No.: egusphere-2024-2869

Title: Measurement report: Crustal materials play an increasing role in elevating particle pH: Insights from 12-year records in a typical inland city of China.

Reviewer #1:

General Comments:

In this article, the authors analyze 12 years of field observation data from Zhengzhou, China, to investigate trends in aerosol composition concentrations and its acidity. This approach is well-aligned with the scope and objectives of the "Measurement Report", making the study highly relevant. However, there are contentious aspects in the discussion and final conclusions of this article. Specifically, whether crustal materials play a dominant role in driving the changes in aerosol acidity remains uncertain. This issue affects several parts of the article, including its main argument and even the title. I believe the authors are capable of making substantial revisions to the article.

Thank you for your careful reading of our paper and valuable comments and suggestions. We believe that we have adequately addressed your comments. To facilitate your review, we used yellow highlights for your comments, green highlights for Reviewer #2, and red color indicating our own corrections in the manuscript.

Major issues:

1. Lines 15-17: Compared to the reduction of ammonia emissions, the reductions in acidic precursors such as SO_2 and NO_x have been more significant, leading to an overall increase in atmospheric acidity (including aerosols, clouds, and precipitation). Studying the trends in aerosol acidity is highly meaningful, but it is essential to consider the combined impact of the reduction in both acidic and basic precursors.

Response: Thanks for your suggestion. This sentence has been modified to: "Particle acidity serves as a key determinant in atmospheric chemical processes. Emerging concerns regarding aerosol acidity trends have been highlighted amid China's sustained initiatives to mitigate emissions of both acidic and alkaline precursors."

2. Lines 19-21: The 12-year observation period and the corresponding years for the PM concentration results do not align. While I understand that the authors began observations in 2011, the abstract should be rephrased to ensure clarity and consistency in the presentation of the time frame.

Response: Sorry for the misunderstanding. This sentence has been modified to: "12-year observational data in Zhengzhou reveal that the annual average $PM_{2.5}$ concentration decreased from 162 ± 81 μg/m^3 in 2011 to 60 ± 41 μg/m^3 in 2022, with the largest reduction in sulfate (73%). Correspondingly, the annual particle pH increased by 0.10 units from 2011 to 2019."

3. Lines 28-29: According to mainstream forecasts regarding the need for further PM reduction under China's carbon peaking and carbon neutrality policy, future emission reduction strategies will primarily focus on acidic precursors. The expression here needs to be more precise and cautious.

Response: Thank you for your comment. This sentence has been modified to: "Therefore, the long-term evolution of particle acidity in North China will require comprehensive consideration of synergistic effects involving acidic precursors, ammonia, and crustal materials."

4. Lines 63-65: There is a lack of logical flow from the previous discussion of acidity changes to the conclusion/summary in this sentence. Additionally, aerosol acidity is unlikely to be neutral or even approach neutrality by nature in general.

Response: Sorry for the misunderstanding. This sentence has been modified to: "The atmospheric behavior of ammonium, governed by gas-particle partitioning processes involving ammonia (NH_3) as the predominant alkaline gas, demonstrates notable stability in concentration levels, with observational records showing less than 5% interannual variation in NH_3 column densities over North China during 2015–2019 (Dong et al., 2023). Under such conditions, the dominant inorganic aerosol component transitions from ammonium sulfate to ammonium nitrate. This compositional shift enhances atmospheric particulate hygroscopicity due to ammonium nitrate's superior

water uptake capability, ultimately elevating particle pH levels through aqueous-phase dilution mechanisms (Pinder et al., 2007, 2008; Heald et al., 2012; Weber et al., 2016).”

5. Lines 66-67: This may not be entirely accurate. The relative contribution of sulfate and nitrate does not directly determine aerosol acidity. The authors need to identify the true driving factors behind the pH trend. In my opinion, the main drivers are the NH_3/NH_4^+ multiphase buffering, ALWC, and non-volatile cations, rather than other components or temperature. This is because, over the long term, the impact of temperature variations on pH is minimal within the same season.

Response: Thank you for your comment. The observed transition in inorganic aerosol composition from ammonium sulfate to ammonium nitrate fundamentally alters aerosol hygroscopicity, as evidenced by deliquescence relative humidity differentials: NH_4NO_3 exhibits DRH = 61% versus 80% for $(NH_4)_2SO_4$ at 298K (ISORROPIA II model). This phase shift enhances water uptake by 38–72% (Wexler and Seinfeld, 1991). The consequent dilution effect on hydrogen ion concentration ($[H^+]$) leads to pH increases.

Therefore, this sentence has been modified to: “This compositional shift enhances atmospheric particulate hygroscopicity due to ammonium nitrate’s superior water uptake capability, ultimately elevating particle pH levels through aqueous-phase dilution mechanisms (Wexler and Seinfeld, 1991; Pinder et al., 2007, 2008; Heald et al., 2012; Weber et al., 2016). For instance, a significant increase in the nitrate-to-sulfate molar ratio from 2014–2017 in Beijing resulted in the particle pH increasing from 4.4

to 5.4 (Xie et al., 2020).”

6. Lines 85-86: Given the limitations, under what circumstances does it go from 4 to 7?.

Response: Thank you for your careful reading of our paper. This sentence has been modified to: “Karydis et al. (2021) framework demonstrated that CM played a critical buffering role in sustaining aerosol pH around 7 across the Middle East arid regions. The model sensitivity tests revealed that under hypothetical dust-free conditions (CM = 0), aerosol acidity would escalate to pH~4 due to NH_4^+/SO_4^{2-} domination.”

7. Lines 93-94: After reviewing the research progress, I suggest concluding with a summary that introduces the focus of this article. Specifically, what makes Zhengzhou and other cities different, what issue this study aims to address based on previous research, and what contributions this study makes. This is essential in scientific writing.

Response: Thank you for your comment. We have added a description in revised version:

“Zhengzhou presents unique atmospheric chemistry that distinguishes it from other mega-cities in North China. As the capital of China’s foremost agricultural province (Henan Province, contributing 18% of national NH_3 emissions), Zhengzhou’s $PM_{2.5}$ composition combined substantial crustal material (15 ± 3% in $PM_{2.5}$ vs. <10% in Beijing) with exceptional ammonia abundance (Huang et al., 2012; Liu et al., 2018;

Wang et al., 2018). This created distinct particle acidity characteristics, maintaining pH 4.5–6.0 compared to lower pH levels (3.3–5.4) in other cities like Beijing (Ding et al.,2019; Zhang et al., 2021). However, two critical research gaps persist: (1) the long-term evolution of CM under control policies remains unquantified; (2) the role of CM on pH buffer capacity in NH_3-enriched environments lacks systematic assessment.

To address these gaps, our study pioneers the first multi-decadal analysis (2011–2022) coupling $PM_{2.5}$ components with thermodynamic modeling through three key innovations: (1) revealing the long-term trends of CM, (2) analyzing the variations of CM sources, and (3) exploring pH trend and its relationship with CM. The resultant findings advance our understanding of urban aerosol acidity chemistry by underscoring the critical role of CM."

8. Line 123: Provide the version of ISORROPIA and the time resolution of the input components.

Response: Thank you for your suggestion. This sentence has been modified to: "The particle pH was calculated using the ISORROPIA-II mode (version 2.1, http://isorropia.eas.gatech.edu). The input data (excluding RH ≤ 30%), including SO_4^{2-}, TNO_3 (HNO_3 + NO_3^-), TNH_x (NH_3+NH_4^+), Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, RH and T, with the temporal resolution aligned with the sampling periods (from 10:00 AM to 9:00 AM the following day)."

9. Line 160: The spring of 2021 saw multiple rare dust storms in the North China Plain, but why was the CM not high in 2021? Additionally, the resolution of the figures in both the main text and SI needs to be improved to at least 300 dpi, as many figures in the SI are unclear.

Response: Thank you for your comments.

"The quality assurance protocol excluded temporally discrete dust storm and precipitation periods to prevent contamination of the source analysis of CM and modeling particle pH, given that such events induce non-representative extremes in both crustal element concentrations and pH values, coupled with elevated PM measurement uncertainties." In the revised manuscript, this quality control protocol description has been incorporated into Section 2.1 of the Methodology chapter.

Additionally, the resolution of the figures in both the main text and SI has been adjusted to 600 dpi.

10. Line 170 (Figure S3): It is recommended to use the same y-axis range for consistency. Regarding the drivers of seasonal variations (increase or decrease), I believe the discussion here lacks sufficient rigor, with an incomplete chain of evidence. I suggest that the authors consider separately discussing natural and anthropogenic sources, especially the impact of spring dust storm events on dust levels. In section 3.3, the source-related discussion is also mentioned, and therefore, this part needs to be strengthened.

Response: Thank you for your comments. We have replotted the Figure S5.

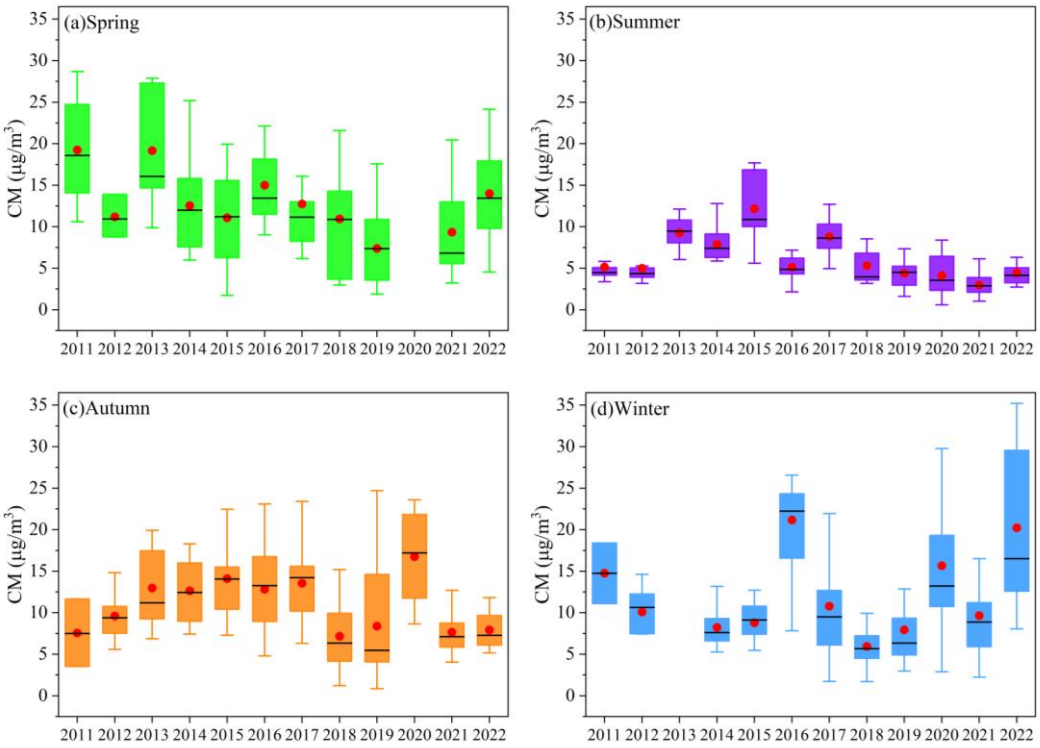


Figure S5. Trends in the CM concentrations in different seasons from 2011 to 2022.

We agree with your comment that the explanation of the seasonal variation characteristics lacked precise evidence. Therefore, we have revised the descriptions for different seasons and added figures showing the trends of wind speed (WS) and relative humidity (RH) changes across different seasons. However, as mentioned earlier, the data for dust storm events have been removed, and therefore, we cannot distinguish between natural and anthropogenic sources of dust. The revised description is as follows:

"Seasonal trends (Fig. S5) reveal significant declines in CM during spring in 2013–2019 with WS decreasing from 2.2 m/s in 2013 to 1.4 m/s in 2019 (Fig. S6) and stable RH (Fig. S7). Similarly, summer CM reductions in 2013–2019 corresponded

with WS declines. These patterns suggest spring-summer CM improvements resulted from the synergistic effects of meteorological changes and dust control policies. Conversely, autumn-winter seasons showed limited CM reductions despite comparable WS decreases in 2013–2019, highlighting the need for enhanced dust emission controls in Zhengzhou during these seasons."

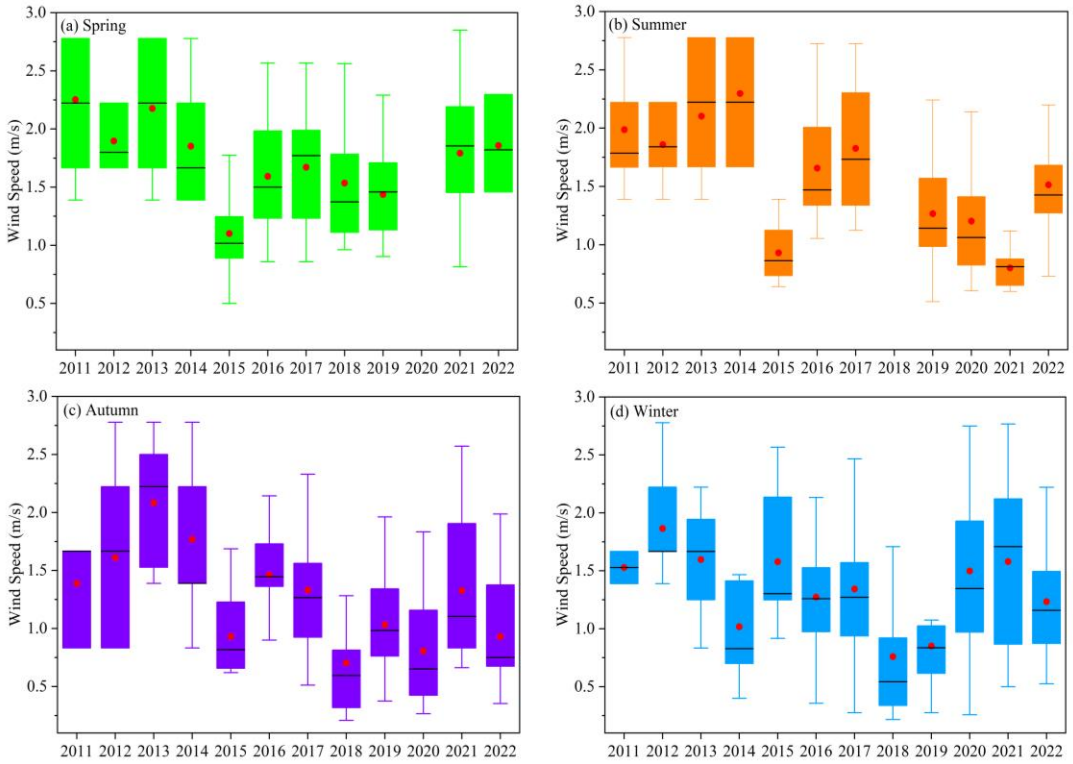


Figure S6 The variation in WS across different seasons from 2011 to 2022.

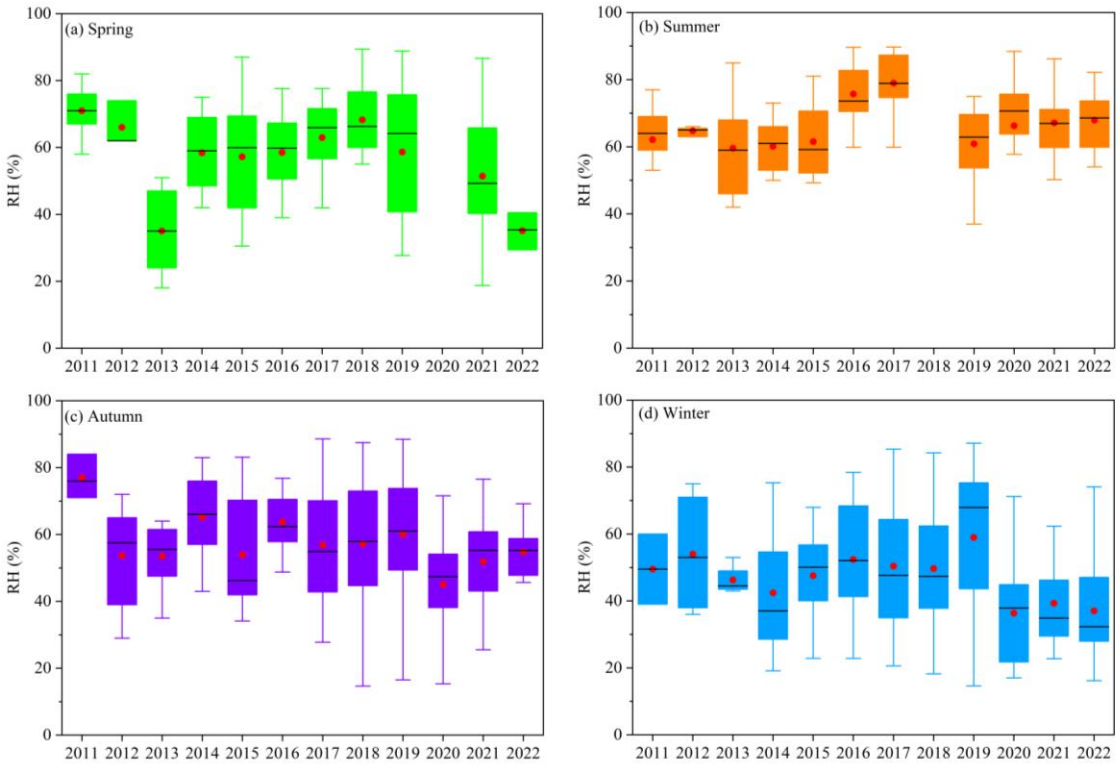


Figure S7 The variation in RH across different seasons from 2011 to 2022.

11. Lines 239-241: I believe ALWC is an important factor influencing pH, and it should not be solely attributed to sulfate. The authors need to carefully consider this point. Specifically, it should be evaluated whether the continuous decrease in ALWC affects pH, and whether this impact might even outweigh the influence of changes in aerosol composition.

Response: Thank you for your comments. We added the description on ALWC:

"According to Equation (2), in addition to H^+ concentration, particle pH is primarily influenced by the dilution effect of ALWC. Moreover, ALWC affects the gas-particle partitioning of semi-volatile compounds, thereby influencing particle acidity (Zuend et al., 2010; Zuend and Seinfeld, 2012). As shown in Fig.5 and Table S6, only

in 2015, 2019, and 2020 did the increases in ALWC concentration (17.6 μg/m³, 4.1 μg/m³, and 11.6 μg/m³, respectively) lead to pH increases of 0.22, 0.06, and 0.14 units. This clearly cannot fully explain the significant pH increase in Zhengzhou since 2013. Notably, since 2013, H^+ concentration has shown a decreasing trend. Particularly, H^+ concentrations decreased by 7.6×10^{-6}, 11.2×10^{-6}, and 7.2×10^{-6} mol/L in 2013, 2015, and 2017, respectively, leading to pH increases of 0.21, 0.36, and 0.42 units. After 2019, a continuous decline in H^+ concentration was observed for three consecutive years, resulting in pH increases of 0.21, 0.13, and 0.2 units in 2020, 2021, and 2022, respectively. These findings indicate that the increase in pH from 2019 to 2022 in Zhengzhou was primarily driven by the reduction in H^+ concentration.

The concentration of H^+ in the aerosol liquid phase is influenced by both chemical composition and meteorological conditions. To further understand the factors affecting ΔpH, we analyzed the variations in $PM_{2.5}$ chemical components and meteorological parameters. Results indicate that the decline in SO_4^{2-} from 2013 to 2018 was the primary cause of the increase in particle pH, as it decreased H^+ and ALWC concentrations (Fig. S11) in aerosol (Ding et al., 2019; Zhang et al., 2021)."

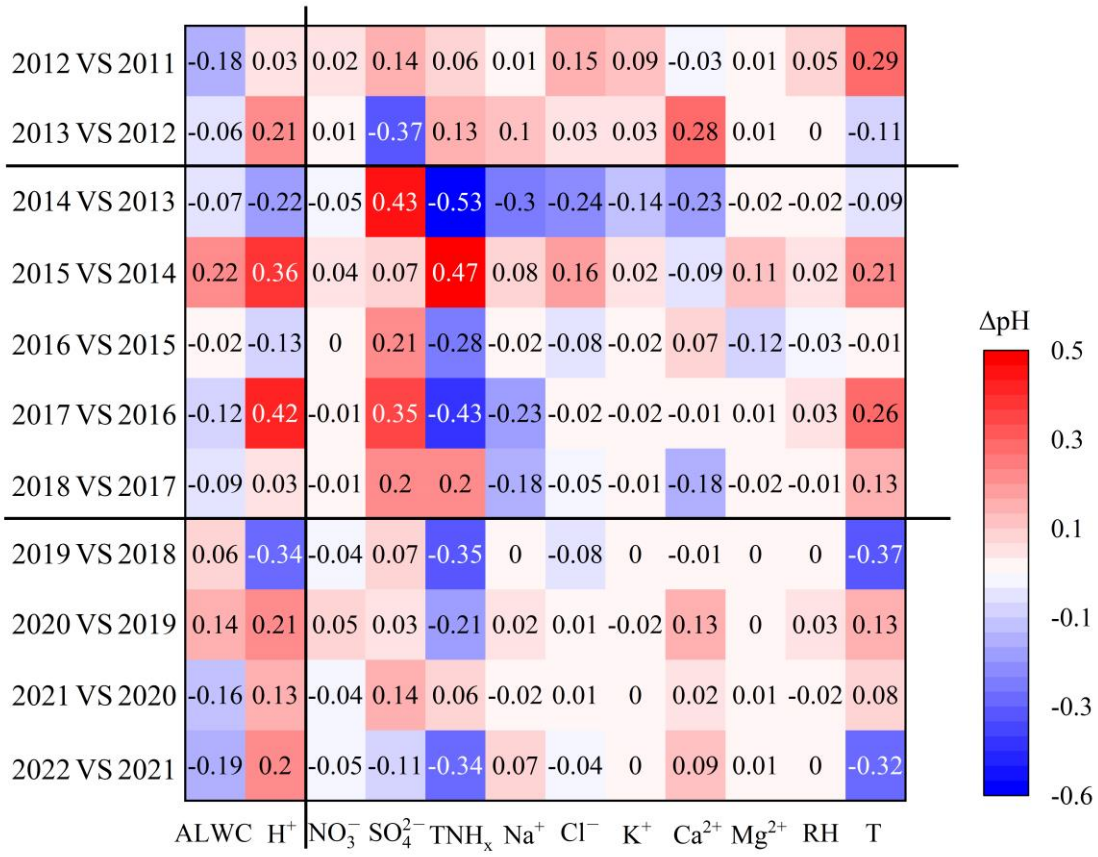


Figure 1. Contribution of each component to the changes in pH (ΔpH) between adjacent years. The difference between ALWC, H^+, particle component concentrations, and meteorological parameters between adjacent years is listed in Table S6.

Table S6. The difference between component concentrations (μg/m^3) and meteorological parameters between adjacent years.

Years	ALWC	H^+(10^{-6})	NO_3^-	SO_4^{2-}	TNH_X	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	RH(%)	T (°C)
2012VS2011	−19.0	−1.5	4.0	−4.6	1.3	0.02	2.0	0.9	−0.2	0.04	−9.6	−5.7
2013VS2012	−4.6	−7.6	2.6	13.0	2.1	0.2	0.4	0.3	1.4	0.1	−2.6	2.1
2014VS2013	−4.5	7.9	−7.3	−14.6	−6.9	−0.4	−3.4	−1.6	−1.1	−0.2	6.6	2.0
2015VS2014	17.6	−11.2	5.2	−1.8	5.5	0.1	2.1	0.4	−0.6	0.6	−5.6	−4.2
2016VS2015	−2.3	3.0	−0.2	−4.5	−3.7	−0.03	−0.1	−0.4	0.5	−0.7	8.0	0.3
2017VS2016	−10.0	−7.2	−2.9	−5.3	−3.6	−0.2	−0.3	−0.2	−0.1	0.1	−6.0	−4.9
2018VS2017	−5.8	−0.3	−0.8	−2.4	1.3	−0.1	−0.8	−0.2	−0.1	−0.1	1.4	−2.8
2019VS2018	4.1	4.8	−3.0	−0.8	−2.2	−0.04	−0.7	−0.03	−0.1	−0.01	−0.1	7.3
2020VS2019	11.6	−3.4	4.9	−0.3	−0.9	0.1	0.1	−0.2	0.7	0.02	−6.6	−2.1
2021VS2020	−12.7	−1.5	−3.6	−2.3	0.2	−0.01	0.03	0.01	0.1	0.04	−2.8	−1.5
2022VS2021	−10.6	−1.5	−5.1	1.9	−1.4	0.03	−0.3	0.01	0.5	0.04	4.7	5.8

12. Lines 280-282: Where is the data for this section sourced from?

Response: This dataset was obtained from the China National Environmental Monitoring Center (CNEMC) and has been referenced in Section 2.1:

"The annual mean $PM_{2.5}$ concentration data for cities in the North China Plain were obtained from the China National Environmental Monitoring Center (CNEMC), available at https://www.cnemc.cn/."

13. Lines 283-286: Although many researchers have done significant work on the impact of ammonia reduction on PM levels, I believe that under China's current policies, future emission reductions will not primarily focus on ammonia. Therefore, the authors need to reconsider whether the focus of this "Measurement Report" should be placed on ammonia. I suggest that the authors revise all statements related to ammonia, including the title.

Response: We sincerely thank the reviewer for their thoughtful and constructive feedback. Your point about the non-primary focus on ammonia reduction under current Chinese policies is well taken, and the sentence has been modified to: "Thus, crustal materials persist as a substantial constituent of atmospheric aerosols in North China, sustaining elevated particle pH levels. Extensive research has established that heightened particle pH inhibits nitrate reduction in aerosols (Ding et al., 2019; Lin et al., 2020; Wen et al., 2018), particularly significant given nitrate's predominant role in

haze formation within this region. Notably, while moderately acidic aerosols demonstrate reduced health impacts, particles with pH < 3 exhibit substantially greater health risks (Shi et al., 2019). Consequently, future environmental management strategies must prioritize real-time assessment of regulatory impacts on particle acidity. This necessitates an integrated approach that simultaneously addresses acidic precursors, alkaline precursors, and crustal material contributions to atmospheric acid chemistry.

Manuscript

Measurement report: Crustal materials play an increasing role in elevating particle pH: Insights from 12-year records in a typical inland city of China.

Hongyu Zhang[1, 2], Shenbo Wang[2, 3]*, Zhangsen Dong[1, 2]*, Xiao Li[2, 3], Ruiqin Zhang[2, 3]

[1] Collage of Chemistry, Zhengzhou University, Zhengzhou, 450000, China

[2] Research Institute of Environmental Sciences, Zhengzhou University, Zhengzhou 450000, China

[3] School of Ecology and Environment, Zhengzhou University, Zhengzhou, 450000, China

* Corresponding authors: Shenbo Wang and Zhangsen Dong

E-mail address: shbwang@zzu.edu.cn and dzszzu1990@163.com

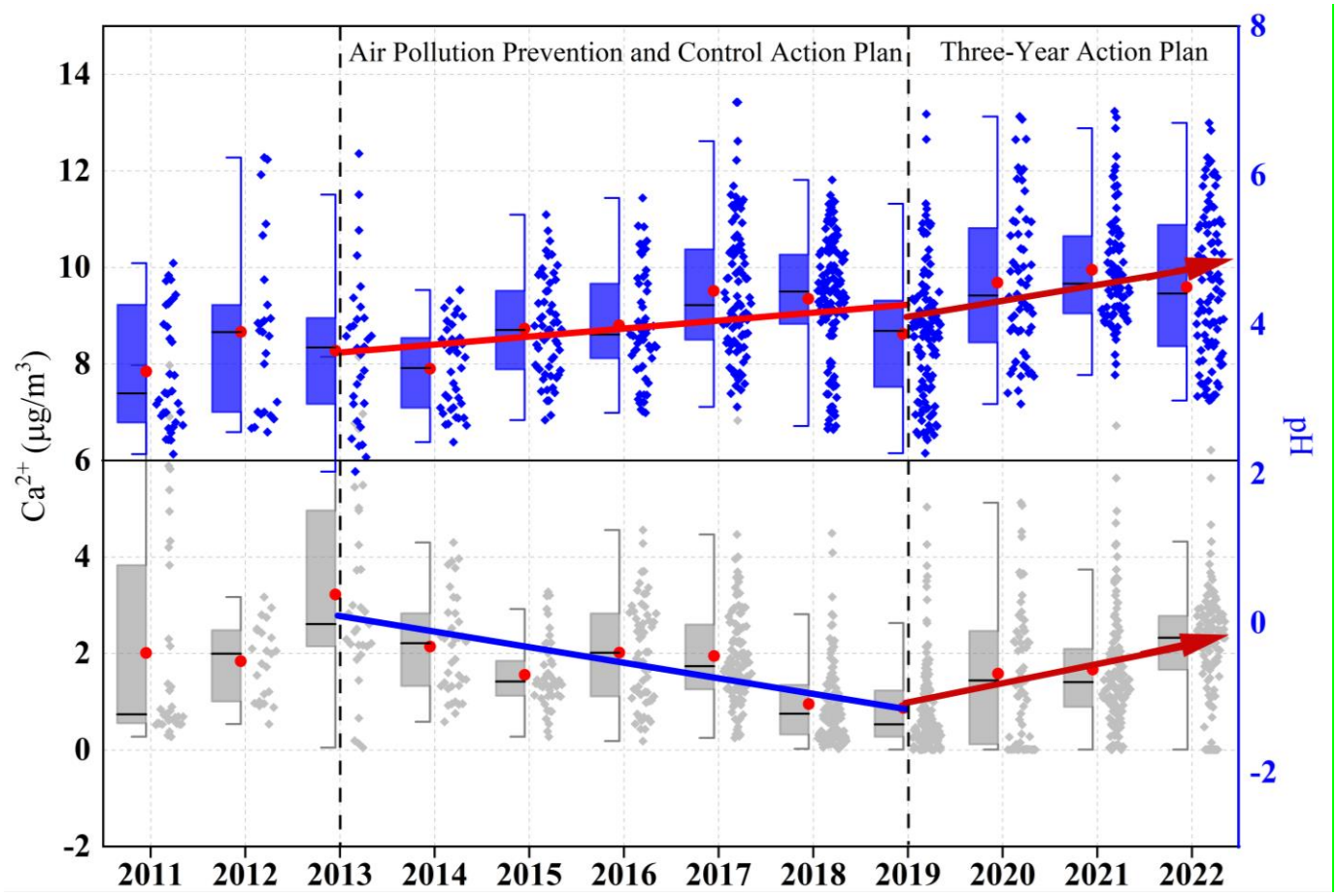
Abstract

Particle acidity serves as a key determinant in atmospheric chemical processes. Emerging concerns regarding aerosol acidity trends have been highlighted amid China's sustained initiatives to mitigate emissions of both acidic and alkaline precursors, especially in North China, which is significantly affected by dust aerosol. 12-year observational data in Zhengzhou reveal that the annual average $PM_{2.5}$ concentration decreased from 162 ± 81 μg/m^3 in 2011 to 60 ± 41 μg/m^3 in 2022, with the largest reduction in sulfate (73%). Correspondingly, the annual particle pH increased by 0.10 units from 2011 to 2019. In addition, the elevated particle pH in 2015 and 2018 was notably influenced by the increase in TNH_x (NH_3 + NH_4^+). Note that the crustal material concentrations and their proportions increased significantly during 2019–2022, which might be responsible for the resuspension of surrounding soil dust. Even though the TNH_x concentration was decreasing, the annual average growth rate of pH values increased to 0.21 units from 2019 to 2022. This phenomenon is not unique to Zhengzhou, as major cities in the North China Plain have also experienced a pronounced upward trend in coarse particles after 2019. Therefore, the long-term evolution of particle acidity in North China will require comprehensive consideration of synergistic effects involving acidic precursors, ammonia, and crustal materials.

Keywords: Dust, aerosol acidity, sources, North China Plain, control measurement

Synopsis: The future ammonia reduction policies in North China may not lead to a rapid increase in particle acidity in the presence of crustal materials., which further elevated the particle pH after 2019.

Graphical abstract:



Highlights:

- Crustal material concentrations and their proportions increased significantly during 2019–2022;
- The resuspension of surrounding soil dust may determine the rebound of crustal material concentrations;
- Rebound in crustal material further elevated the particle pH.

1 Introduction

Particle acidity is a critical parameter that affects atmospheric chemistry, such as the gas-particle

partitioning of semi-volatile and volatile species (Surratt et al., 2010; Guo et al., 2016), the solubility of metals (Tao and Murphy, 2019), acid-catalyzed reactions (Rengarajan et al., 2011), and acid deposition (Mao et al., 2009), thereby determining aerosol concentration and chemical composition, as well as impacting human health, ecosystems, and climate (Li et al., 2017; Pye et al., 2020; Su et al., 2020; Nenes et al., 2021). Generally, the global fine particulate matter ($PM_{2.5}$, aerodynamic diameter ≤ 2.5 μm) exhibits a bimodal pH distribution ranging from 1–3 (e.g., in the United States and Europe) (Guo et al., 2015; Battaglia et al., 2017; Masiol et al., 2020; Zhang et al., 2021) and 4–5 (e.g., in East Asia) (Kim et al., 2022; Sharma et al., 2022). The atmosphere rich in gaseous ammonia (NH_3) and crustal material (CM) shows significant pH buffering effects (Wang et al., 2020; Zheng et al., 2020; Karydis et al., 2021), which is a dominant factor that drives the high particle pH in East Asia (Karydis et al., 2021; Zhang et al., 2021; Kim et al., 2022; Sharma et al., 2022).

In recent years, the changing trends in particle pH have become a research focus, especially in China, in response to air pollution control policies, i.e. Air Pollution Prevention and Control Action Plan (2013–2018) and Three-Year Action Plan (2018–2020). The annual average $PM_{2.5}$ concentration in Beijing dropped by 64% from 89.5 μg/m³ in 2013 to 32 μg/m³ in 2023 (MEP, 2023), with a clear downward trend of sulfate concentration, and nitrate surpassing sulfate as the primary component (Zhai et al., 2019; Zhou et al., 2019; Li et al., 2023). The atmospheric behavior of ammonium, governed by gas-particle partitioning processes involving ammonia (NH_3) as the predominant alkaline gas, demonstrates notable stability in concentration levels, with observational records showing less than 5% interannual variation in NH_3 column densities over North China during 2015–2019 (Dong et al., 2023). Under such conditions, the dominant inorganic aerosol component transitions from ammonium sulfate

to ammonium nitrate. This compositional shift enhances atmospheric particulate hygroscopicity due to ammonium nitrate's superior water uptake capability, ultimately elevating particle pH levels through aqueous-phase dilution mechanisms (Wexler and Seinfeld, 1991; Pinder et al., 2007, 2008; Heald et al., 2012; Weber et al., 2016). For instance, a significant increase in the nitrate-to-sulfate molar ratio from 2014–2017 in Beijing resulted in the particle pH increasing from 4.4 to 5.4 (Xie et al., 2020). Moreover, increased NH_3 concentrations raised particle pH by 0.3–0.4 units from 2014/2015 to 2018/2019 in Beijing (Song et al., 2019). Over Europe and North America, the pH has increased strongly from about 2.8 and 2.2 during the 1970s to 3.9 and 3.3 in 2020 respectively, especially during the 1990s, with significantly increasing NH_3 emission (Karydis et al., 2021). On the contrary, modeling results indicate a continuous decline in pH in East Asia from 1970 to 2020 due to sharp increases in SO_2 and NO_x emissions (Karydis et al., 2021). In addition, the $PM_{2.5}$ pH showed a slight decrease of 0.13 from 2018 to 2022 summer in Beijing due to the change in total nitrate (NO_3^- + HNO_3) (Li et al., 2023). Moreover, Zhou et al. (2022) found a decreasing pH trend from 2011 to 2019 in eastern China, primarily influenced by temperature, followed by sulfate and non-volatile cations. Similarly, Nah et al. (2023) observed a decreasing pH trend from 2011 to 2020 in Hong Kong, attributing it to temperature and sulfate levels. Thus, concerns have been raised about the potential increase in the acidity of aerosol and precipitation due to China's ongoing efforts to reduce ammonia emissions, which pose severe health risks and acid deposition (Liu et al., 2019; Shi al., 2019).

In addition to NH_3, CM is another key alkaline substance, that buffers particle pH. Ca^{2+} can form insoluble $CaSO_4$ with sulfate, reducing sulfate concentration in the aqueous phase of aerosol, and thus lowering H^+ and aerosol liquid water content (ALWC) concentrations and enhancing particle pH (Ding

et al., 2019; Karydis et al., 2021). Moreover, non-volatile cations can lower the molar ratio of ammonia to sulfate, leading to an increase in particle pH (Zheng et al., 2022). Karydis et al. (2021) framework demonstrated that CM played a critical buffering role in sustaining aerosol pH around 7 across the Middle East arid regions. The model sensitivity tests revealed that under hypothetical dust-free conditions (CM = 0), aerosol acidity would escalate to pH~4 due to NH_4^+/SO_4^{2-} domination. Wang et al. (2022) reported that non-volatile cations accounted for approximately 8–17% of hourly aerosol pH variation. Li et al. (2023) indicated that the buffering effect of cations was the major reason for the relatively small pH changes from 2018 to 2022 in Beijing, emphasizing that reducing coarse particle emissions in the future could significantly decrease particle pH. In addition, there was a rising trend in the contribution of CM to particle pH in Tianjin, China (Shi et al., 2017). Therefore, it is evident that CM has a significant impact on the variation of particle pH, especially in North China, which is significantly affected by dust aerosol, but the trend of CM concentration and its long-term implication is still lacking unfortunately.

Zhengzhou presents unique atmospheric chemistry that distinguishes it from other mega-cities in North China. As the capital of China's foremost agricultural province (Henan Province, contributing 18% of national NH_3 emissions), Zhengzhou's $PM_{2.5}$ composition combined substantial crustal material (15 ± 3% in $PM_{2.5}$ vs. <10% in Beijing) with exceptional ammonia abundance (Huang et al., 2012; Liu et al., 2018; Wang et al., 2018). This created distinct particle acidity characteristics, maintaining pH 4.5–6.0 compared to lower pH levels (3.3–5.4) in other cities like Beijing (Ding et al.,2019; Zhang et al., 2021). However, two critical research gaps persist: (1) the long-term evolution of CM under control policies remains unquantified; (2) the role of CM on pH buffer capacity in NH_3-

enriched environments lacks systematic assessment.

To address these gaps, our study pioneers the first multi-decadal analysis (2011–2022) coupling $PM_{2.5}$ components with thermodynamic modeling through three key innovations: (1) revealing the long-term trends of CM, (2) analyzing the variations of CM sources, and (3) exploring pH trend and its relationship with CM. The resultant findings advance our understanding of urban aerosol acidity chemistry by underscoring the critical role of CM.

2 Experiment and method

2.1 Instruments and Measurements

Sampling was conducted on the fourth-floor platform at Zhengzhou University (34.75° N, 113.61° E) in Zhengzhou, China. The sampling site (Fig. S1), approximately 14 m above the ground, is primarily surrounded by residential areas with well-developed transportation networks and no significant industrial sources. There are two highways located 3 km to the south and 7 km to the east. Additionally, a coal-fired power plant located 6 km to the east was shut down in 2020, and a gas-fired power plant is situated 3 km to the south.

Samples were collected using a high-volume sampler (TE-6070D, Tisch, USA) and air particulate samplers (TH-16A, Tianhong, China) from April 2011 to December 2022. Two quartz filters and two Teflon filters were used daily from 10:00 AM to 9:00 AM the next day, resulting in a total of 5848 samples. After excluding abnormal data due to instrument malfunctions, 4228 valid samples were obtained. Detailed information on the samples is provided in Table S1. Organic carbon (OC) and elemental carbon (EC) were analyzed using a carbon analyzer (Model 5L, Sunset Laboratory, USA).

Water-soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were measured using ion chromatography (ICS-90 and ICS-900 models, Dionex, USA) (Yu et al., 2017; Jiang et al., 2018). Elements were analyzed using a wavelength dispersive X-ray fluorescence spectrometer (S8 TIGER, Bruker, Germany) to determine concentrations of Fe, Na, Mg, Al, Si, Cl, K, Ca, V, Ni, Cu, Zn, Cr, Mn, Co, Cd, Ga, As, Se, Sr, Sn, Sb, Ba, and Pb (Tremper et al., 2018). Meteorological conditions, including temperature (T), relative humidity (RH), and wind speed (WS) were obtained using an automatic weather station (Wang et al., 2019). Blank filters were also routinely analyzed with each batch of samples to detect sample contamination and provide quality assurance on the elemental concentrations. Detailed analytical methods and quality control are described in the supplement (Text S1). The method detection limits and measurement uncertainties are summarized in Table S2. The quality assurance protocol excluded temporally discrete dust storm and precipitation periods to prevent contamination of the source analysis of CM and modeling particle pH, given that such events induce non-representative extremes in both crustal element concentrations and pH values, coupled with elevated PM measurement uncertainties. The annual mean $PM_{2.5}$ concentration data for cities in the North China Plain were obtained from the China National Environmental Monitoring Center (CNEMC), available at https://www.cnemc.cn/.

2.2 Data Analysis

2.2.1 Mass reconstruction

The calculation method for CM is as follows (Tian et al., 2016):

$$[CM]=1.89\times[Al] + 2.14\times[Si] + 1.4\times[Ca] + 1.43\times[Fe]+1.94[Ti] \quad (1)$$

where [Al], [Si], [Ca], [Fe] and [Ti] represent the concentrations of the respective elements (μg/m^3), but Ti was not measured.

2.2.2 Thermodynamic model

The particle pH was calculated using the ISORROPIA-II mode (version 2.1, http://isorropia.eas.gatech.edu). The input data (excluding RH ≤ 30%), including SO_4^{2-}, TNO_3 (HNO_3 + NO_3^-), TNH_x (NH_3+NH_4^+), Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, RH and T, with the temporal resolution aligned with the sampling periods (from 10:00 AM to 9:00 AM the following day). Input data (excluding RH ≤ 30%) included SO_4^{2-}, TNO_3 (HNO_3 + NO_3^-), TNH_x (NH_3+NH_4^+), Ca^{2+}, K^+, Na^+, Mg^{2+}, Cl^-, RH and T. The concentrations of hydrogen ions in air (H^+_{air}) and ALWC were calculated using the aerosol equilibrium composition system Na^+-K^+-Ca^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-}-NO_3^--Cl^--H_2O H^+_{air} (Fountoukis and Nenes, 2007). pH values were calculated using the following formula:

$$pH = -\log_{10} H^+_{aq} \cong -\log_{10} \frac{1000 H^+_{air}}{ALWC_i + ALWC_o} \cong -\log_{10} \frac{1000 H^+_{air}}{ALWC_i} \quad (2)$$

$$ALWC_o = \frac{m_{org}\rho_w}{\rho_w} \frac{\kappa_{org}}{\left(\frac{1}{RH} - 1\right)} \quad (3)$$

where $ALWC_i$ and $ALWC_o$ refer to the ALWC for inorganic and organic components, respectively. m_{org} denotes the mass of organic aerosol, ρ_w is the density of water (1.0 g/cm^3), ρ_{org} is the density of organic material (1.4 g/cm^3) (Guo et al., 2015), k_{org} is the hygroscopicity parameter for organic aerosol (0.087) (Chang et al., 2010; Li et al., 2016). The ISORROPIA-II model operated under metastable conditions in the forward mode. Due to the lack of measured data for gaseous HNO_3 and NH_3, TNO_3 was represented solely by NO_3^-. The concentration of NH_3 was simulated based on a linear regression

equation proposed by Wei et al. (2023), who used the same data as this study from 2013 to 2020:

$$NH_3 = 19.909 \times RH + 0.559 \times T - 0.35 \times NH_4^+ + 0.123 \times NO_3^- + 2.159 \times Cl^- - 0.224 \times SO_4^{2-} - 154.923 \quad (4)$$

where NO_3^-, SO_4^{2-}, NH_4^+, and Cl^- correspond to their respective concentrations (μg/m^3). To validate the applicability of Equation 4 for annual NH_3 estimation and pH simulation in Zhengzhou, this study utilized both observed NH_3 data (from a Thermo Scientific URG-9000D ambient ion monitor, USA) and calculated NH_3 values derived from Equation 4 at the same monitoring site throughout 2022, inputting them into the thermodynamic model for pH simulation. As shown in Figure S2, pH values calculated from observed and simulated NH_3 exhibit good agreement ($r = 0.97$, $P < 0.01$). Furthermore, NH_3 concentrations modeled by ISORROPIA demonstrate a significant correlation ($r = 0.95$, $P < 0.01$) with that simulated NH_3 by Equation 4. These results collectively demonstrate the reliability of the NH_3 estimation method in this study.

2.2.3 HYSPLIT analysis

Backward trajectories were calculated using the mixed-particle Lagrangian integrated trajectory method (HYSPLIT, https:// www.ready.noaa.gov/HYSPLIT_traj.php). Meteorological input data were from the Global Data Assimilation System (GDAS) with 3D wind vectors, temperature, relative humidity, geopotential height, surface pressure, and boundary layer diagnostics. 24-h backward trajectories were simulated for air masses above 1000 m above ground level in Zhengzhou. While the surface elevation of Zhengzhou is approximately 100 m above sea level (ASL), setting the height at 1000 m ASL takes into account the minimum altitude needed to traverse the average elevation of the Taihang Mountains (ranging from 1000 to 1500 m ASL). This ensures that the simulated trajectory paths over this topographical barrier are physically realistic.

The Angle Distance algorithm was used to cluster air mass trajectories, enabling the identification of dominant air mass directions and potential pollution sources affecting the study site during different periods. The optimal number of clusters was determined by evaluating the spatial variance (SPVAR) of each trajectory from the cluster mean and the total spatial variance (TSV). The final classification was selected just before the second rapid increase in TSV. The underlying principle is that TSV initially rises sharply during clustering, then increases gradually; however, once the number of clusters reaches a certain threshold, TSV surges again, indicating that the merged clusters are highly dissimilar, marking the end of the classification process. The classification results correspond to the different air mass categories before this final merging step. The mean trajectories of these clusters represent the primary airflow patterns at the target site during the analysis period (Wang et al., 2009). Subsequently, trajectories from two periods, 2013–2018 and 2019–2022, were clustered separately to analyze the variations between the two policy implementation periods.

3 Results and discussion

3.1 Temporal variations in chemical components

Over the past twelve years, the Chinese government implemented the Air Pollution Prevention and Control Action Plans (2013–2018) and the Three-Year Action Plan (2018–2020). The Air Pollution Prevention and Control Action Plan focused on reducing $PM_{2.5}$ concentrations in key regions and aiming to cut $PM_{2.5}$ levels by 10–25% in priority areas over five years. To achieve these goals, it adopted several measures. In terms of industrial restructuring, it mandated the elimination of a large amount of outdated production capacity in industries such as iron/steel and cement to optimize the

industrial structure and reduce high-pollution production. For emission standards, it set strict requirements for multiple industrial sectors, especially coal-fired power plants, and gradually introduced ultra-low emission requirements to control pollutants like SO_2, NO_x, and PM. Regarding energy transition, it promoted a shift from coal to cleaner energy sources, including capping coal consumption in certain regions and restricting the construction of small-scale coal-fired boilers. Subsequently, the Three-Year Action Plan was carried out to continue improving air quality with a broader scope of regions under control, further reducing pollutant emissions and enhancing the overall air quality index. The measures included enhanced transportation controls, such as introducing stricter vehicle emission standards (like National VI standards for vehicles) and establishing diesel truck exclusion zones in many cities to reduce emissions from the transportation sector. It also adopted precision governance through grid-based environmental supervision, dividing areas into small grids for more accurate and efficient monitoring of pollution sources. Additionally, it strengthened the legal and institutional framework by revising relevant laws, such as the Air Pollution Prevention and Control Law, to strengthen legal penalties for environmental violations and implementing an environmental tax system to encourage enterprises to reduce emissions.

The long-term trends in $PM_{2.5}$ concentrations and its chemical components in Zhengzhou from 2011 to 2022 are depicted in Fig. 1, with annual average concentrations listed in Table 1. Correspondingly, the annual average concentration of $PM_{2.5}$ in Zhengzhou decreased from 162 ± 81 $\mu g/m^3$ in 2011 to 60 ± 41 $\mu g/m^3$ in 2022, representing a reduction of approximately 63%. In particular, the reduction rate reached 72% after 2013. As for chemical components, the largest reductions were observed in SO_4^{2-} (79%), decreasing from 38.0 ± 19.9 $\mu g/m^3$ in 2013 to 7.9 ± 4.5 $\mu g/m^3$ in 2022,

followed by EC (76%). Additionally, the concentrations of NH_4^+ and NO_3^- also significantly decreased by 68% and 56%, respectively. The proportion of each component in $PM_{2.5}$ (Fig. S3) reveals a decrease in SO_4^{2-}, K^+, and Cl^-, indicating effective control measures targeting coal and biomass combustion (Lei et al., 2021). However, the proportions of NO_3^- and OC in $PM_{2.5}$ rose from 11% and 12% in 2013 to 13% and 17% in 2022, respectively, similar to the trend observed in the North China Plain (Wen et al., 2018; Zhai et al., 2019; Li et al., 2023).

3.2 Temporal variations in CM

Notably, there is no clear declining trend in the CM concentration, with a rebound observed during 2020–2022 (Fig. 1i). Furthermore, the proportion of CM in $PM_{2.5}$ exhibits a significant upward trend (Fig. S3). To further analyze its trend, sampling data were divided into three periods corresponding to governmental stages: 2011–2013, when no special control measures were implemented; 2013–2019, coinciding with the implementation of the Air Pollution Prevention and Control Action Plan; and 2019–2022, coinciding with the Three-Year Action Plan. During these periods, Henan Province and Zhengzhou City implemented several dust control policies summarized in Table S3. As shown in Fig. 2a and 2b, the mass concentration of CM peaked at 14.6 ± 8.3 μg/m^3 in 2013, accounting for 8% of $PM_{2.5}$. To evaluate the inter - annual change trend of CM, the Mann - Kendall method, Sen's slope, and Least - Squares (LS) slope were comprehensively used with the results presented in Table S4. From 2013 to 2019, the CM concentration notably decreased from 14.6 ± 8.3 to 8.5 ± 7.8 μg/m^3, with an annual average decline rate of 0.81 μg/(m^3·year) from LS slope [0.015 μg/(m^3·year) from Sen's slope]. Apart from control measures, the interannual meteorological analysis shows (Fig. S4) WS

exhibited a declining trend, with a decrease rate of 43%, while RH showed an increasing trend at a rate of 8% from 2013 to 2019, under which conditions that were unfavorable for dust resuspension (Wang et al., 2013, 2018). Seasonal trends (Fig. S5) reveal significant declines in CM during spring in 2013–2019 with WS decreasing from 2.2 m/s in 2013 to 1.4 m/s in 2019 (Fig. S6) and stable RH (Fig. S7). Similarly, summer CM reductions in 2013–2019 corresponded with WS declines. These patterns suggest spring-summer CM improvements resulted from the synergistic effects of meteorological changes and dust control policies. Conversely, autumn-winter seasons showed limited CM reductions despite comparable WS decreases in 2013–2019, highlighting the need for enhanced dust emission controls in Zhengzhou during these seasons. As for the individual crustal elements in Fig. S8, Ca exhibited the highest average annual decline rate of 33% during 2013–2019, followed by Al. Si showed a less pronounced decline, attributed to its association with soil dust, where control measures for exposed soil are lacking (Zhang et al., 2020). In addition, the Ca^{2+} concentration as depicted in Fig. 2c decreased from 3.2 ± 2.1 μg/m^3 in 2013 to 2.2 ± 1.1 μg/m^3 in 2019, with an approximate annual average decline rate of 0.32 μg/(m^3·year) from LS slope [4.14E–03 μg/(m^3·year) from Sen's slope] in Table S4, further demonstrating the decline in dust source. It was worth noting that the proportions of CM, Ca, Al, Fe, Si, and Ca^{2+} in $PM_{2.5}$ have shown consecutive annual increases from 2013 to 2019, with CM proportion increasing from 8% in 2013 to 14% in 2019, indicating that CM reduction lagged behind $PM_{2.5}$ reduction efforts in Zhengzhou during this period. Additionally, both concentration and proportion of Ca^{2+} in 2022 (2.2 ± 1.1 μg/m^3 and 14%) were higher than in other cities of China, such as Beijing (1.0 μg/m^3 and 2.8%), Tianjin (0.5 μg/m^3 and 1.4%), and Xiamen (0.48 μg/m^3 and 1.5%) (Shi et al., 2017; Xu et al., 2025; Zhang et al., 2021). These results indicate that CM remained an

important component of $PM_{2.5}$ in Zhengzhou City.

During 2019–2022, both CM and Ca^{2+} concentrations exhibited significant rebounds, with annual growth rates of 0.24 and 0.4 μg/(m^3·year) from LS slope [5.80E–03 and 5.42E–03 μg/(m^3·year) from Sen's slope], respectively, and their proportions increased from 14% and 2% in 2019 to 22% and 5% in 2022. CM concentrations rebounded in all seasons, particularly in winter (Fig. S5). Changes in meteorological conditions may be a significant factor contributing to these concentration rebounds, accompanied by the average WS increased by 0.14 m/s and RH decreased by 7% from 2020 to 2022 (Fig. S4, S6, and S7), facilitating dust resuspension. Furthermore, the lack of more effective dust control measures, as indicated by the absence of significant changes in the dust control policies from the Air Pollution Prevention and Control Action Plan and Three-Year Action Plan, may be another important factor contributing to the rebound of dust.

3.3 Sources of CM

Elemental ratios were employed to characterize the sources of CM, with the Ca/Al ratio widely recognized as a reliable indicator of sandy origin (Zhang et al., 2017). In addition, significant variations in Ca/Si ratios (Table S5) were observed among different dust sources (Road, Construction, Piles, Soil). Fig. 3a illustrates the trend in Ca/Si ratios from 2011 to 2022. After 2013, Ca/Si ratios showed a declining trend annually, with the average ratio decreasing from a peak of 1.6 in 2016 to a lowest of 0.4 in 2022. Compared with Ca/Si ratios from different types of dust sources, the effect of road and construction dust on CM has gradually decreased. This may be attributed to the implementation of dust control measures such as enclosure, shielding, and dust suppression at construction and demolition

sites, as well as dust control on ground surfaces and roads (Table S5). During 2019–2022, the average Ca/Si ratio remained below 1, with a mean of 0.4 in 2022, indicating that soil dust predominantly contributed to CM. Currently, measures for controlling soil-suspended dust are limited, primarily relying on long-term strategies such as afforestation and increasing urban green coverage, thus requiring a longer process and sustained investment.

Sand dust transport serves as a significant source of CM in the North China Plain (Zhang et al., 2024). The Ca/Al ratio from 2016 to 2022 (Fig. 3b) shows minimal variation, with annual averages ranging between 1.5 and 2.5, indicating no significant changes in the source regions of sand. The transport trajectories reveal that the predominant pathways for long-distance transport of sand dust originated from Inner Mongolia, passing through Shaanxi and Shanxi provinces. Compared to 2013–2018 (45%), the influence of long-distance transport decreased to 25% during 2019–2022. In contrast, local transport within Henan province and short-distance transport from Shandong province showed a noticeable increase. These findings suggest that the rebound in CM concentrations during 2019–2022 in Zhengzhou might be responsible for the resuspension of surrounding soil dust.

3.4 Long-term trend of particle pH

Are shown in Fig. 4 and Table S4, pH values showed a clearly increasing trend after 2014. From 2013 to 2019, the annual pH increased by 0.11 units from the LS slope [9.15E–04 units from Sen's slope], reaching a maximum median value of 4.45 (Mean: 4.35) in 2018. Note that the annual average growth rate of pH values increased to 0.21 units from LS slope [2.93E–03 units from Sen's slope] from 2019 to 2022, with a maximum median value of 4.42 (Mean: 4.51) in 2022. Seasonally, pH values

showed increasing trends in spring, summer, and autumn, and notably increased in winter from 2020 to 2022 (Fig. S9). The increasing trend in pH values observed in this study is similar to the findings in Beijing (Song et al., 2019; Xie et al., 2020), presumably attributable to the comparable chemical composition trends and meteorological conditions. In contrast, Shanghai and Hong Kong display divergent trends (Nah et al., 2023; Zhou et al., 2022). This disparity might be ascribed to the stronger buffering effect exerted by NH_3 and dust in Zhengzhou than marine aerosols (Na^+/Cl^-) in these coastal cities (Shi et al., 2017; Liu et al., 2019). Moreover, the relatively higher temperatures and more abundant rainfall in Shanghai and Hong Kong could also contribute to the distinct trends observed in their pH values.

Sensitivity analyses were conducted to explore the dominant factors driving the elevated particle pH in Zhengzhou by giving a range for one parameter (i.e., TNH_x) and average values for other parameters (i.e., SO_4^{2-}, NO_3^-, Na^+, Cl^-, Ca^{2+}, K^+, Mg^{2+}, RH, and T) input into the ISORROPIA-II model. Are shown in Fig. S10, particle pH increases with the cation concentrations (e.g., TNH_x, K^+, Ca^{2+}, Mg^{2+}, and Na^+) and decreases with anions concentrations (e.g., SO_4^{2-} and NO_3^-). Additionally, RH does not significantly affect pH, whereas an increase in T leads to a noticeable decrease in particle pH.

Based on the sensitivity analysis curves, the pH values corresponding to a variable in different years were calculated according to the average values of this variable in different years (Table S6). The difference in pH values of this variable between two adjacent years was defined as ΔpH which is illustrated in Fig. 5. According to Equation (2), in addition to H^+ concentration, particle pH is primarily influenced by the dilution effect of ALWC. Moreover, ALWC affects the gas-particle partitioning of semi-volatile compounds, thereby influencing particle acidity (Zuend et al., 2010; Zuend and Seinfeld,

2012). As shown in Fig.5 and Table S6, only in 2015, 2019, and 2020 did the increases in ALWC concentration (17.6 μg/m³, 4.1 μg/m³, and 11.6 μg/m³, respectively) lead to pH increases of 0.22, 0.06, and 0.14 units. This clearly cannot fully explain the significant pH increase in Zhengzhou since 2013. Notably, since 2013, H^+ concentration has shown a decreasing trend. Particularly, H^+ concentrations decreased by 7.6×10^{-6}, 11.2×10^{-6}, and 7.2×10^{-6} mol/L in 2013, 2015, and 2017, respectively, leading to pH increases of 0.21, 0.36, and 0.42 units. After 2019, a continuous decline in H^+ concentration was observed for three consecutive years, resulting in pH increases of 0.21, 0.13, and 0.2 units in 2020, 2021, and 2022, respectively. These findings indicate that the increase in pH from 2019 to 2022 in Zhengzhou was primarily driven by the reduction in H^+ concentration.

The concentration of H^+ in the aerosol liquid phase is influenced by both chemical composition and meteorological conditions. To further understand the factors affecting ΔpH, we analyzed the variations in $PM_{2.5}$ chemical components and meteorological parameters. Results indicate that the decline in SO_4^{2-} from 2013 to 2018 was the primary cause of the increase in particle pH, as it decreased H^+ and ALWC concentrations (Fig. S11) in aerosol (Ding et al., 2019; Zhang et al., 2021). The average SO_4^{2-} concentration decreased by 14.6 and 5.3 μg/m^3, resulting in a pH increase of 0.43 and 0.35 units from 2013 to 2014 and 2016 to 2017, respectively, which was comparable to an increased rate of 0.3 units in East Asia due to SO_2 emission controls since 2016 (Karydis et al., 2021). As another acidic ion, the decrease in nitrate concentration did not significantly contribute to the pH increases, consistent with findings from Ding et al. (2019) and Zhang et al. (2021). This is primarily because NO_3^- declined more slowly compared to sulfate ions and exceeded sulfate concentrations after 2016, under which conditions that nitrate-rich particles can absorb twice the amount of water that sulfate-rich particles,

leading to an increase in ALWC concentration and inhibiting pH decline (Lin et al., 2020; Xie et al., 2020). On the other hand, increases in particle pH in 2015 and 2018 were notably influenced by changes in TNH_x with concentrations increased by 5.5 and 1.3 μg/m^3, respectively. Increased TNH_x concentrations could react with SO_4^{2-} or NO_3^- and consume a substantial amount of H^+, thereby raising particulate matter pH values (Seinfeld et al., 1998; Zhang et al., 2021). Substantial decreases in T in 2015 (4.2℃), 2017 (4.9℃), and 2018 (2.8℃), favoring NH_3 partitioning into the particle phase and reducing H^+ concentrations, drove increases in particle pH (Tao and Murphy, 2019).

During the period from 2020 to 2022, the influence of SO_4^{2-} on particle pH gradually decreased, with a decrease in concentration from 0.3 to 2.3 μg/m^3 (Table S6) only bringing about a pH decrease of 0.03 to 0.14 (Fig. 5). Moreover, a rebound in SO_4^{2-} concentration to 7.9 ± 4.5 μg/m^3 in 2022 even resulted in a decrease of 0.11 units in pH instead. On the other hand, TNHx began to show a slight annual decline (0.9 to 2.2 μg/m^3), resulting in a significant decrease in pH (0.21–0.35). Consequently, the increase in pH values was closely related to the rise in Ca^{2+} concentration. Ca^{2+} is less volatile and competes preferentially with NH_3 to neutralize anions such as SO_4^{2-} to form insoluble $CaSO_4$, which precipitates from the aerosol aqueous phase (Ding et al., 2019; Karydis et al., 2021), thereby reducing H^+ concentrations (Fig. S11) and subsequently lowering particle acidity. Specifically, increases of 0.7 and 0.5 μg/m^3 in Ca^{2+} concentrations led to pH increases of 0.13 and 0.09 units in 2020 and 2022, respectively, making Ca^{2+} a primary controlling factor for pH elevation.

4 Conclusions

The annual average $PM_{2.5}$ concentration in Zhengzhou decreased from 212.4 ± 101.5 μg/m^3 in

2013 to 59.5 ± 41.2 μg/m^3 in 2022, with the largest reduction in SO_4^{2-}. As for CM, their concentrations notably decreased from 2013 to 2019, because of effective dust control measures, as well as decreased wind speed and increased relative humidity. However, the proportions of CM in $PM_{2.5}$ have shown consecutive annual increases. In addition, CM concentrations and their proportions increased significantly during 2019–2022, which might be responsible for the resuspension of surrounding soil dust. Correspondingly, the annual pH increased by 0.11 units from 2013 to 2019 mainly due to the decline in SO_4^{2-}, increased TNH_x, or decreased temperature. During the period from 2020 to 2022, the annual average growth rate of pH values increased to 0.21 units from 2019 to 2022, which was determined by the rise in Ca^{2+} concentration.

5 Implication

Control measures implemented by the Chinese government have proven effective in reducing dust, but this study reveals that the crustal materials in $PM_{2.5}$ rebounded after 2019. This phenomenon is not unique to Zhengzhou, as major cities in the North China Plain have also experienced a pronounced upward trend in coarse particles after 2019 (Fig. S12). Thus, crustal materials persist as a substantial constituent of atmospheric aerosols in North China, sustaining elevated particle pH levels. Extensive research has established that heightened particle pH inhibits nitrate reduction in aerosols (Ding et al., 2019; Lin et al., 2020; Wen et al., 2018), particularly significant given nitrate's predominant role in haze formation within this region. Notably, while moderately acidic aerosols demonstrate reduced health impacts, particles with pH < 3 exhibit substantially greater health risks (Shi et al., 2019). Consequently, future environmental management strategies must prioritize real-time assessment of

regulatory impacts on particle acidity. This necessitates an integrated approach that simultaneously addresses acidic precursors, alkaline precursors, and crustal material contributions to atmospheric acid chemistry.

Data availability

All the data presented in this article can be accessed through https://doi.org/10.5281/zenodo.14032007 (Zhang, 2024).

Supporting Information

Additional data, figures, and tables, some of which are referenced directly within the manuscript, and detailed descriptions of field measurements and samples.

Author contributions

Shenbo Wang designed this study. Hongyu Zhang and Zhangsen Dong analyzed the data and prepared the manuscript with the contributions of all coauthors. Xiao Li conducted measurements. Ruiqin Zhang provided funding acquisition. All authors have read and agreed to the published version of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgment

This work was supported by the National Key Research and Development Program of China (No. 2024YFC3713701), the China Postdoctoral Science Foundation (2023 M733220), the Zhengzhou $PM_{2.5}$ and O_3 Collaborative Control and Monitoring Project (20220347 A), and the National Key R&D Program of China No. 2017YFC0212400.

Funding Sources

This work was supported by the National Key Research and Development Program of China (No. 2024YFC3713701), the China Postdoctoral Science Foundation (2023 M733220), the Zhengzhou $PM_{2.5}$ and O_3 Collaborative Control and Monitoring Project (20220347 A), and the National Key Research and Development Program of China (No. 2017YFC0212400).

References

Battaglia, M. A.; Douglas, S.; Hennigan, C.: Effect of the urban heat island on aerosol pH, Environ. Sci. Technol., 51, 13095–13103, https://doi.org/10.1021/acs.est.7b02786, 2017.

Chang, R. Y. W.; Slowik, J. G.; Shantz, N. C.; Vlasenko, A.; Liggio, J.; Sjostedt, S. J.; Leaitch, W. R.; Abbatt, J. P. D. The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation. Atmos. Chem. Phys., 10, 5047–5064, https://doi.org/10.5194/acp-10-5047-2010, 2010.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939–7954, https://doi.org/10.5194/acp-19-7939-2019, 2019.

Dong, J., Li, B., Li, Y., Zhou, R., Gan, C., Zhao, Y., Liu, R., Yang, Y., Wang, T., and Liao, H.:

Atmospheric ammonia in China: Long-term spatiotemporal variation, urban-rural gradient, and influencing factors, Sci. Total Environ., 883, 163733, https://doi.org/10.1016/j.scitotenv.2023.163733, 2023.

Fountoukis, C and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols, Atmos. Chem. Phys., 7, 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, 10,355–310,376, https://doi.org/10.1002/2016JD025311, 2016.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211–5228, https://doi.org/10.5194/acp-15-5211-2015, 2015.

Heald, C.; Collett, J. J.; Lee, T.; Benedict, K.; Schwandner, F.; Li, Y.; Clarisse, L.; Hurtmans, D. R.; Van, D. M.; Clerbaux, C.; Coheur, P. F., Philip, S.; Martin, R. V.; Pye, T.: Atmospheric ammonia and particulate inorganic nitrogen over the United States, Atmos. Chem. Phys., 12, 10295–10312, https://doi.org/10.5194/acp-12-10295-2012, 2012.

Huang, X., Song, Y., Li, M., Li, J., Huo, Q., Cai, X., Zhu, T., Hu, M., and Zhang, H.: A high-resolution ammonia emission inventory in China, Global. Biogeochem. Cy., 26, GB1030, https://doi.org/10.1029/2011GB004161, 2012.

Jiang, N.; Duan, S.; Yu, X.; Zhang, R.; Wang, K. Comparative major components and health risks of toxic elements and polycyclic aromatic hydrocarbons of $PM_{2.5}$ in winter and summer in Zhengzhou: Based on three-year data. Atmos. Res., 213, 173–184, https://doi.org/10.1016/j.atmosres.2018.06.008, 2018.

Karydis, V. A., Tsimpidi, A. P., Pozzer, A., and Lelieveld, J.: How alkaline compounds control atmospheric aerosol particle acidity, Atmos. Chem. Phys., 21, 14983–15001, https://doi.org/10.5194/acp-21-14983-2021, 2021.

Kim, Y., Park, O., Park, S. H., Kim, M. J., Kim, J.-J., Choi, J.-Y., Lee, D., Cho, S., and Shim, S.: $PM_{2.5}$ pH estimation in Seoul during the KORUS-AQ campaign using different thermodynamic models, Atmos. Environ., 268, 118787, https://doi.org/10.1016/j.atmosenv.2021.118787, 2022.

Lei, L., Zhou, W., Chen, C., He, Y., Li, Z., Sun, J., Tang, X., Fu, P., Wang, Z., and Sun, Y.: Long-term characterization of aerosol chemistry in cold season from 2013 to 2020 in Beijing, China, Environ. Pollut., 268, 115952, https://doi.org/10.1016/j.envpol.2020.115952, 2021.

Li, C.; Hu, Y.; Chen, J.; Ma, Z.; Ye, X.; Yang, X.; Wang, L.; Wang, X.; Mellouki, A. Physiochemical properties of carbonaceous aerosol from agricultural residue burning: Density, volatility, and hygroscopicity. Atmos. Environ., 140, 94–105, https://doi.org/10.1016/j.atmosenv.2016.05.052, 2016.

Li, W., Xu, L., Liu, X., Zhang, J., Lin, Y., Yao, X., Gao, H., Zhang, D., Chen, J., Wang, W., Harrison, R. M., Zhang, X., Shao, L., Fu, P., Nenes, A., and Shi, Z.: Air pollution-aerosol interactions produce more bioavailable iron for ocean ecosystems, Sci. Adv., 3, e1601749, https://doi.org/10.1126/sciadv.1601749, 2017.

Li, Y., Lei, L., Sun, J., Gao, Y., Wang, P., Wang, S., Zhang, Z., Du, A., Li, Z., Wang, Z., Kim, J. Y., Kim, H., Zhang, H., and Sun, Y.: Significant reductions in secondary aerosols after the Three-Year Action Plan in Beijing summer, Environ. Sci. Technol., 57, 15945–15955, https://doi.org/10.1021/acs.est.3c02417, 2023.

Lin, Y., Zhang, Y., Fan, M, and Bao, M.: Heterogeneous formation of particulate nitrate under ammonium-rich regimes during the high-$PM_{2.5}$ events in Nanjing, China, Atmos. Chem. Phys., 20, 3999–4011, https://doi.org/10.5194/acp-20-3999-2020, 2020.

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

Liu, Z., Gao, W., Yu, Y., Hu, B., Xin, J., Sun, Y., Wang, L., Wang, G., Bi, X., Zhang, G., Xu, H., Cong, Z., He, J., Xu, J., and Wang, Y.: Characteristics of $PM_{2.5}$ mass concentrations and chemical species

in urban and background areas of China: emerging results from the CARE-China network, Atmos. Chem. Phys., 18, 8849-8871, https://doi.org/10.5194/acp-18-8849-2018, 2018.

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, 5622–5629, https://doi.org/10.1016/j.atmosenv.2009.07.054, 2009.

Masiol, M., Squizzato, S., Formenton, G., Khan, M. B., Hopke, P. K., Nenes, A., Pandis, S. N., Tositti, L., Benetello, F., Visin, F., and Pavoni, B.: Hybrid multiple-site mass closure and source apportionment of $PM_{2.5}$ and aerosol acidity at major cities in the Po Valley, Sci. Total Environ., 704, 135287, https://doi.org/10.1016/j.scitotenv.2019.135287, 2020.

MEP (Ministry of Environment Protection), 2023. https://www.mee.gov.cn/ywdt/hjywnews/202406/t20240605_1075031.shtml, Accessed date:5 June 2024.

Nah, T., Lam, Y. H., Yang, J., and Yang, L.: Long-term trends and sensitivities of $PM_{2.5}$ pH and aerosol liquid water to chemical composition changes and meteorological parameters in Hong Kong, South China: Insights from 10-year records from three urban sites, Atmos. Environ., 302, https://doi.org/10.1016/j.atmosenv.2023.119725, 2023.

Nenes, A., Pandis, S. N., Kanakidou, M., Russell, A. G., Song, S., Vasilakos, P., and Weber, R. J.: Aerosol acidity and liquid water content regulate the dry deposition of inorganic reactive nitrogen, Atmos. Chem. Phys., 21, 6023–6033, https://doi.org/10.5194/acp-21-6023-2021, 2021.

Pinder, R., Adams, P., and Pandis, S.: Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the eastern United States, Environ. Sci. Technol., 41, 380–386, https://doi.org/10.1021/es060379a, 2007.

Pinder, R., Gilliland, A., and Dennis, R.: Environmental impact of atmospheric NH_3 emissions under present and future conditions in the eastern United States, Geophys. Res. Lett., 35, 28, https://doi.org/10.1029/2008gl033732, 2008.

Pye, H. O. T.; Nenes, A.; Alexander, B.; Ault, A. P.; Barth, M. C.; Clegg, S. L.; Collett Jr, J. L.; Fahey, K. M.; Hennigan, C. J.; Herrmann, H.; Kanakidou, m.; Kelly, J. T.; Ku, L.; McNeill, V. F.; Riemer, N.; Schaefer, T.; Shi, G.; Tilgner, A.; Walker, J.T.; Wang, T.; Weber, R.; Xing, J.; Zaveri, R. A.; Zuend, A. The acidity of atmospheric particles and clouds. Atmos. Chem. Phys., 20, 4809–4888,

https://doi.org/10.5194/acp-20-4809-2020, 2020.

Rengarajan, R., Sudheer, A. K., and Sarin, M. M.: Aerosol acidity and secondary organic aerosol formation during wintertime over urban environment in western India, Atmos. Environ., 45, 1940–1945, https://doi.org/10.1016/j.atmosenv.2011.01.026, 2011.

Seinfeld, J. H., Pandis, S. N., and Noone, K. J.: Atmospheric chemistry and physics: From air pollution to climate change, Phys. Today., 51, 88–90, https://doi.org/10.1063/1.882420, 1998.

Sharma, B., Jia, S., Polana, A. J., Ahmed, M. S., Haque, R. R., Singh, S., Mao, J., and Sarkar, S.: Seasonal variations in aerosol acidity and its driving factors in the eastern Indo-Gangetic Plain: A quantitative analysis, Chemosphere., 305, 135490, https://doi.org/10.1016/j.chemosphere.2022.135490, 2022.

Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A., and Russell, A. G.: pH of aerosols in a polluted atmosphere: source contributions to highly acidic aerosol, Environ. Sci. Technol., 51, 4289–4296, https://doi.org/10.1021/acs.est.6b05736, 2017.

Shi, X., Nenes, A., Xiao, Z., Song, S., Yu, H., Shi, G., Zhao, Q., Chen, K., Feng, Y., and Russell, A. G.: High-resolution data sets unravel the effects of sources and meteorological conditions on nitrate and its gas-particle partitioning, Environ. Sci. Technol., 53, 3048–3057, https://doi.org/10.1021/acs.est.8b06524, 2019.

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. B.: 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, 752–760, https://doi.org/10.1021/acs.estlett.9b00621, 2019.

Su, H., Cheng, Y., and Pöschl, U.: New Multiphase Chemical Processes Influencing Atmospheric Aerosols, Air Quality, and Climate in the Anthropocene, Acc. Chem. Res., 53, 2034–2043, https://doi.org/10.1021/acs.accounts.0c00246, 2020.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, Proc. Natl. Acad. Sci., 107, 6640–6645, https://doi.org/10.1073/pnas.0911114107, 2010.

Tao, Y. and Murphy, J. G.: The sensitivity of $PM_{2.5}$ acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites, Atmos. Chem. Phys., 19, 9309–9320, https://doi.org/10.5194/acp-19-9309-2019, 2019.

Tian, Y.; Chen, G.; Wang, H.; Huang-Fu, Y.; Shi, G.; Han, B.; and Feng, Y.: Source regional contributions to $PM_{2.5}$ in a megacity in China using an advanced source regional apportionment method. Chemosphere., 147, 256–263, https://doi.org/10.1016/j.chemosphere.2015.12.132, 2016.

Tremper, A.; Font, A.; Priestman, M.; Hamad, S.; Chung, T.; Pribadi, A.; Brown, R.; Goddard, S.; Grassineau, N.; Petterson, K.; Kelly, F.; Green, D.: Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols, Atmos. Meas. Tech., 11, 3541–3557, https://doi.org/10.5194/amt-11-3541-2018, 2018.

Wang, C., Yin, S., Bai, L., Zhang, X., Gu, X., Zhang, H., Lu, Q., and Zhang, R.: High-resolution ammonia emission inventories with comprehensive analysis and evaluation in Henan, China, 2006–2016, Atmos. Environ., 193, 11–23, https://doi.org/10.1016/j.atmosenv.2018.08.063, 2018.

Wang, G., Chen, J., Xu, J., Yun, L., Zhang, M., Li, H., Qin, X., Deng, C., Zheng, H., Gui, H., Liu, J., and Huang, K.: Atmospheric processing at the Sea-Land interface over the South China Sea: Secondary aerosol formation, aerosol acidity, and role of sea salts, J. Geophys. Res. Atmos., 127, https://doi.org/10.1029/2021jd036255, 2022.

Wang, L., Du, H., Chen, J., Zhang, M., Huang, X., Tan, H., Kong, L., and Geng, F.: Consecutive transport of anthropogenic air masses and dust storm plume: Two case events at Shanghai, China, Atmos. Res., 127, 22–33, https://doi.org/10.1016/j.atmosres.2013.02.011, 2013.

Wang, S., Yin, S., Zhang, R., Yang, L., Zhao, Q., Zhang, L., Yan, Q., Jiang, N., and Tang, X.: Insight into the formation of secondary inorganic aerosol based on high-time-resolution data during haze episodes and snowfall periods in Zhengzhou, China, Sci. Total Environ., 660, 47–56, https://doi.org/10.1016/j.scitotenv.2018.12.465, 2019.

Wang, S.; Wang, L.; Li, Y.; Wang, C.; Wang, W.; Yin, S.; Zhang, R.; Effect of ammonia on fine-particle pH in agricultural regions of China: comparison between urban and rural sites, Atmos. Chem. Phys., 20, 2719–2734, https://doi.org/10.5194/acp-20-2719-2020, 2020.

Wang, Y., Zhang, X., and Draxler, R.: TrajStat: GIS-based software that uses various trajectory

statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environ. Model. Softw., 24, 938–939, https://doi.org/10.1016/j.envsoft.2009.01.004, 2009.

Wang, Z., Pan, X., Uno, I., Chen, X., Yamamoto, S., Zheng, H., Li, J., and Wang, Z.: Importance of mineral dust and anthropogenic pollutants mixing during a long–lasting high PM event over East Asia, Environ. Pollut., 234, 368–378, https://doi.org/10.1016/j.envpol.2017.11.068, 2018.

Weber, R.; Guo, H.; Russell, A.; Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geoscience., 9, 282–285, https://doi.org/10.1038/ngeo2665, 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., 458, 15, https://doi.org/10.1016/10.1016/j.jhazmat.2023.131970, 2023.

Wen, L., Xue, L., Wang, X., Xu, C., Chen, T., Yang, L., Wang, T., Zhang, Q., and Wang, W.: Summertime fine particulate nitrate pollution in the North China Plain: increasing trends, formation mechanisms and implications for control policy, Atmos. Chem. Phys., 18, 11261–11275, https://doi.org/10.5194/acp-18-11261-2018, 2018.

Wexler, A. S. and Seinfeld, J. H.: Second-generation inorganic aerosol model, Atmos. Environ., Part A. General Topics, 25, 2731-2748, https://doi.org/10.1016/0960-1686(91)90203-J, 1991.

Xie, Y., Wang, G., Wang, X., Chen, J., Chen, Y., Tang, G., Wang, L., Ge, S., Xue, G., Wang, Y., and Gao, J.: Nitrate-dominated $PM_{2.5}$ and elevation of particle pH observed in urban Beijing during the winter of 2017, Atmos. Chem. Phys., 20, 5019–5033, https://doi.org/10.5194/acp-20-5019-2020, 2020.

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.

Yu, F., Yan, Q., Jiang, N., Su, F., Zhang, L., Yin, S., Li, Y., Zhang, R., and Chen, L.: Tracking pollutant

597 characteristics during haze events at background site Zhongmu, Henan Province, China, Atmos.
598 Pollut. Res., 8, 64–73, https://doi.org/10.1016/j.apr.2016.07.005, 2017.
599 Zhai, S.; Jacob, DJ.; Wang, X.; Shen, L.; Li, K.; Zhang, Y.; Gui, K.; Zhao, T.; Liao, H. Fine particulate
600 matter ($PM_{2.5}$) trends in China, 2013–2018: separating contributions from anthropogenic
601 emissions and meteorology, Atmos. Chem. Phys., 19, 11031–11041, https://doi.org/10.5194/acp-
602 19-11031-2019, 2019.
603 Zhang, B., Shen, H., Liu, P., Guo, H., Hu, Y., Chen, Y., Xie, S., Xi, Z., Skipper, T. N., and Russell, A.
604 G.: Significant contrasts in aerosol acidity between China and the United States, Atmos. Chem.
605 Phys., 21, 8341–8356, https://doi.org/10.5194/acp-21-8341-2021, 2021.
606 Zhang, G., Ding, C., Jiang, X., Pan, G., Wei, X., and Sun, Y.: Chemical compositions and sources
607 contribution of atmospheric particles at a typical steel industrial urban site, Sci. Rep., 10, 7654,
608 https://doi.org/10.1038/s41598-020-64519-x, 2020.
609 Zhang, Z., Dong, Z., Zhang, C., Qian, G., and Lei, C.: The geochemical characteristics of dust material
610 and dust sources identification in northwestern China, J. Geochem. Explor., 175, 148–155,
611 https://doi.org/10.1016/j.gexplo.2016.11.006, 2017.
612 Zhang, Z., Kuang, Z., Yu, C., Wu, D., Shi, Q., Zhang, S., Wang, Z., and Liu, D.: Trans–boundary dust
613 transport of dust storms in Northern China: A study utilizing ground–based lidar network and
614 CALIPSO satellite, Remote sens.,16, 1196, https://doi.org/10.3390/rs16071196, 2024.
615 Zheng, G., Su, H., and Cheng, Y.: Revisiting the key driving processes of the decadal trend of aerosol
616 acidity in the U.S, Acs. Environ. Au., 2, 346–353, https://doi.org/10.1021/acsenvironau.1c00055,
617 2022.
618 Zheng, G., Su, H., Wang, S., Andreae, M. O., Pöschl, U., and Cheng, Y.: Multiphase buffer theory
619 explains contrasts in atmospheric aerosol acidity, Science., 369, 1374–1377,
620 https://doi.org/10.1126/science.aba3719, 2020.
621 Zhou, M., Zheng, G., Wang, H., Qiao, L., Zhu, S., Huang, D., An, J., Lou, S., Tao, S., Wang, Q., Yan,
622 R., Ma, Y., Chen, C., Cheng, Y., Su, H., and Huang, C.: Long-term trends and drivers of aerosol
623 pH in eastern China, Atmos. Chem. Phys., 22, 13833–13844, https://doi.org/10.5194/acp-22-
624 13833-2022, 2022.

Zhou, W., Gao, M., He, Y., Wang, Q., Xie, C., Xu, W., Zhao, J., Du, W., Qiu, Y., Lei, L., Fu, P., Wang, Z., Worsnop, D. R., Zhang, Q., and Sun, Y.: Response of aerosol chemistry to clean air action in Beijing, China: Insights from two-year ACSM measurements and model simulations, Environ Pollut., 255, 113345, https://doi.org/10.1016/j.envpol.2019.113345, 2019.

Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, Atmos. Chem. Phys., 12, 3857–3882, https://doi.org/10.5194/acp-12-3857-2012, 2012.

Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols, Atmos. Chem. Phys., 10, 7795–7820, https://doi.org/10.5194/acp-10-7795-2010, 2010.

Figures

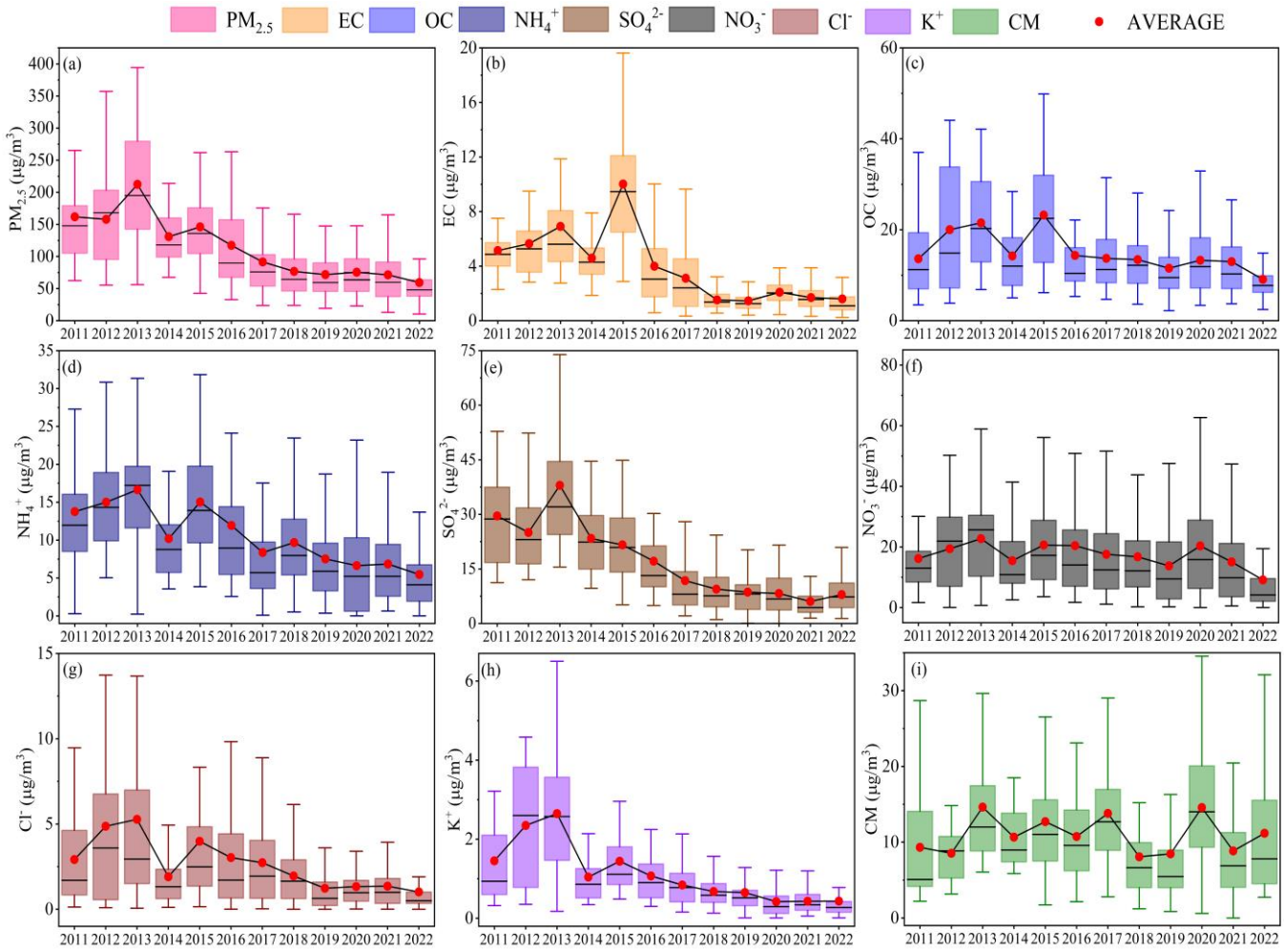
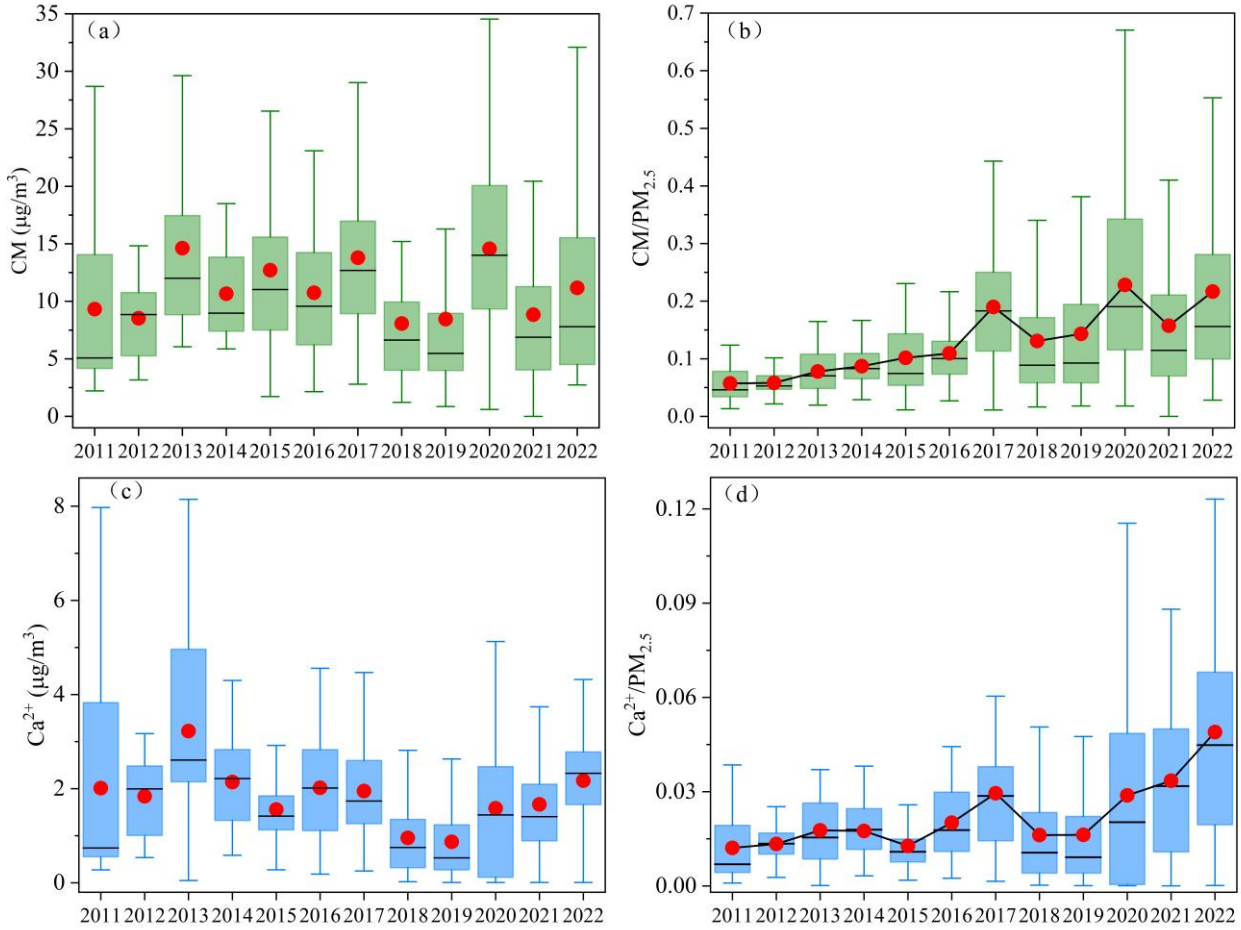


Figure 2. Long-term trends in the concentrations of $PM_{2.5}$ and its chemical components in from 2011 to 2022 in Zhengzhou. Box plots depict annual averages (red dots) and medians (black lines), the top, middle, and bottom lines represent the 75, 50, and 25 percentiles of statistical data, respectively, and the upper and lower whiskers represent the 90 and 10 percentiles of statistical data, respectively.



642

643 Figure 3. (a) and (c) Long-term trends in CM and Ca^{2+} concentrations in Zhengzhou from 2011 to
644 2022, respectively. Box plots depict annual averages (red dots) and medians (black lines). (b) and (d)
645 Long-term trends in the proportions of CM and Ca^{2+} in $PM_{2.5}$, respectively.

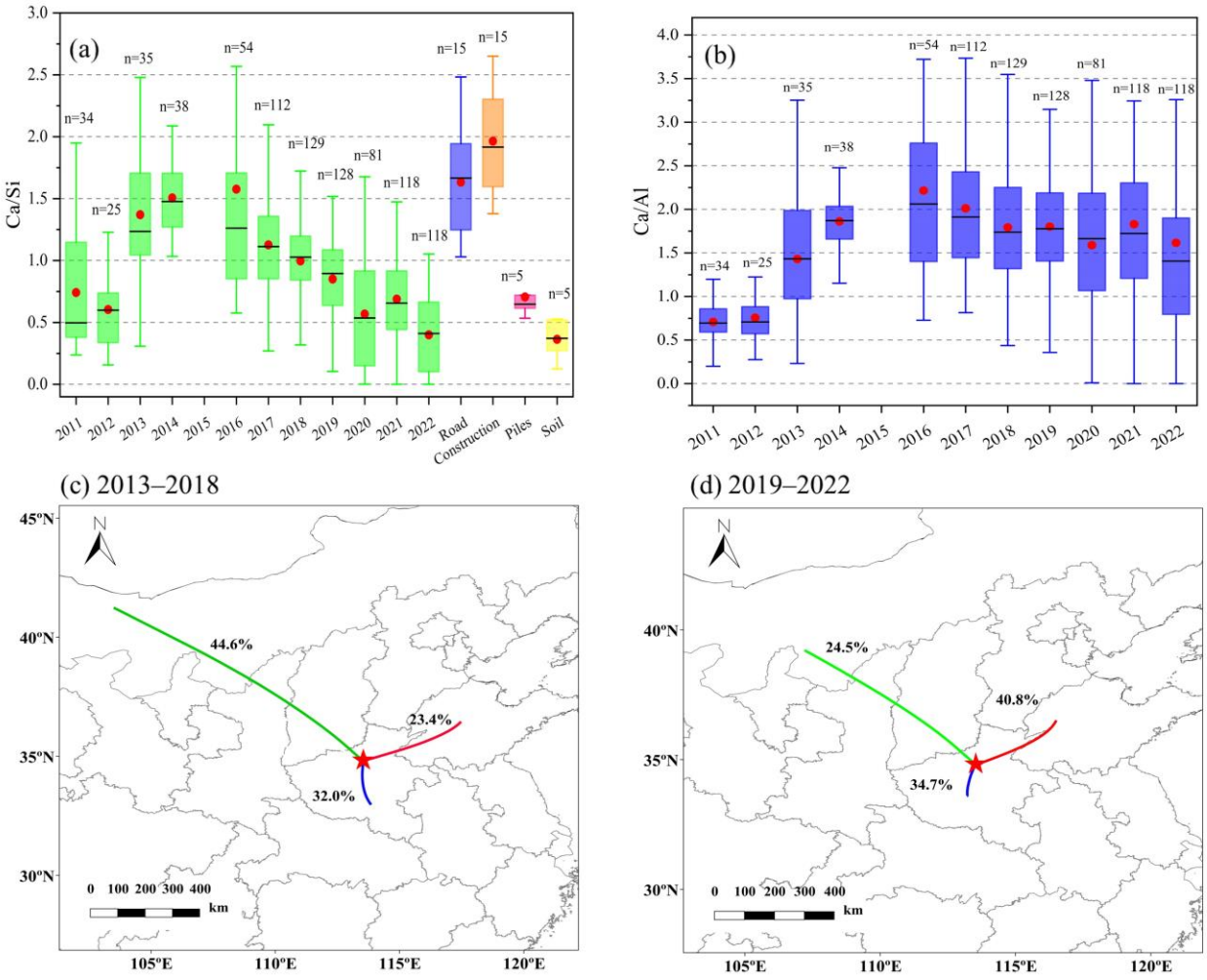


Figure 4. (a) The annual Ca/Si ratios in Zhengzhou from 2011 to 2022 compared with those in various dust sources (specific values and references in Table S5). The red dots and black lines in the box plots represent the annual averages and medians, respectively, with n indicating the sample size. (b) The Ca/Al ratios in Zhengzhou from 2011 to 2022. The red dots and black lines in the box plots represent the annual averages and medians, respectively, with n indicating the sample size. (c) and (d) The transport pathways of CM during 2013–2018 and 2019–2022, respectively.

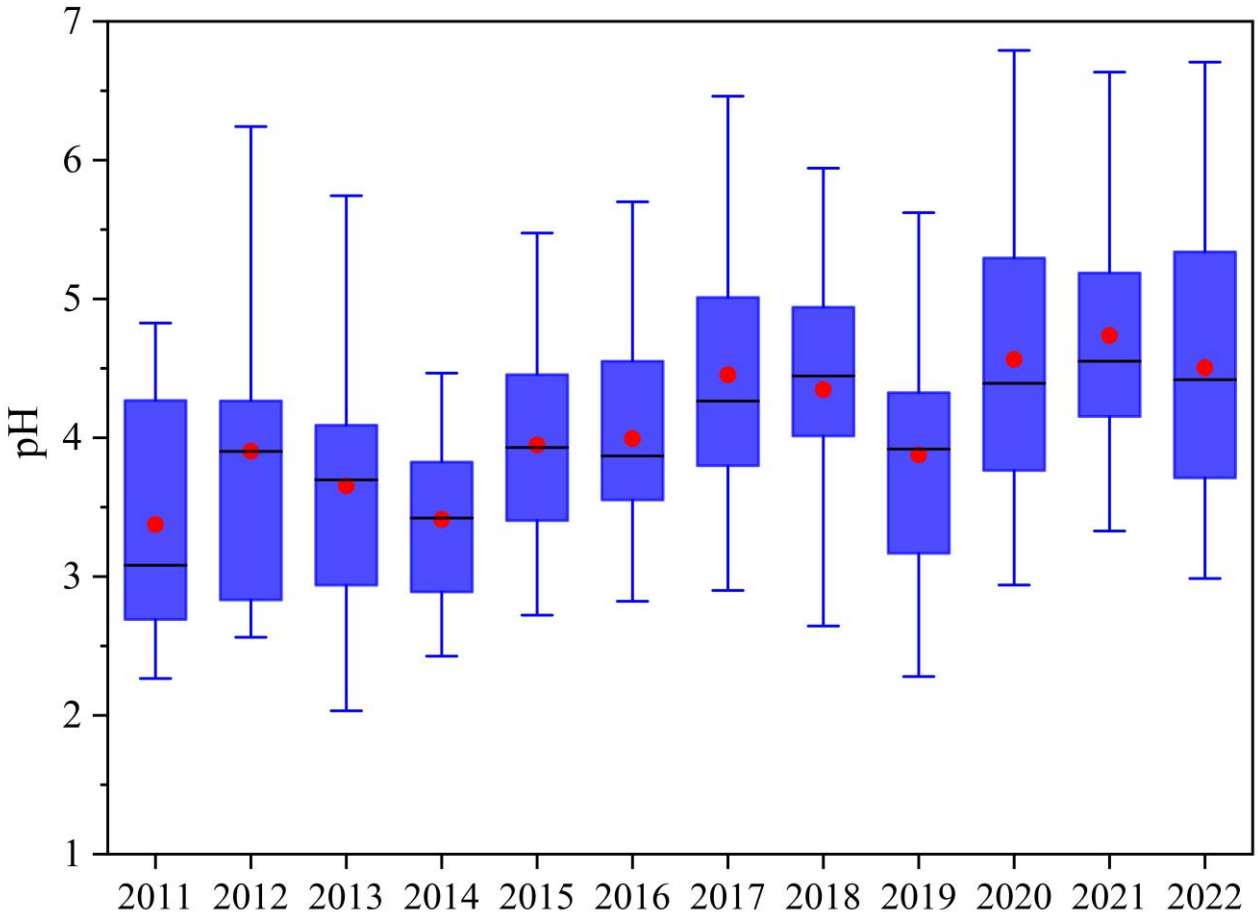


Figure 5. The time series of particle pH in Zhengzhou from 2011 to 2022. In the boxplots, red dots and black lines represent the annual mean and median values, respectively.

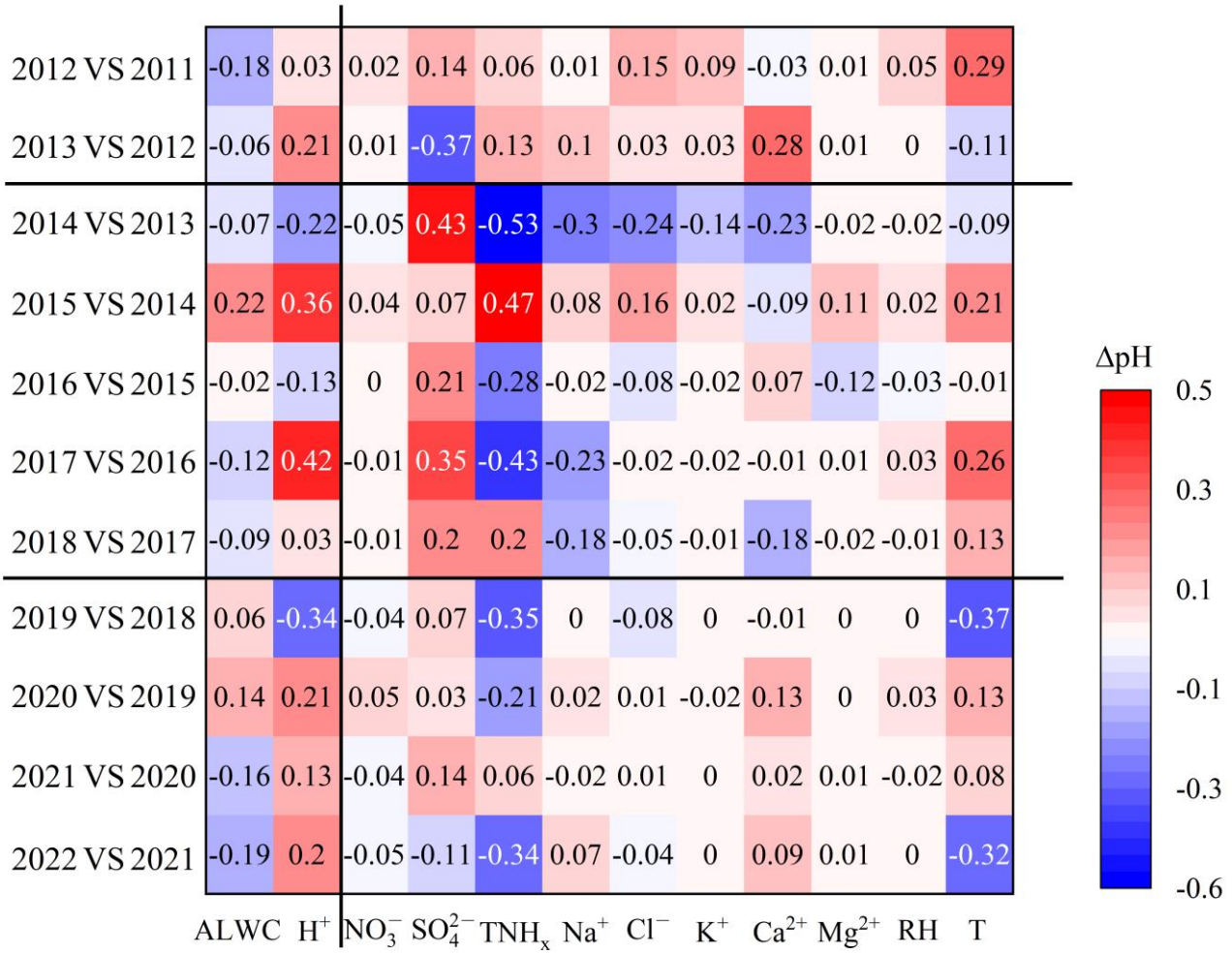


Figure 6. Contribution of each component to the changes in pH (ΔpH) between adjacent years. The difference between component concentrations and meteorological parameters between adjacent years is listed in Table S6.

Table

Table 1. Annual average concentrations of $PM_{2.5}$ and its components from 2011 to 2022 in Zhengzhou, China (μg/m^3).

Years	$PM_{2.5}$	EC	OC	NO_3^-	SO_4^{2-}	NH_4^+	CM	Ca^{2+}
2011	161.9 ± 81.4	5.1 ± 2.1	13.6 ± 8.6	16.2 ± 11.2	29.6 ± 14.3	13.8 ± 8.3	9.3 ± 7.3	2.0 ± 2.2
2012	157.9 ± 71.2	5.6 ± 2.5	20.0 ± 13.4	20.2 ± 13.7	25.0 ± 11.2	15.0 ± 7.1	8.5 ± 3.4	1.8 ± 0.8
2013	212.4 ± 101.5	6.9 ± 3.8	21.5 ± 10.4	22.7 ± 13.2	38.0 ± 19.9	17.1 ± 6.9	14.6 ± 8.3	3.2 ± 2.1
2014	130.8 ± 48.7	4.6 ± 2.0	14.2 ± 8.2	15.5 ± 10.8	23.4 ± 9.3	10.2 ± 6.2	10.7 ± 4.4	2.1 ± 1.0
2015	146.1 ± 61.0	10.0 ± 4.7	23.2 ± 11.6	20.6 ± 14.5	21.6 ± 9.8	15.7 ± 7.5	12.7 ± 6.8	1.6 ± 0.7
2016	117.4 ± 73.5	4.0 ± 2.8	14.4 ± 10.0	20.4 ± 18.7	17.1 ± 11.3	11.9 ± 10.6	10.8 ± 5.3	2.0 ± 1.1
2017	91.5 ± 61.1	3.1 ± 2.5	13.7 ± 7.5	17.6 ± 15.9	11.8 ± 11.6	8.4 ± 7.9	13.8 ± 6.5	2.0 ± 1.0
2018	76.8 ± 41.6	1.5 ± 0.7	13.4 ± 7.3	16.7 ± 13.5	9.4 ± 6.0	9.7 ± 6.1	8.1 ± 5.7	1.0 ± 0.8
2019	68.4 ± 34.8	1.5 ± 0.8	11.5 ± 6.8	13.8 ± 13.9	8.6 ± 6.4	7.5 ± 6.1	8.5 ± 7.8	0.9 ± 0.9
2020	75.5 ± 31.8	2.1 ± 0.9	13.3 ± 7.9	18.6 ± 14.2	8.3 ± 5.6	6.7 ± 6.6	14.6 ± 7.6	1.6 ± 1.4
2021	71.5 ± 45.9	1.7 ± 0.9	13.0 ± 8.0	15.1 ± 15.1	6.1 ± 4.5	6.8 ± 6.0	8.9 ± 7.0	1.7 ± 1.2
2022	59.5 ± 41.1	1.6 ± 1.5	9.1 ± 8.1	10.0 ± 14.4	7.9 ± 4.5	5.5 ± 5.4	11.2 ± 8.3	2.2 ± 1.1

Supplement materials:

Text S1 Instruments and Measurements.

Samples were collected using a high-volume sampler (TE-6070D, Tisch, USA) and air particulate samplers (TH-16A, Tianhong, China) from April 2011 to December 2022. Two quartz filters and two Teflon filters were used daily from 10:00 AM to 9:00 AM the next day, resulting in a total of 5848 samples. After excluding abnormal data due to instrument malfunctions, 4228 valid samples were obtained. Detailed information on the samples is provided in Table S1.

Organic carbon (OC) and elemental carbon (EC) were analyzed using a carbon analyzer (Model 5L, Sunset Laboratory, USA). The analysis of EC and OC was conducted in two stages. In the first stage, the filter membrane was placed in a quartz heating furnace under a pure helium atmosphere. As the temperature gradually increased to approximately 580°C, OC was volatilized and released. In the second stage, heating continued in a mixed atmosphere of 2% oxygen and 98% helium. When the temperature reached approximately 870°C, EC underwent oxidative decomposition and was released. During the helium flow transmission, OC and EC released at different temperatures were completely oxidized to CO_2 in a MnO_2 oxidation furnace and subsequently reduced to CH_4 for detection by a flame ionization detector (FID). The detection limits for both OC and EC were 0.2 μg/cm². Before each sample analysis, calibration was performed using a standard sucrose solution. Additionally, parallel tests were conducted every ten samples to ensure accuracy.

Water-soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were measured using ion chromatography (ICS-90 and ICS-900 models, Dionex, USA). Half of the $PM_{2.5}$ filter was

cut into pieces and ultrasonically extracted with 20 mL of Milli-Q water for 30 min, followed by filtering through a 0.45 mm polytetrafluoroethylene syringe filter before analysis. The cation concentrations were determined by an IonPacASll-HC4 mm anion separation column and an IonPacAGll-HC4 mm guard column, with 20 mM methane sulfonate as an eluent at 0.8 mL/min. The anions were measured by an IonPacCS12A cation separation column and an IonPacCG12A guard column, with a solution of 8.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$ as an eluent at 1.0 mL/min. The regression coefficients (R^2) of the calibration curves were over 0.9996 for all ions, except NH_4^+ (0.9988), which showed a quadratic response.

Elements were analyzed using a wavelength dispersive X-ray fluorescence spectrometer (S8 TIGER, Bruker, Germany) to determine concentrations of Fe, Na, Mg, Al, Si, Cl, K, Ca, V, Ni, Cu, Zn, Cr, Mn, Co, Cd, Ga, As, Se, Sr, Sn, Sb, Ba, and Pb (Tremper et al., 2018), which has been approved by the United States Environmental Protection Agency (Chow and Watson, 1994). The spectrometer was equipped with an X-ray tube featuring close coupling among the tube, sample, and detector, ensuring high efficiency and optimal excitation of elements within the sample. Before analysis, the instrument was calibrated using a series of high-quality, self-prepared standards. Calibration procedures were conducted following established methods (Chow and Watson, 1994). To assess potential contamination and ensure data quality, blank filters were routinely analyzed alongside each batch of samples.

Figures

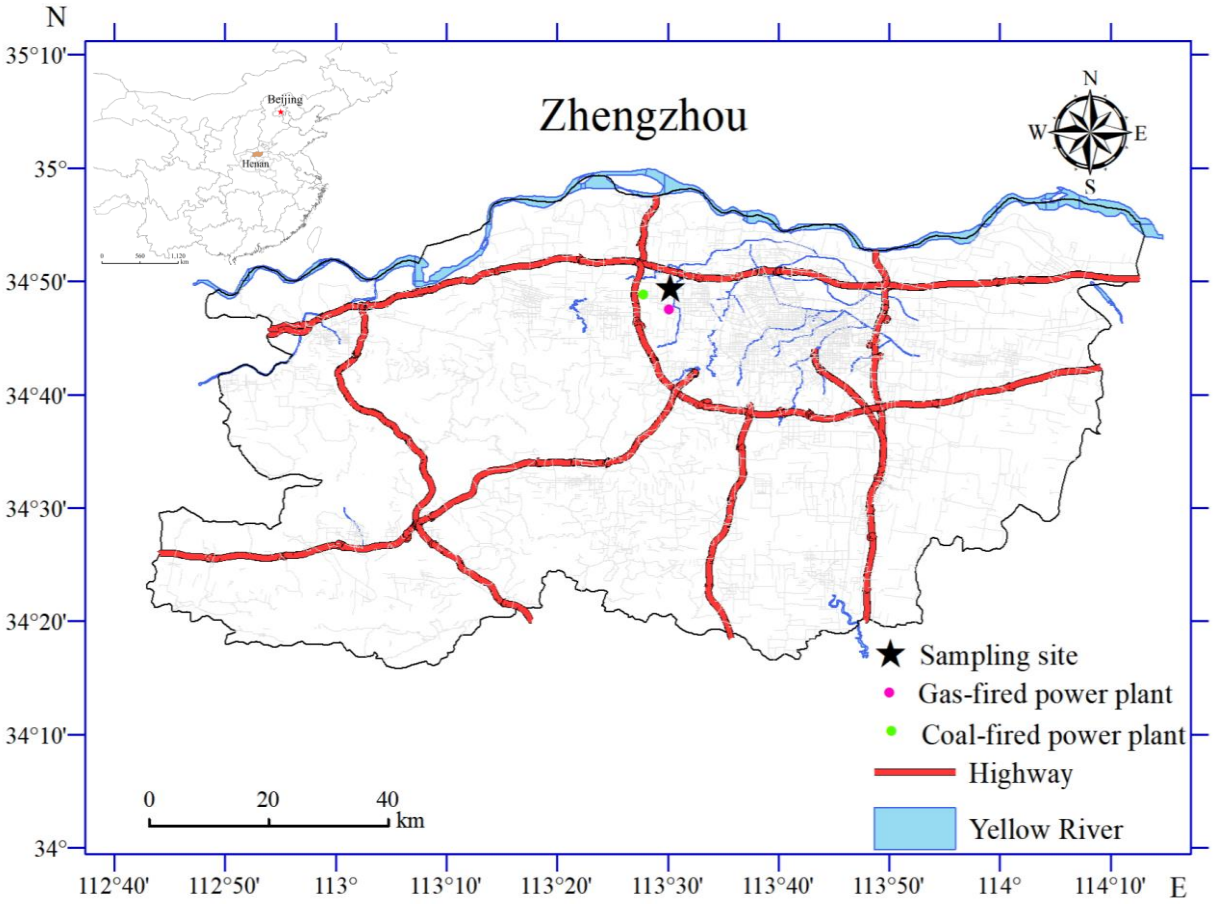


Figure S1.Sampling site in Zhengzhou, China. © 2019 National Geomatics Center of China. All rights reserved.

.

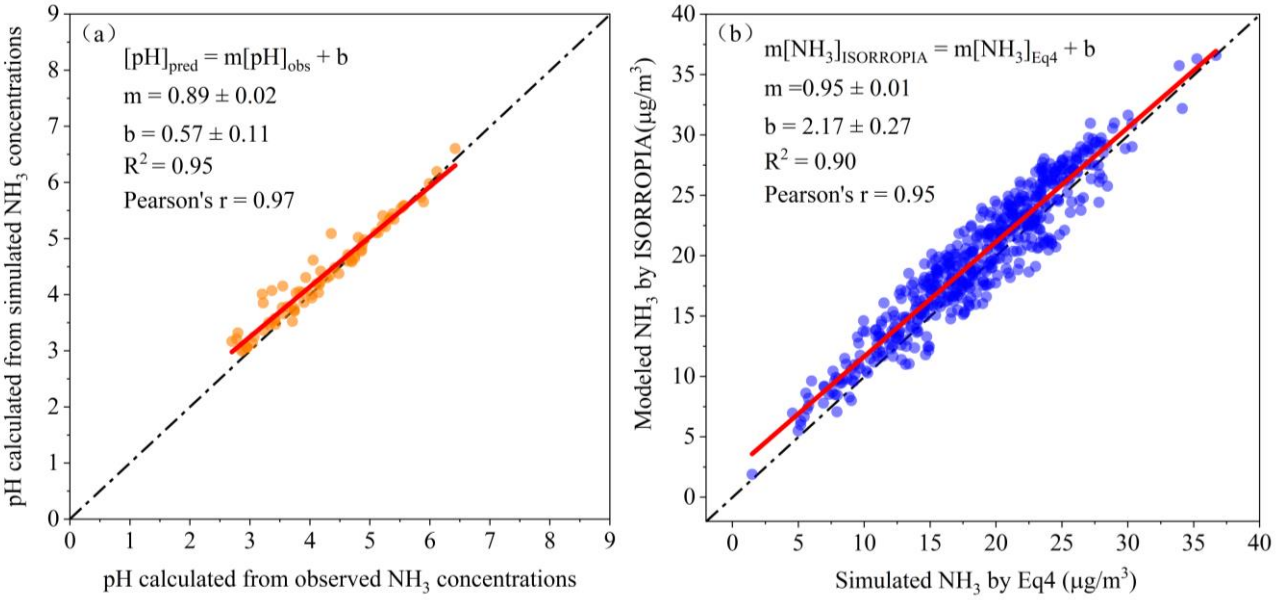


Figure S2. Verification of the NH_3 Method.

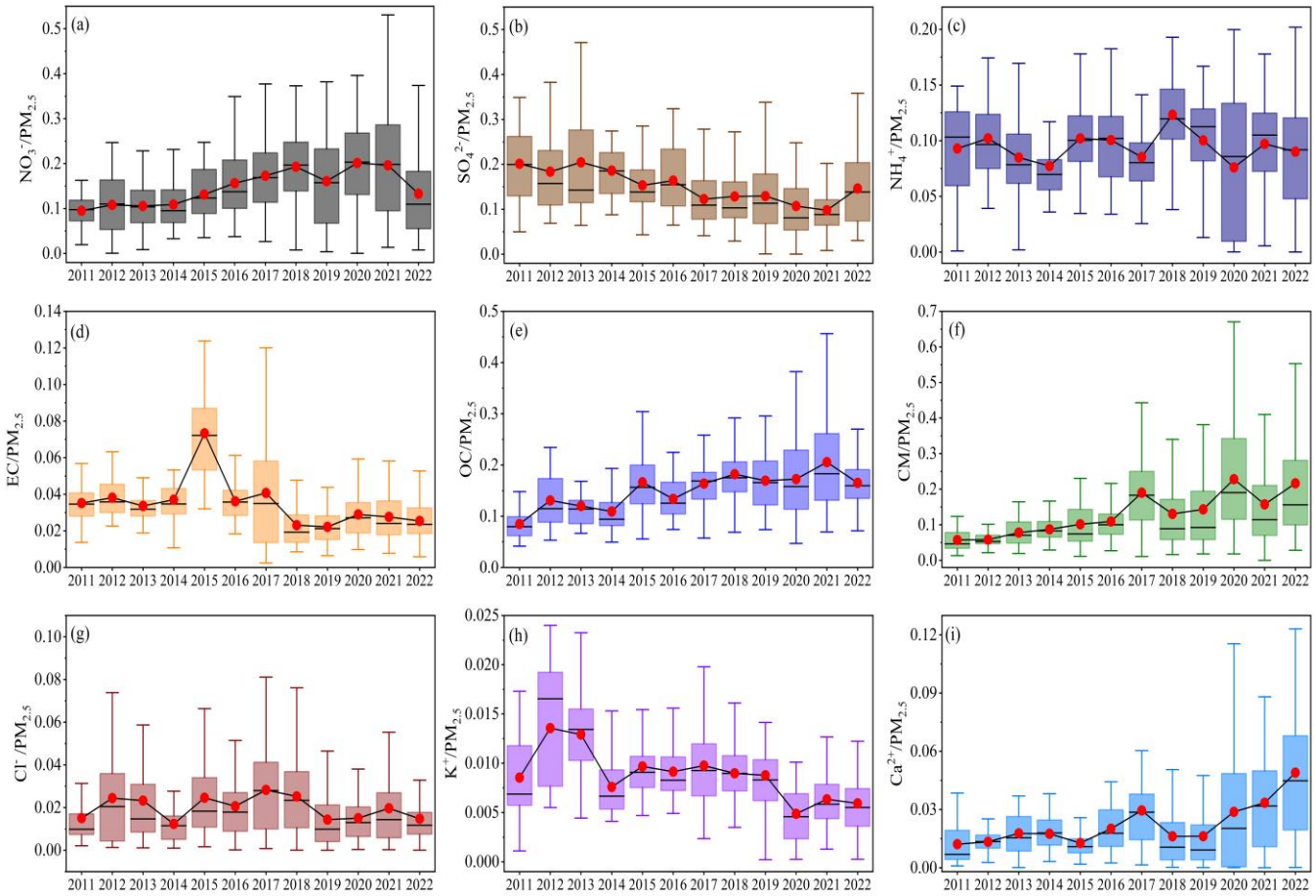


Figure S3. Trends in the proportions of chemical components in $PM_{2.5}$ from 2011 to 2022.

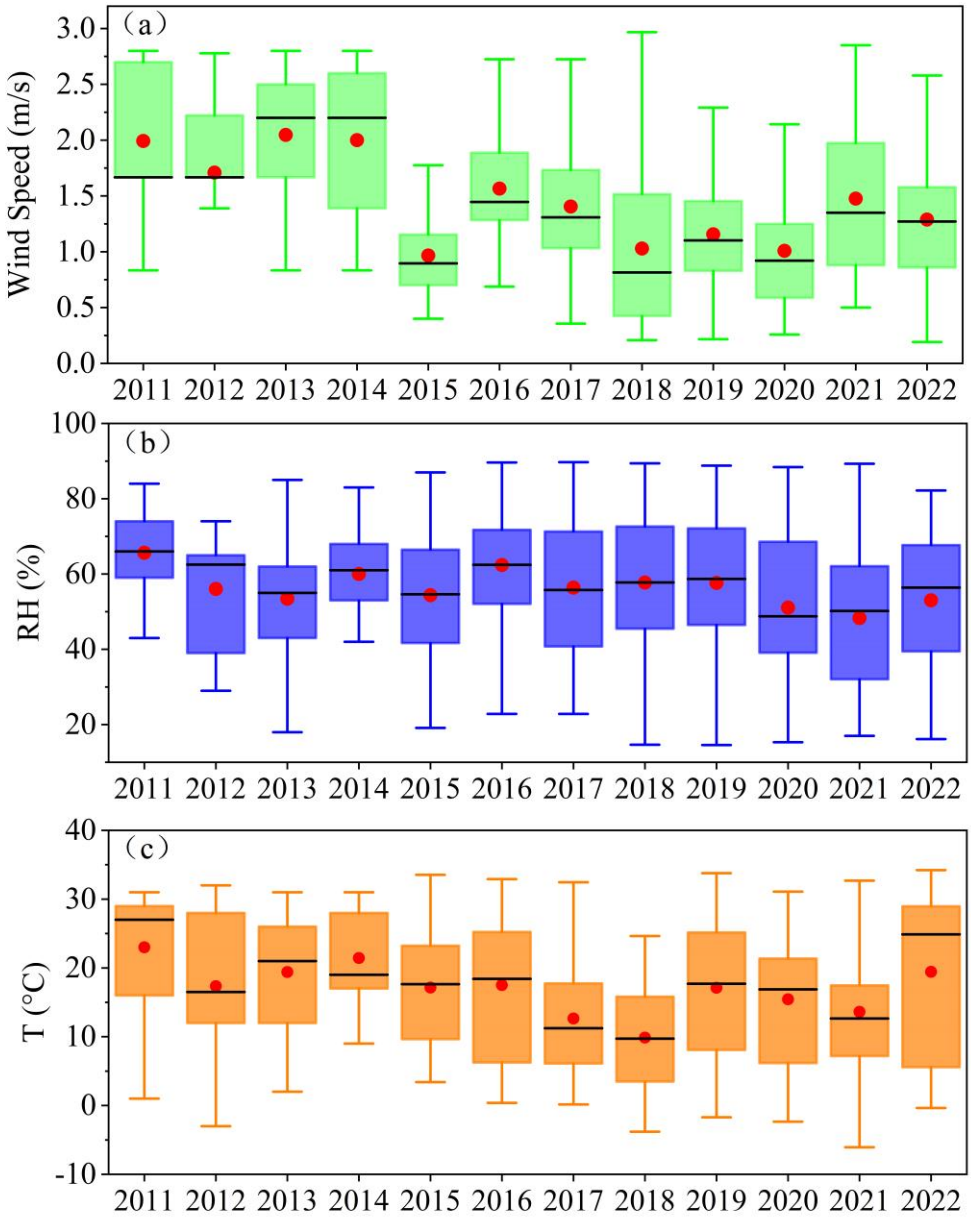


Figure S4. Trends in the meteorological parameters from 2011 to 2022.

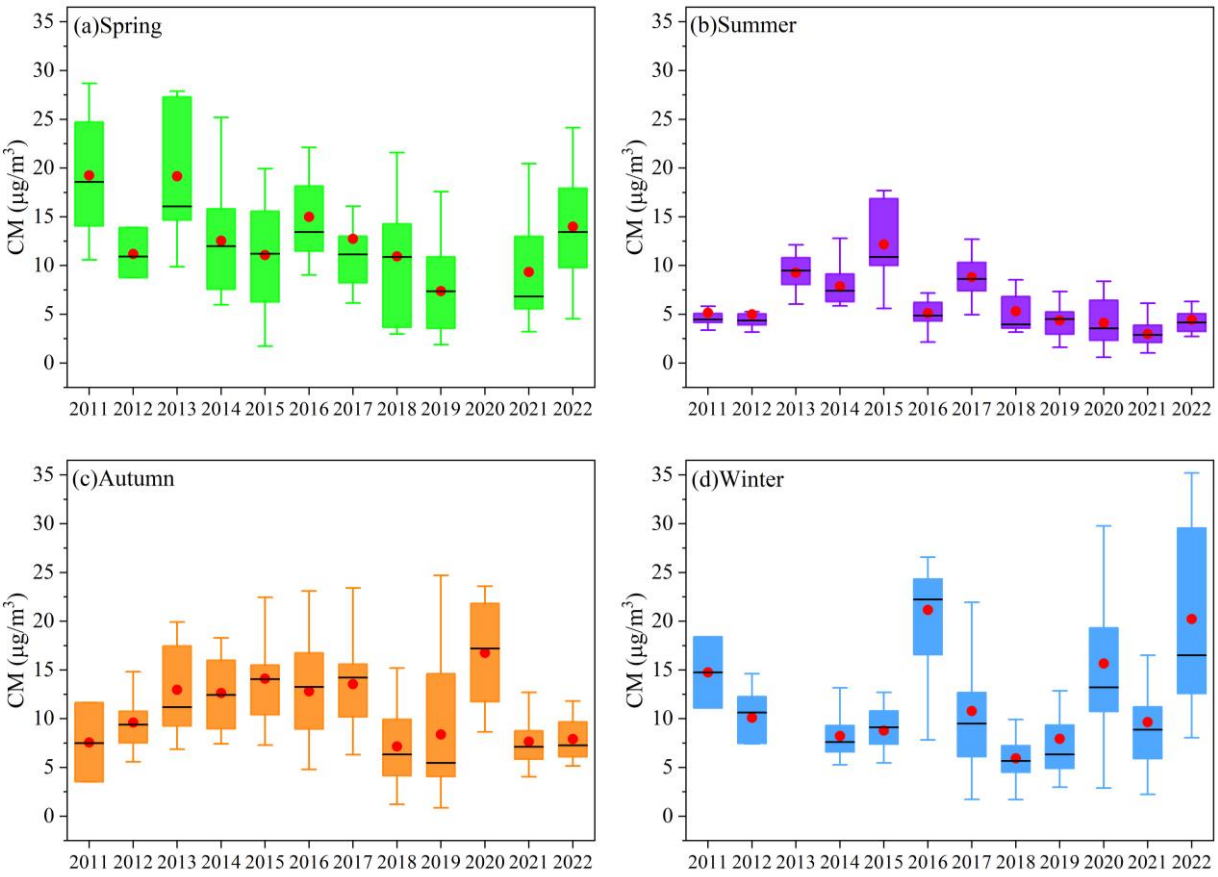


Figure S5. Trends in the CM concentrations in different seasons from 2011 to 2022.

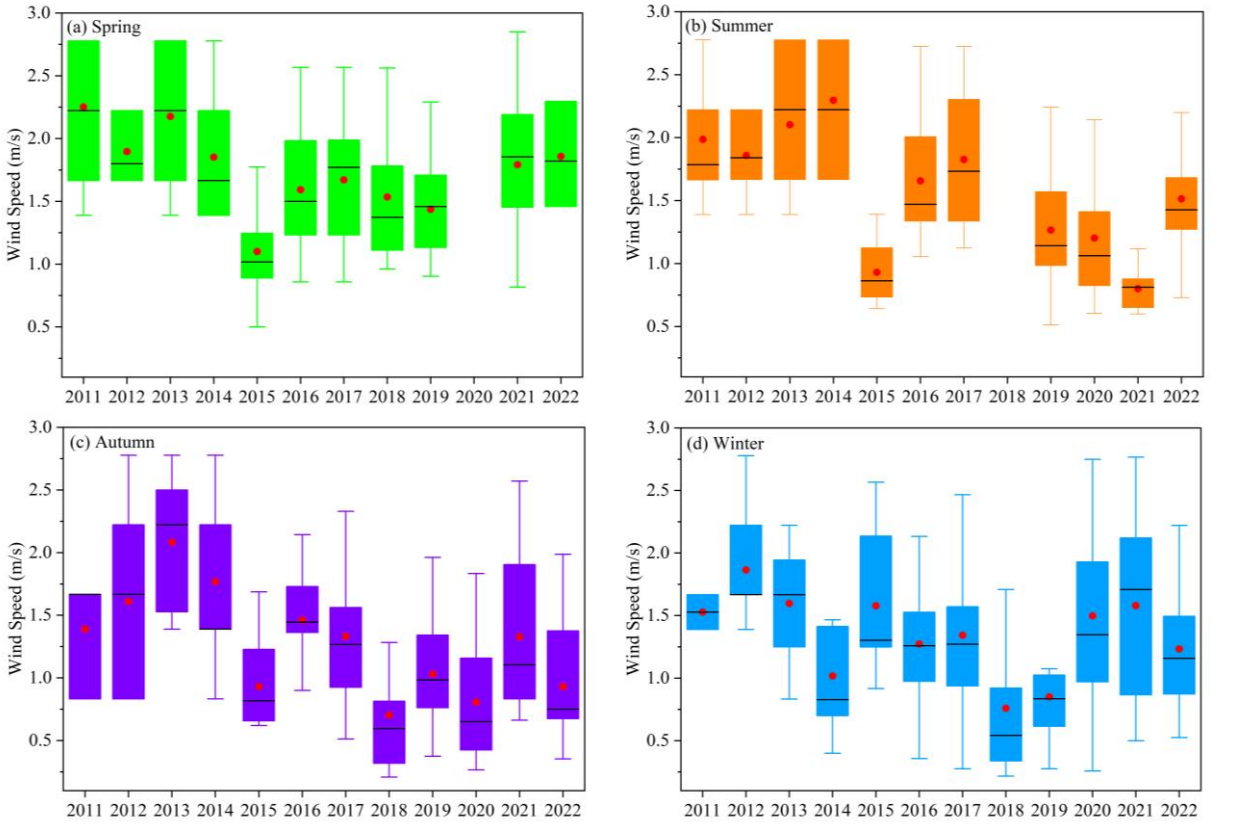


Figure S6. The variation in WS across different seasons from 2011 to 2022.

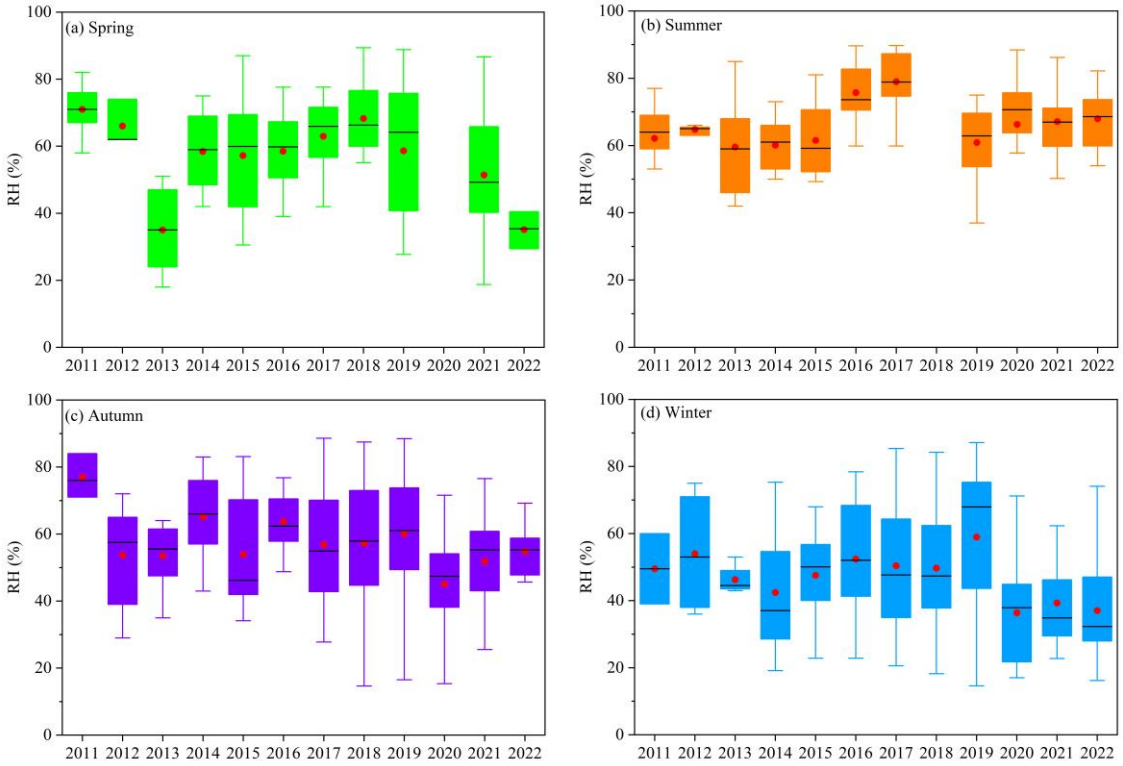


Figure S7. The variation in RH across different seasons from 2011 to 2022.

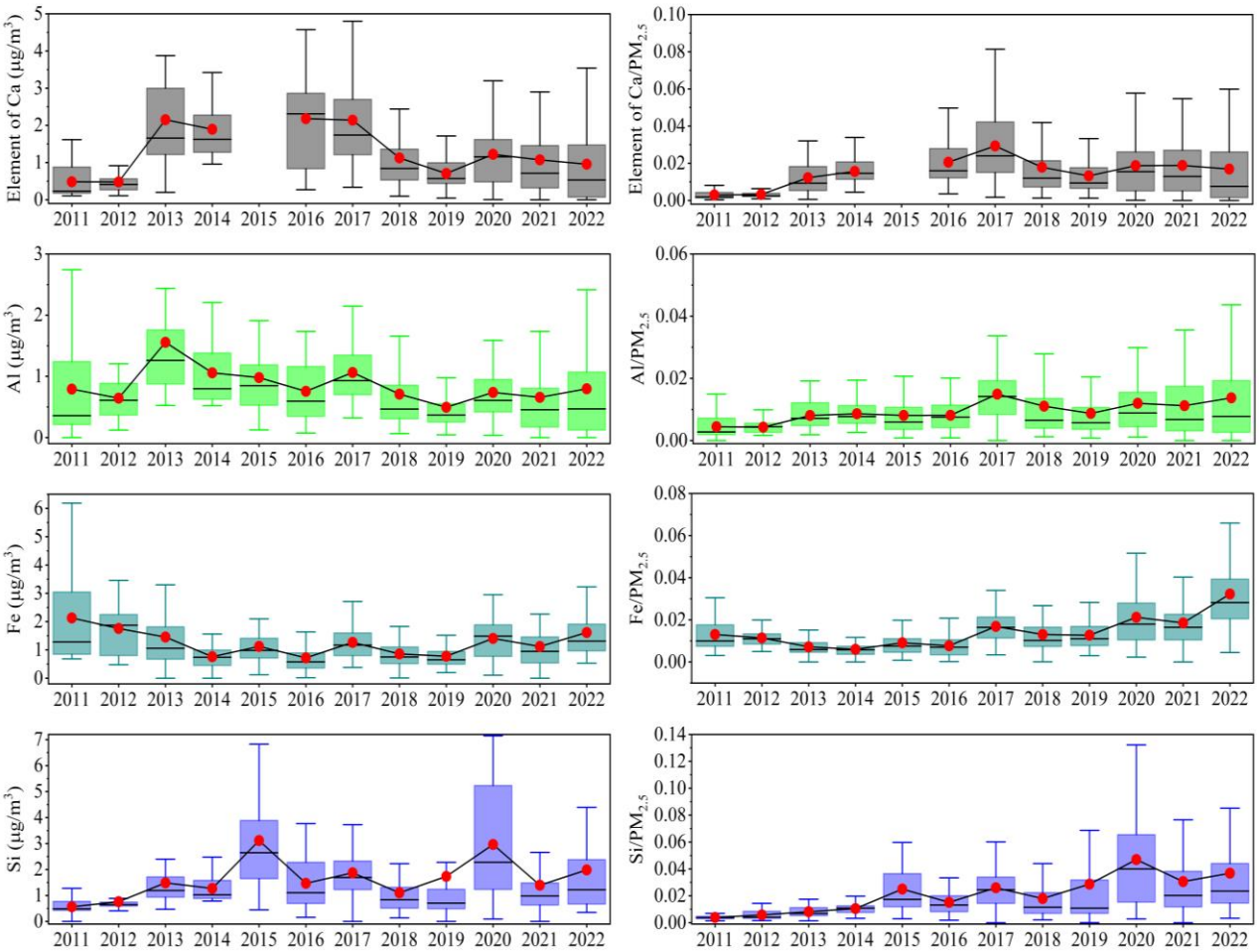


Figure S8. Trends in the concentrations of crustal elements and their proportions in $PM_{2.5}$ from 2011 to 2022.

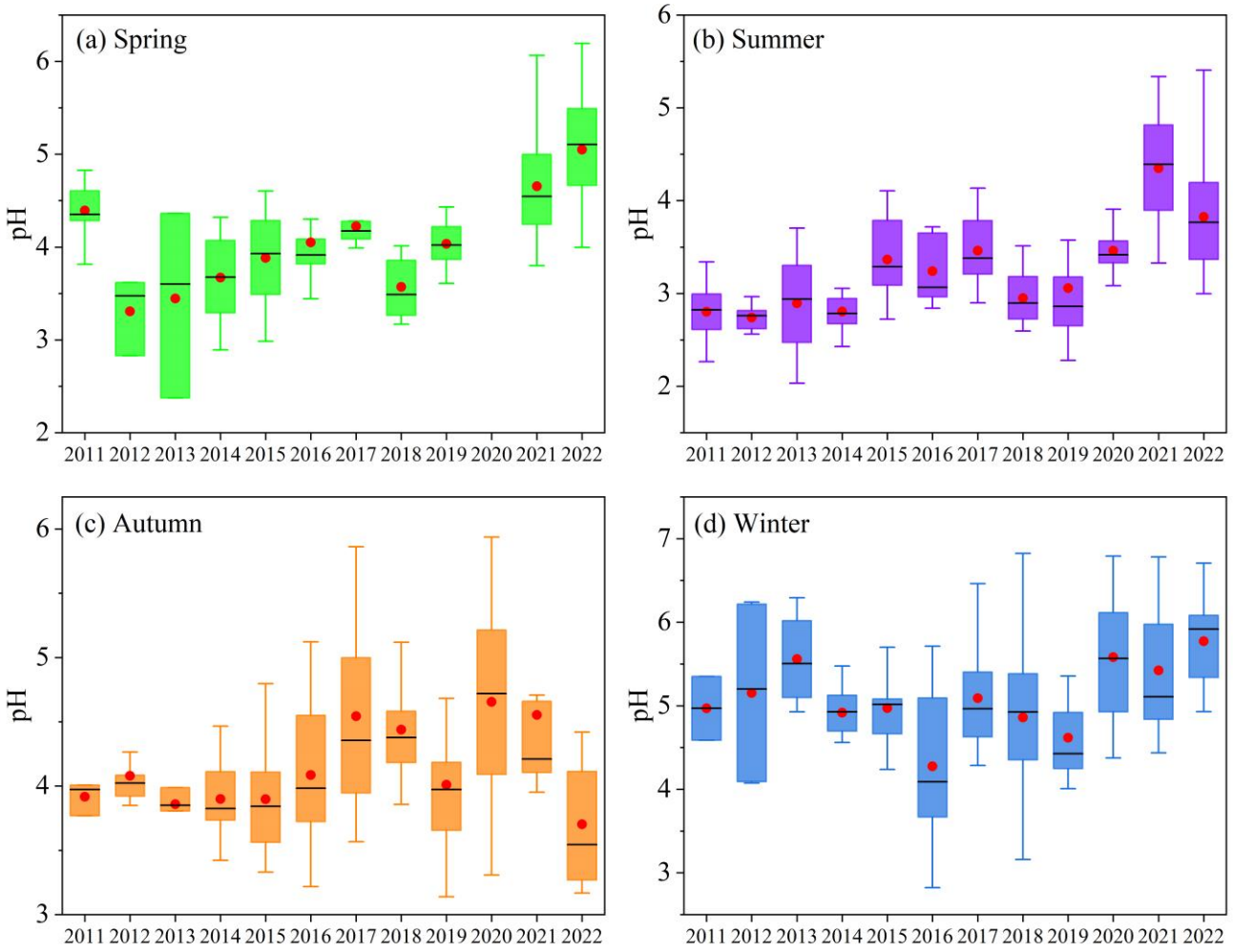


Figure S4. Trends in the particle pH in different seasons from 2011 to 2022.

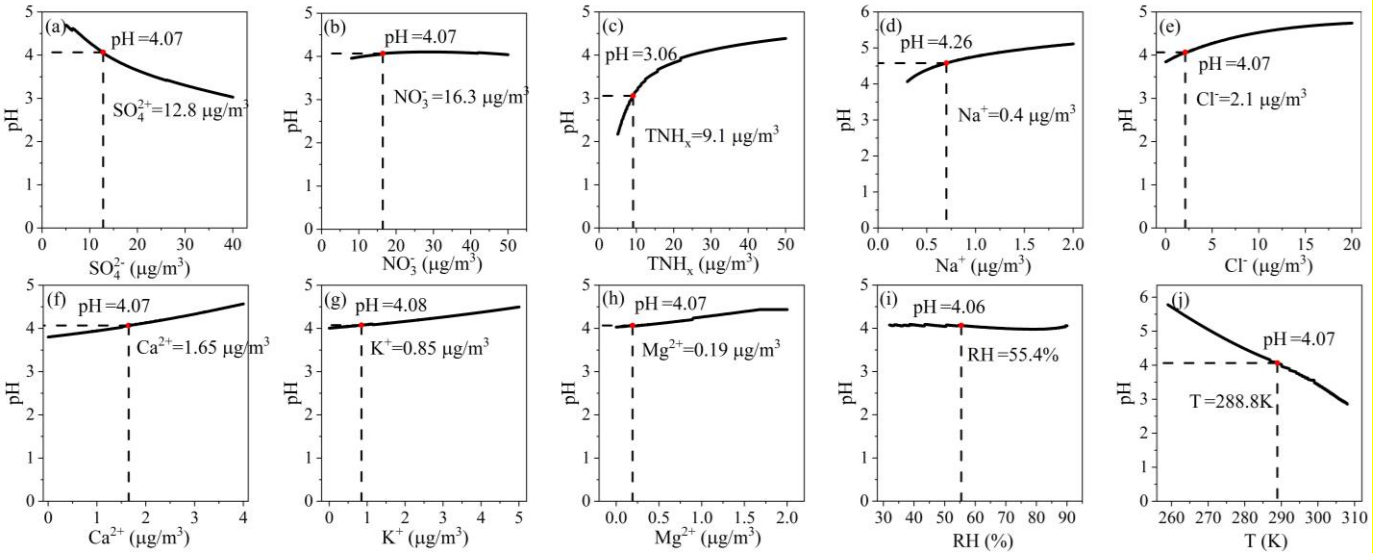
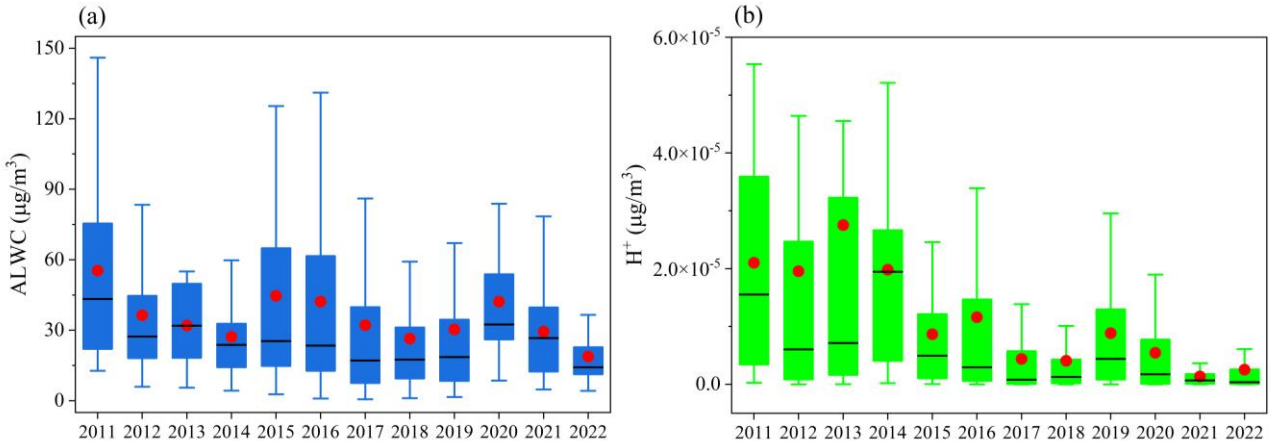


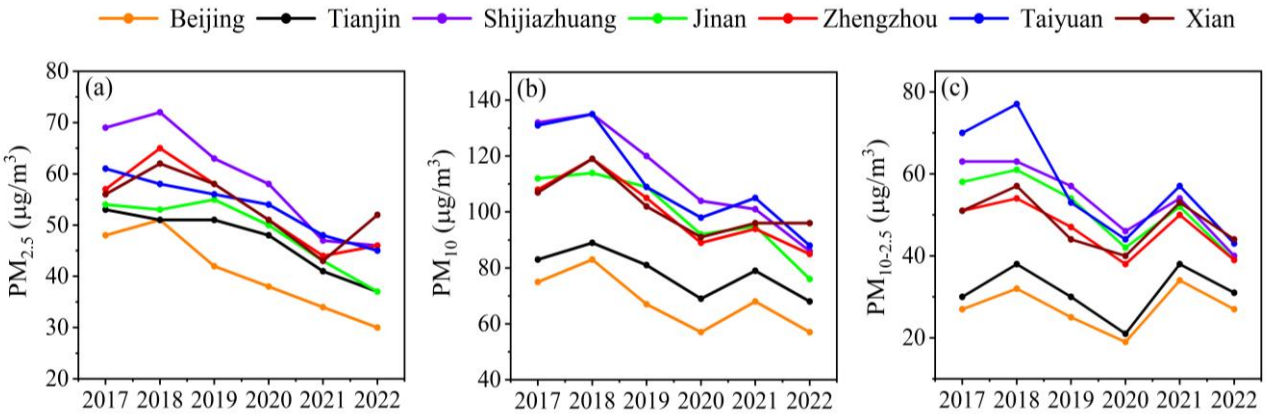
Figure S5. Sensitivity analysis of input parameters to particle pH. The dashed line represents the average of the observational data from 2011 to 2022.



739

740 Figure S6. Trends in aerosol liquid water content (ALWC) and H^+ concentrations from 2011 to 2022

741



742

743 Figure S7. Trends in the annual average concentrations of $PM_{2.5}$, PM_{10}, and $PM_{10-2.5}$ in provincial
744 capitals in the North China Plain.

745

746 **Tables**

747 Table S1. Information on sampling date and numbers.

Years	Sampling date	The effective number of samples
2011	April 7–20 July 1–31 October 28–December 2 December 11–November 23	188
2012	February 25–26 April 21–May 6 July 22–August 2 October 17–November 1 December 8–25	140
2013	February 25–March 6 April 1–May 1 June 5–July 30 September 20–October 13 December 2–18	184
2014	April 1–May 5 June 18–July 20 October 7–24 December 30–31	180
2015	January 1–15 April 1–20 July 1–20 October 9–24	248
2016	January 6–22 April 8–30 July 9–31 October 1–20 December 29–31	252
2017	January 1–20 April 18–May 4 July 1–26 October 14–December 31	480
2018	January 1–31 April 1–30 July 1–31 October 9–December 31	600
2019	January 1–31 April 1–30 July 1–31 September 2–October 31 November 12–30 December 21–31	592

2020	January 1–20 June 5–July 31 October 6–November 13 December 15–31	332
2021	January 1–31 March 16–April 30 July 1–August 8 October 17–December 31	540
2022	January 1–4 April 1–May 3 July 1–August 11 September 5–October 11 December 10–31	492
Total		4228

748
749
750
751 Table S2. The method detection limit (MDL) and measurement uncertainties (Unc) of individual
752 components

	MDLs (μg/m^3)	Unc (%)
EC	0.1	13.1
OC	0.1	9.8
Na^+	0.005	9.6
NH_4^+	0.011	10.1
K^+	0.006	9.5
Mg^{2+}	0.002	9.3
Ca^{2+}	0.017	8.8
F^-	0.001	8.2
Cl^-	0.001	9.3
NO_3^-	0.015	10.1
SO_4^{2-}	0.031	9.9
Na	0.003	10.9
Mg	0.002	10.6
Al	0.004	9.2
Si	0.005	9.3
Cl	0.008	9.5
K	0.005	9.4
Ca	0.01	9.4
V	0.008	57.9
Ni	0.006	96.6
Cr	0.02	24.7
Mn	0.02	16.8
Fe	0.03	9.3
Co	0.009	79.6
Cu	0.005	5.8
Zn	0.003	8.4
Ga	0.005	84.7
As	0.008	27.4

Se	0.006	25.7
Sr	0.006	22.8
Cd	0.03	68.6
Sn	0.02	42.0
Sb	0.02	73.6
Ba	0.02	15.6
Pb	0.02	13.4

Table S3. Control measures for dust implemented by Henan Province and Zhengzhou government

Release time	Policies	Regulatory focus
2013.9	Regulations on Reducing Pollutant Emissions in Henan Province	Road, Construction
2014.8	Temporary Regulations on Dust Control Management at Construction Sites in Henan Province	Construction
2016.7	Implementation Plan for Controlling Dust Pollution in Henan Province	Road, Construction
2018.2	Regulations on the Prevention and Control of Atmospheric Pollution in Henan Province	Road, Construction, Piles
2019.4	Special Action Plan for Fine Management of Dust Pollution Prevention and Control at Construction Sites in Zhengzhou City, 2019	Construction
2019.8	Enhanced Action Plan for Intensive Dust Control at Construction Sites in 2019	Construction
2021.1	Special Governance Plan for Key Project Dust Pollution in Zhengzhou	Road, Construction, Piles

759 Table S4. Analysis of the inter - annual trends of CM and Ca^{2+} concentrations and pH during different periods using multiple methods.

	2011–2013			2013–2019			2019–2022		
	CM	Ca^{2+}	pH	CM	Ca^{2+}	pH	CM	Ca^{2+}	pH
MK-*Z*	3.01	2.70	1.41	–9.74	–13.62	3.00	2.48	8.21	5.12
MK-*p*	0.003	0.007	0.159	<2.2 E–16	<2.2E–16	0.003	0.013	2.20E–16	2.99E–07
Sen's slope	0.082	0.023	7.10E–03	–0.015	–4.14E–03	9.15E–04	5.80E–03	5.42E–03	2.93E–03
LS slope	2.65	0.61	/	–0.81	–0.32	0.11	0.24	0.40	0.21

760 ** MK-*Z* and MK-*p* represent the trend (Z) and significance (*p*) calculated by the Mann - Kendall method using daily data, respectively; Sen's

761 slope represents the Sen slope using daily data; LS slope represents the Least - Squares slope using annual data. All the above calculations were

762 performed using the R language (R version 4.0.2).

763

764 Table S5. The ratios of Ca/Si in the source spectrum of different dust sources in China

Dust source	City	Ca/Si	Reference
Road dust	Xi'an	2.04	http://www.klacp.ac.cn/wgPMzypfypk/ycy/201706/t20170610_375562.html
	Yinchuan	2.48	
	Lanzhou	1.67	
	Beijing	1.25	
	Tianjin	1.03	
	Baoding	1.16	
	Shijiazhuang	1.98	
	Handan	1.83	
	Shenyang	1.81	
	Changsha	1.92	
	Chongqing	1.38	
	Chengdu	1.17	
	Kunming	1.94	
	Taiyuan	1.55	
	Nanjing	1.28	
Construction dust	Xi'an	1.69	http://www.klacp.ac.cn/wgPMzypfypk/ycy/201706/t20170610_375562.html
	Yinchuan	1.84	
	Lanzhou	2.33	
	Beijing	2.65	
	Tianjin	1.46	
	Baoding	1.58	
	Shijiazhuang	1.38	
	Handan	1.86	
	Shenyang	1.92	
	Changsha	2.30	
	Chongqing	2.52	
	Chengdu	2.15	
	Kunming	1.60	
	Taiyuan	1.92	
	Nanjing	2.26	
Piles dust	Xi'an	0.72	(Yang, 2016)
	Tianjin	0.57	(Zhang et al., 2018)
	Taiyuan	0.61	(Bi et al., 2007)
	Jinan	1.01	(Bi et al., 2007)
	/	0.65	http://www.nkspap.com:9091/Index.aspx
Soil dust	Nanchang	0.37	(Xu et al., 2019)
	Xi'an	0.27	(Yang, 2016)
	Jincheng	0.13	(Wang et al., 2016)
	Wuhan	0.52	(Gong and Luo, 2018)
	/	0.53	http://www.nkspap.com:9091/Index.aspx

765

Table S6. The difference between component concentrations (μg/m^3) and meteorological parameters between adjacent years.

Years	ALWC	$H^+(10^{-6})$	NO_3^-	SO_4^{2-}	TNH_X	Na^+	Cl^-	K^+	Ca^{2+}	Mg^{2+}	RH(%)	T (°C)
2012VS2011	-19.0	-1.5	4.0	-4.6	1.3	0.02	2.0	0.9	-0.2	0.04	-9.6	-5.7
2013VS2012	-4.6	-7.6	2.6	13.0	2.1	0.2	0.4	0.3	1.4	0.1	-2.6	2.1
2014VS2013	-4.5	7.9	-7.3	-14.6	-6.9	-0.4	-3.4	-1.6	-1.1	-0.2	6.6	2.0
2015VS2014	17.6	-11.2	5.2	-1.8	5.5	0.1	2.1	0.4	-0.6	0.6	-5.6	-4.2
2016VS2015	-2.3	3.0	-0.2	-4.5	-3.7	-0.03	-0.1	-0.4	0.5	-0.7	8.0	0.3
2017VS2016	-10.0	-7.2	-2.9	-5.3	-3.6	-0.2	-0.3	-0.2	-0.1	0.1	-6.0	-4.9
2018VS2017	-5.8	-0.3	-0.8	-2.4	1.3	-0.1	-0.8	-0.2	-0.1	-0.1	1.4	-2.8
2019VS2018	4.1	4.8	-3.0	-0.8	-2.2	-0.04	-0.7	-0.03	-0.1	-0.01	-0.1	7.3
2020VS2019	11.6	-3.4	4.9	-0.3	-0.9	0.1	0.1	-0.2	0.7	0.02	-6.6	-2.1
2021VS2020	-12.7	-1.5	-3.6	-2.3	0.2	-0.01	0.03	0.01	0.1	0.04	-2.8	-1.5
2022VS2021	-10.6	-1.5	-5.1	1.9	-1.4	0.03	-0.3	0.01	0.5	0.04	4.7	5.8

References

Bi, X., Feng, Y., Wu, J., Wang, Y., and Zhu, T.: Source apportionment of PM_{10} in six cities of northern China, Atmospheric Environment., 41, 903–912, https://doi.org/10.1016/j.atmosenv.2006.09.033, 2007.

Chow, J.C., Watson, J.G., 1994. Guidelines for PM_{10} sampling and analysis applicable to receptor modeling. Washington, DC7 US Environmental Protection Agency, Office of Air Quality Planning and Standards, EPA-452/R-94-009.

Gong, P. and Luo, Y.: Study on the characteristics of source profiles in Wuhan, Journal of Nanjing University of Information Science & Technology., 10, 579–589, https://doi.org/10.13878/j.cnki.jnuist.2018.05.008， 2018.

Tremper, A.; Font, A.; Priestman, M.; Hamad, S.; Chung, T.; Pribadi, A.; Brown, R.; Goddard, S.; Grassineau, N.; Petterson, K.; Kelly, F.; Green, D.: Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols, Atmos. Meas. Tech., 11, 3541–3557, https://doi.org/10.5194/amt-11-3541-2018, 2018.

Wang, Y., Peng, L., Li, L., Wang, Y., Zhang, T., Liu, H., and Mu, L.: Chemical compositions and sources apportionment of re-suspended dust in Jincheng, Environmental Science., 37, 82–87, https://doi.org/10.13227/j.hjkx.2016.01.012 , 2016.

Xu, Y., Gong, X., and Zhang, W.: Construction and characteristic analysis of $PM_{2.5}$ source profiles of typical emissions in Nanchang City, Chemical Engineer., 33, 41–43, https://doi.org/10.16247/j.cnki.23-1171/tq.20190841, 2019.

Yang, Y.: The Chemical Compositions and Source Apportionment of Particulate matter of Open Sources in Xi'an, 42–43, https://doi.org/10.27393/d.cnki.gxazu.2016.000073, 2016.

Zhang, J., Wei, E., Wu, L., Fang, X., Li, F., Yang, Z., Wang, T., and Mao, H.: Elemental composition and health risk assessment of PM_{10} and $PM_{2.5}$ in the roadside microenvironment in Tianjin, China, Aerosol and Air Quality Research., 18, 1817–1827, https://doi.org/10.4209/aaqr.2017.10.0383, 2017.