis of influencing factors to aerosol pH and its responses to $PM_{2.5}$ and O_3 pollution in a coastal city. J. Environ. Sci., 151, 284–297, https://doi.org/10.1016/j.jes.2024.03.044, 2025.