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 #2:

General Comments:

The authors have addressed most of my comments. However, there are still a few places that require clarification before the manuscript can be accepted.

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 green highlights for your comments, and red color indicating our own corrections in the manuscript.

Major Comment:

1. Section 2.2.3: The author stated that the choice of 1000 m ASL as the receptor height was based on the elevation of the Taihang Mountains (1000 – 1500 m ASL). I am not convinced that using 100 m ASL as the receptor height in the HYSPLIT model will lead to unrealistic results. In fact, using 100 m ASL does not influence the movement of an air mass; it can still have a trajectory above 1000 m.

To support the selection of 1000 m ASL, the authors must show consistent HYSPLIT results, irrespective of whether a receptor height of 100 meters or 1000 meters ASL is used during a chosen period for a case study. Otherwise, I recommend that the authors redo the analysis using a receptor height of 100 meters, as this height is more representative of conditions within the boundary layer due to its proximity to the surface.

Response: Thanks for your comment. Upon carefully revisiting the HYSPLIT model documentation and relevant literature, we recognize that selecting a receptor height of 100 m ASL is indeed more appropriate for studying boundary-layer transport processes, as it better represents near-surface pollutant dynamics. In response to your suggestion, we have re-simulated all trajectories using 100 m ASL as the receptor height and updated the methodology, results, and figures in the revised manuscript:

Section 2.2.3

"24-hour backward trajectories were simulated for air masses arriving at 100 m above ground level in Zhengzhou, a receptor height aligned with the city's average elevation (~100 m above sea level) to capture near-surface pollutant transport dynamics within the boundary layer."

Section 3.3

"The transport trajectories (Fig. 3c and 3d) reveal that a marked decline in the contribution of long-distance sand dust transport originating from Inner Mongolia (via Shaanxi and Shanxi provinces) from 13.9% during 2013–2018 to 7.2% in 2019–2022. In contrast, local transport within Henan province and short-distance transport from Shandong province exhibited contrasting increases. These findings suggest that the rebound in CM concentrations during 2019–2022 in Zhengzhou might be responsible for the resuspension of surrounding soil dust."

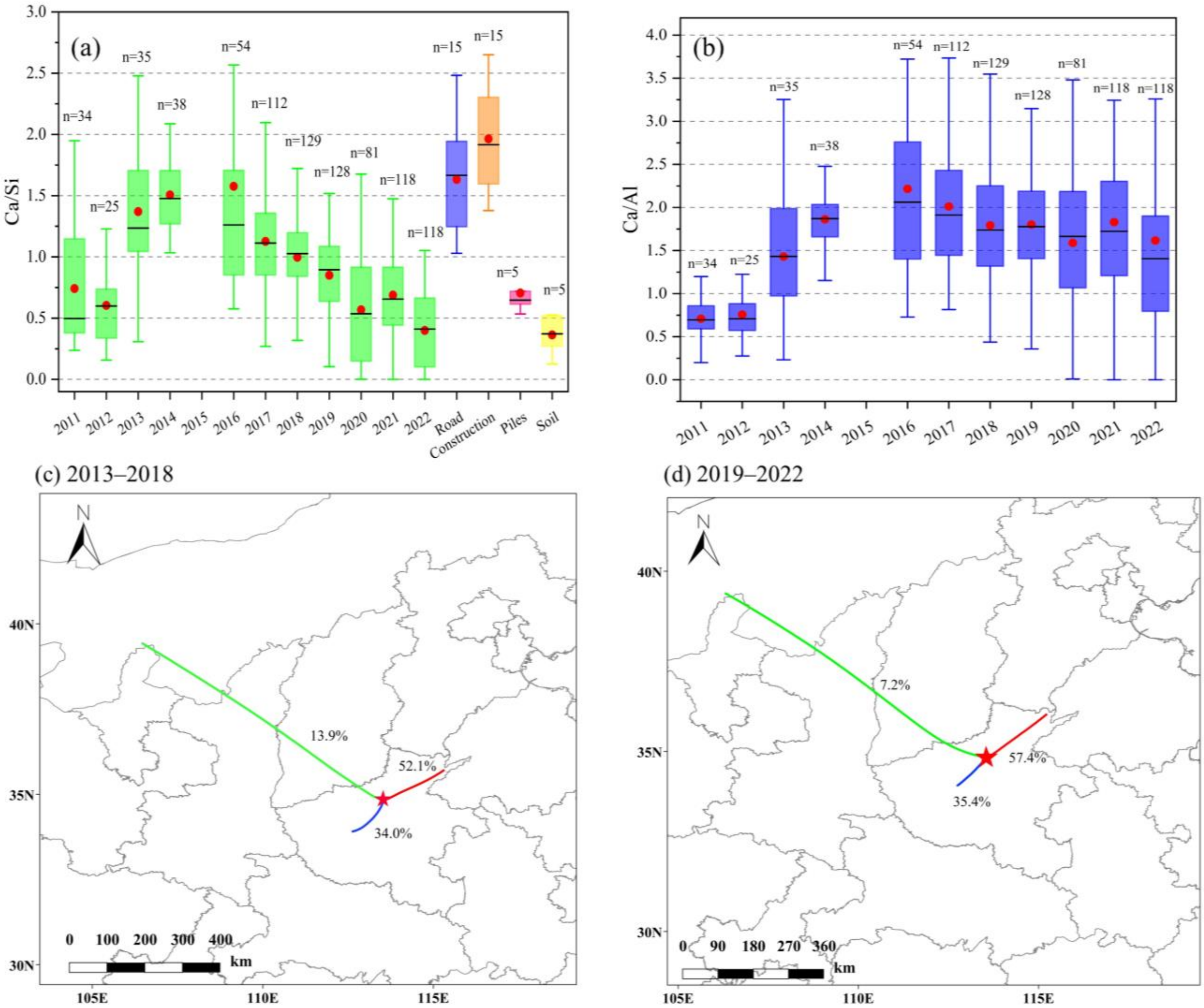

Figure 3. (a) The annual Ca/Si ratios in Zhengzhou from 2011 to 2022 compared with those in various dust sources (specific values and references in Table S5). The red dots and black lines in the box plots represent the annual averages and medians, respectively, with n indicating the sample size. (b) 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.

Minor Comment:

1. Figure S2: Could the authors clarify why there are more data points in Fig S2 (b) compared with Fig S2 (a)?

Response: We sincerely apologize for the lack of clarity in the original figure. The difference in data points between Figures S2(a) and S2(b) arises because Figure S2(a) validation of pH estimates derived from 2022 observational data vs. simulated NH_3 concentrations using Equation 4, while Figure S2(b) compares NH_3 concentrations derived from 12-year (2011–2022) ISORROPIA-II simulations against Equation 4 calculations.

To resolve this ambiguity, we have revised the figure caption to explicitly state the temporal parameters and calculation methods. The updated caption now reads:

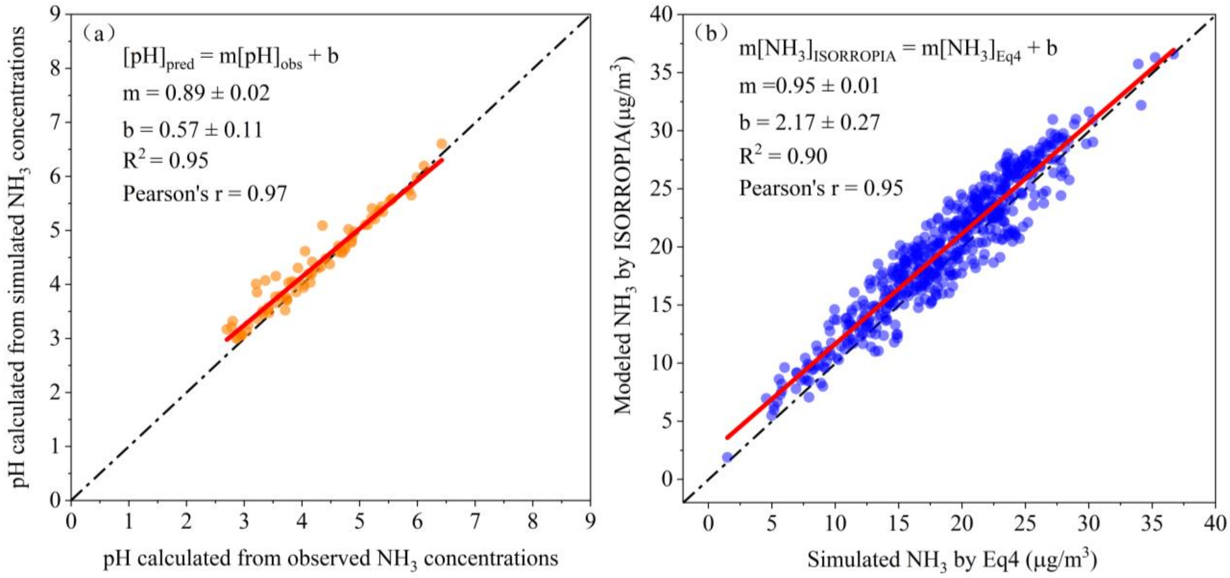

Figure S2. (a) Validation of pH estimates derived from observed vs. simulated NH_3 concentrations in 2022. Red line: linear regression fit. (b) Cross-validation of NH_3 concentrations calculated by the ISORROPIA thermodynamic model and Equation 4 (2011–2022). Red line: linear regression fit.

2. Lines 190 – 201: The statement is too descriptive and long to follow. The authors need to include a plot showing the SPVAR and TSV as a function of cluster number in the SI.

Response: Thanks for your comment. We have made the following revisions to this section:

"Trajectories from 2013–2018 and 2019–2022 were independently clustered via the Angle Distance algorithm to compare policy-driven variations (Wang et al., 2009). The optimal cluster number (three, Figure S3) was determined by tracking total spatial variance (TSV), with classification finalized at the inflection point preceding the second TSV surge."

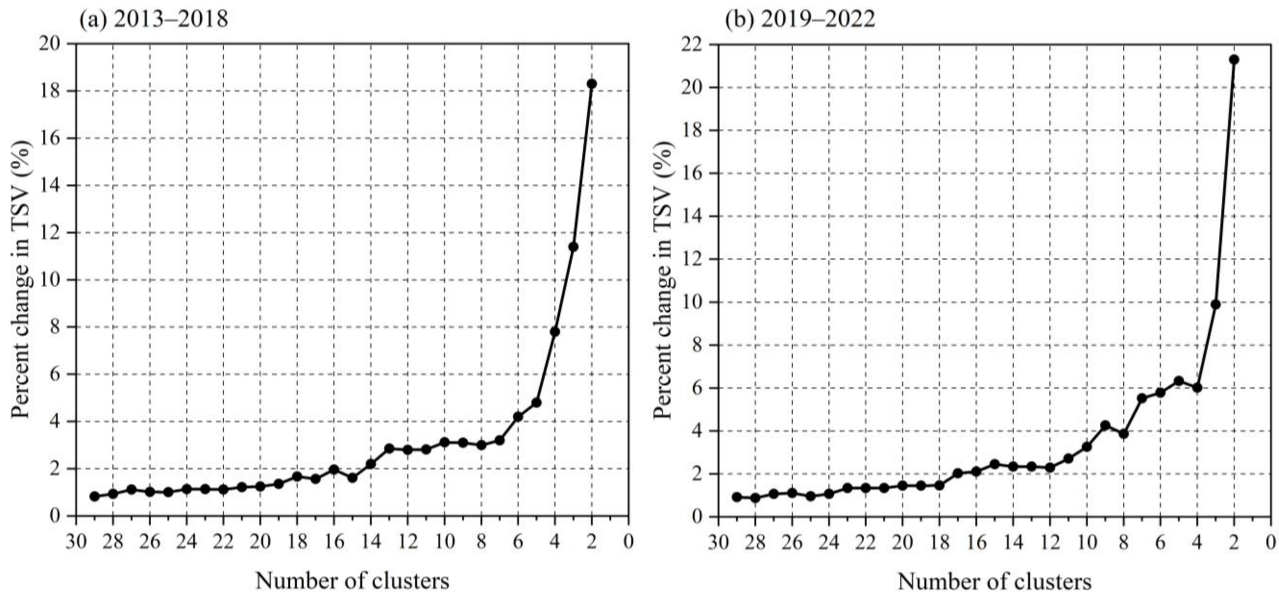

Figure S3. Evolution of total spatial variance (TSV) and optimal cluster number determination for backward trajectories under two policy phases: (a) 2013–2018; (b) 2019–2022.

3. Line 207: What are the priority areas?

Response: Sorry for the misunderstand. This sentence has been modified to: "The 2013–2018 policy prioritized end-of-pipe controls in power generation and heavy industries, mandating ≥10% PM_{10} reduction nationwide and region-specific $PM_{2.5}$ reduction targets (25% for Beijing-Tianjin-Hebei, 20% for Yangtze River Delta, and 15% for Pearl River Delta)."

4. Lines 204 – 224: The information is very descriptive and reads like a report. It needs to be properly shortened to improve the readability.

Response: Thanks for your comments. We have modified this section:

"Over the past twelve years, the Chinese government has implemented two major policies to mitigate air pollution: the Air Pollution Prevention and Control Action Plans (2013–2018) and the Three-Year Action Plan (2018–2020), with key targets and measures detailed in Tables S3 and S4. The 2013–2018 policy prioritized end-of-pipe controls in power generation and heavy industries, mandating ≥10% PM_{10} reduction nationwide and region-specific $PM_{2.5}$ reduction targets (25% for Beijing-Tianjin-Hebei, 20% for Yangtze River Delta, and 15% for Pearl River Delta). Subsequently, the 2018–2020 campaign shifted toward structural reforms and multi-pollutant synergistic governance, enforcing ≥15% nationwide SO_2/NO_x emission cuts and ≥18% $PM_{2.5}$ reduction in non-compliant cities relative to 2015 levels."

Table S3. Major emission reduction measures were implemented during the Air Pollution Prevention and Control Action Plan (2013–2018) and the Three-Year Action Plan (2018–2020)

	Air Pollution Prevention and Control Action Plan	Three-Year Action Plan
Industrial Restructuring	Elimination of a large amount of outdated production capacity in industries. Cement to optimize the industrial structure Reduce high-pollution production	Continued phase-out of outdated production capacity (e.g., steel, cement) Strengthen ultra-low emission retrofitting in sectors such as steel and coking
Energy Transition	Capping coal consumption in certain regions Restricting the construction of small-scale coal-fired power plants	Deepen regional coal consumption control Expand clean heating coverage in rural areas
Promote clean fuels in the residential sector	Ultra-low emission retrofitting in the power sector Comprehensive retrofitting of coal-fired boilers	Continue raising emission standards in the power sector Introduce ultra-low emission requirements for non-power sectors (e.g., steel, coking)
Mobile Source Control	Initial elimination of high-emission (yellow-label) vehicles	Full implementation of China VI emission standards Set up low-emission zones for diesel trucks

	Promotion of China V emission standards	Promote the replacement of vehicles with new energy vehicles
Coordinated Control of Multiple Pollutants	Focus on SO_2, NO_x, and $PM_{2.5}$	Incorporate VOCs (Volatile Organic Compounds) and NH_3 (ammonia) into joint control Strengthen control over industrial solvent use and agricultural emissions
Innovative Governance Models	Regional joint prevention and control (key regions such as Beijing–Tianjin–Hebei)	Grid-based and precise supervision (micro-zoning and dynamic management)

Table S4. The Comparison of Key Indicators Between the Air Pollution Prevention and Control Action Plan (2013–2018) and the Three-Year Action Plan (2018–2020).

	Air Pollution Prevention and Control Action Plan	Three-Year Action Plan
$PM_{2.5}$	Beijing-Tianjin-Hebei region: ≥25% reduction Yangtze River Delta region: ≥20% reduction Pearl River Delta region: ≥15% reduction	$PM_{2.5}$ concentrations to be reduced by more than 18% (vs. 2015)
PM_{10}	National PM_{10} concentration to decrease by ≥10%	No explicit targets
SO_2/NO_x	No explicit targets	National SO_2 and NO_x emissions to be reduced by ≥15% (vs. 2015)
Number of good air quality days	"Annual improvement" in good air days	>80% annually in prefecture-level and above cities
Number of heavily polluted days	No explicit targets	25% reduction in heavy pollution days (vs. 2015)

5. The response to "What was the set activity coefficient of H in the model?" needs to be included in the section of the method.

Response: Done!

"The concentrations of hydrogen ions in air (H^{+}_{air}) and ALWC were derived from the Na^+-K^+-Ca^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-}-NO_3^--Cl^--H_2O equilibrium composition system. Activity coefficients for H^+ and OH^- were fixed at unity, while other ion pairs (e.g., H^+-Cl^-) employed the Kusik-Meissner parameterization for ionic activity calculations (Fountoukis and Nenes, 2007)."

6. Lines 314 – 315: Could the authors include references to support the statement "the comparable chemical composition trends and meteorological conditions"?

Response: Thank you for your comments. We have added relevant literature citations to support this viewpoint:

"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 (Liu et al., 2017; Wang et al., 2020; Xu et al., 2015)."

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213–5221, https://doi.org/10.1002/2017GL073210, 2017.

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, J.; Gao, J.; Che, F.; Wang, Y.; Lin, P.; Zhang, Y.: Dramatic changes in aerosol composition during the 2016–2020 heating seasons in Beijing–Tianjin–Hebei region and its surrounding areas: The role of primary pollutants and secondary aerosol formation, Sci. Total Environ., 849, 157621, https://doi.org/10.1016/j.scitotenv.2022.157621, 2022.

7. Lines 318 – 319: More discussion needs to be provided on how higher temperatures and more rainfall drive the distinct pH trends in Shanghai and Hong Kong.

Response: Thanks for your suggestion. We have added a discussion:

"Moreover, these coastal cities' warm climates amplify pH declines. Elevated temperatures reduce ALWC through moisture evaporation, concentrating H^+ and directly lowering pH. Concurrently, heat-enhanced NH_3 volatilization from particulate NH_4^+ weakened acid neutralization (Zhou et al., 2022; Nah et al., 2023)."

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.

Zhou, M., Zheng, G., Wang, H., Qiao, L., Zhu, S., Huang, D., An, J., Lou, S., Tao, S., Wang, Q., Yan, R., Ma, Y., Chen, C., Cheng, Y., Su, H., and Huang, C.: Long-term trends and drivers of aerosol pH in eastern China, Atmos. Chem. Phys., 22, 13833–13844, https://doi.org/10.5194/acp-22-13833-2022, 2022.

Rainfall data has been removed from this study; therefore, the influence of rainfall on pH values will no longer be discussed.