Reply to Anonymous Referee #2

Comments: The manuscript explores the impact of dust pollution on aerosol pH and nitrate gas-particle partitioning. By combining field observations, thermodynamic modeling, and machine learning techniques, this study provides a comprehensive analysis of how different dust scenarios affect urban aerosol pH and gas-particle partitioning chemistry of nitrate. I would consider the publication of this article once the authors have addressed the following comments.

Reply: We thank the reviewer for his/her positive and constructive comments on this manuscript. We have modified the related content according to the comments.

1) (English) The language and grammar of the manuscript should be improved. In some of these instances, bad grammar prevents understanding the main point of the sentence. I will point in the minor comment section to these parts of the text, with a recommendation on how to change the text, based on my understanding of what the main point of it is.

Reply: Thank you for your valuable comments. We have carefully reviewed the language and grammar issues you highlighted and revised the corresponding sections to improve clarity and readability. These changes aim to ensure that the main points of the manuscript are conveyed more effectively. We sincerely appreciate your suggestions, which have helped enhance the overall quality of the manuscript.

2) L. 47: “Dust particles also engage in heterogeneous reactions with gaseous nitric acid, buffering acidic species and modulating pH dynamics.” This is a priori reasonable description, due to the alkalinity of carbonate minerals. It would be good to have references here to support it. A recently published article in EST provides a thorough explanation of how aerosol acidification responds to the buffering capacity of carbonate minerals during Asian dust storms (https://pubs.acs.org/doi/10.1021/acs.est.4c12370).

Reply: Thank you for your insightful comment. We have carefully reviewed the suggested reference (https://pubs.acs.org/doi/10.1021/acs.est.4c12370), which indeed offers a comprehensive explanation of the buffering effects of carbonate minerals on aerosol acidification during Asian dust storms. As it directly supports and enriches our discussion on the role of dust in modulating aerosol pH, we have now cited this study at the appropriate place in the revised manuscript. We appreciate your recommendation, which has strengthened the scientific grounding of our work.

3) L. 75: “atmospheric setting” to “atmospheric experiment”

Reply: Thank you for the suggestion. We have revised “atmospheric setting” to “atmospheric experiment” as recommended to better reflect the context and improve clarity.

4) L. 231-236: The authors claim that the abundance of nitrate in aged dust particles during long-range transport dust storms was higher than during local dust periods, whereas sulfate abundance was greater during local dust periods than in long-range transport dust storms. You attribute this to the stronger atmospheric dilution and dispersion effects on nitrate during dust storms. You mean that long-range transport dilutes nitrate? If so, a decrease in nitrate contribution should be observed along the dust transport from Xuzhou to Zhenjiang to Suzhou. In reality, however, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ coatings preferentially form on aged mineral particles containing calcite and dolomite. Moreover, the number of $Ca(NO_3)_2$-coated particles increases with dust transport distance due to the relatively low deliquescence relative humidities (>11%) (see Li et al., ACP, 2009, https://doi.org/10.5194/acp-9-1863-2009; Tobo et al., PNAS, 2010, http://www.pnas.org/cgi/doi/10.1073/pnas.1008235107; A. Laskin and T. W. Wietsma, JGR-A, 2005, doi:10.1029/2004JD005206). Given that calcite and dolomite are widely present in Asian dust particles, it is expected that during the dust storm period, the relative contribution of Ca^{2+} and Mg^{2+} increased across all three cities, with an average rise of approximately 10% compared to the local dust period. (your Figure 3). Therefore, the authors should thoroughly study more relevant literatures to provide a more reasonable explanation. Furthermore, the higher sulfate content in long-range transported dust particles likely originates from the presence of weakly soluble $CaSO_4$.

Reply: Thank you for this insightful comment and valuable references. We have revised the manuscript accordingly and cited the suggested studies to strengthen our discussion. As shown in Figure 3, the relative contribution of nitrate was indeed lower during dust storm periods compared to local dust events, whereas sulfate showed the opposite trend. This pattern was likely driven by the combined influence of meteorological conditions and dust-related chemical processes.

Specifically, nitrate, which is often formed locally through gas-particle conversion processes, is more sensitive to dispersion effects during dust storms than sulfate, which typically has stronger regional characteristics and may be less impacted by local meteorological changes. To further evaluate this hypothesis, we applied a random forest regression model coupled with SHAP analysis. Meteorological parameters (listed in Table S4) were used as input predictors, while nitrate and sulfate concentrations served as the respective response variables. As shown in Fig. S2, the aggregated SHAP values for meteorological variables associated with dispersion processes (e.g., winds, planetary boundary layer height) revealed a stronger influence on nitrate concentrations than on sulfate. This suggests that meteorological dilution has a more pronounced effect on nitrate, helping to explain its reduced relative abundance during dust storms. Meanwhile, the relatively stable SHAP responses for sulfate – and some increases during dust storm periods – may point to contributions from long-range transport of sulfate-containing particles. However, this interpretation would benefit from further verification through chemical transport modeling.

In addition, we fully agree with the reviewer that chemical aging processes during dust transport likely contribute to nitrate formation. As reported in previous studies (Li and Shao, 2009; Tobo et al., 2010; Laskin et al., 2005), $Ca(NO_3)_2$ and $Mg(NO_3)_2$ coatings preferentially form on aged dust particles containing calcite and dolomite, with their abundance increasing along transport paths due to low deliquescence relative humidities. Given the widespread presence of these minerals in Asian dust, it is reasonable to expect enhanced formation of nitrate salts during long-range transport. Our measurements support this, as shown in Figure 3, where the relative contributions of Ca^{2+} and Mg^{2+} increased by approximately 10% during the dust storm period across all three cities compared to local dust events. This highlights the importance of both physical dispersion and chemical processing in shaping the observed aerosol composition. Nevertheless, further quantitative analysis of these factors requires comprehensive aerosol chemical measurements and atmospheric chemical transport modeling in future studies.

We have modified the manuscript which can be found on lines 241 – 260 in the revised manuscript.

5) L. 318: "During dust storms, the mean aerosol pH values were 5.50 ± 1.65 in Xuzhou, 5.44 ± 1.69 in Zhenjiang, and 5.30 ± 1.67 in Suzhou. Under local dust conditions, these values were lower, at 4.12 ± 0.52, 3.92 ± 0.32, and 3.74 ±0.69 respectively." As the author pointed out, dust particles were more acidified by more secondary acidic aerosols (SO_4^{2-}, NO_3^-) formed on dust surfaces along with dust long-distance transport, eventually leading to the decrease of pH.

However, why does a similar trend also appear during local dust events?

Reply: Thank you for the comment. The observed decrease in aerosol pH during local dust events across the three cities was primarily attributed to the reduction in ambient NH_3 concentrations. As shown in Table S1–S3, the average NH_3 concentrations during local dust events were 13.24 ± 4.28 μg m^{-3} in Xuzhou, 9.27 ± 3.99 μg m^{-3} in Zhenjiang, and 6.16 ± 3.51 μg m^{-3} in Suzhou. As discussed in Section 3.2, NH_3 was identified as the most influential chemical species affecting aerosol pH. Therefore, the decrease in NH_3 concentrations during local dust conditions likely played a dominant role in driving the observed reduction in aerosol pH.

6) L. 359: "This indicates that dust storm conditions have a significantly stronger positive contribution to the particle-phase fraction of nitrate. The presence of dust particles facilitates the conversion of nitrate to the particulate phase, highlighting the significant influence of dust storms on nitrate partitioning in the atmosphere." Does this contradict the previous description of stronger atmospheric dilution and dispersion effects on nitrate? similar to Comment 5.

Reply: We thank the reviewer for the comment. The influence of dust storms on nitrate can indeed be understood from two distinct perspectives. In earlier sections, we focused on the physical processes of atmospheric dilution and dispersion, which primarily lead to a decrease in the absolute mass concentration of nitrate aerosols. In contrast, the discussion in Lines 384 – 387 centers on the thermodynamic gas-particle partitioning process. Specifically, in Section 3.3, we used machine learning methods to analyze how dust storms affect aerosol pH and the particle-phase fraction of nitrate ($\varepsilon(NO_3^-)$). While overall nitrate concentrations may decrease due to dispersion, the presence of alkaline mineral components (e.g., Ca^{2+}) in dust elevates aerosol pH and thereby promotes the partitioning of nitrate into the particle phase. Therefore, the observed increase in $\varepsilon(NO_3^-)$ reflects a relative enhancement in particle-phase nitrate formation and does not contradict the decline in total nitrate concentrations caused by atmospheric dispersion.

7) Figure 9: Please label the different dust pollution conditions along with Ca^{2+} concentrations in the figure.

Reply: Thank you for the valuable suggestion. We have now labeled the different dust pollution conditions along with the corresponding Ca^{2+} concentrations in Figure 9a. To better represent the variation in calcium ion levels, we included Ca^{2+} concentrations typical of local dust events (0.5 μg m^{-3}), and, using the ISORROPIA-II model, we simulated changes in $\varepsilon(NO_3^-)$ and NH_4^+ + NO_3^- under three emission reduction scenarios. We have updated the manuscript as follows: "*For the simulation,* Ca^{2+} *concentration was set to 0.1 to 0.7 μg* m^{-3} *for local dust conditions and ranged from 1.0 to 3.0 μg* m^{-3} *for dust storm conditions.*" The revised figure is shown below:

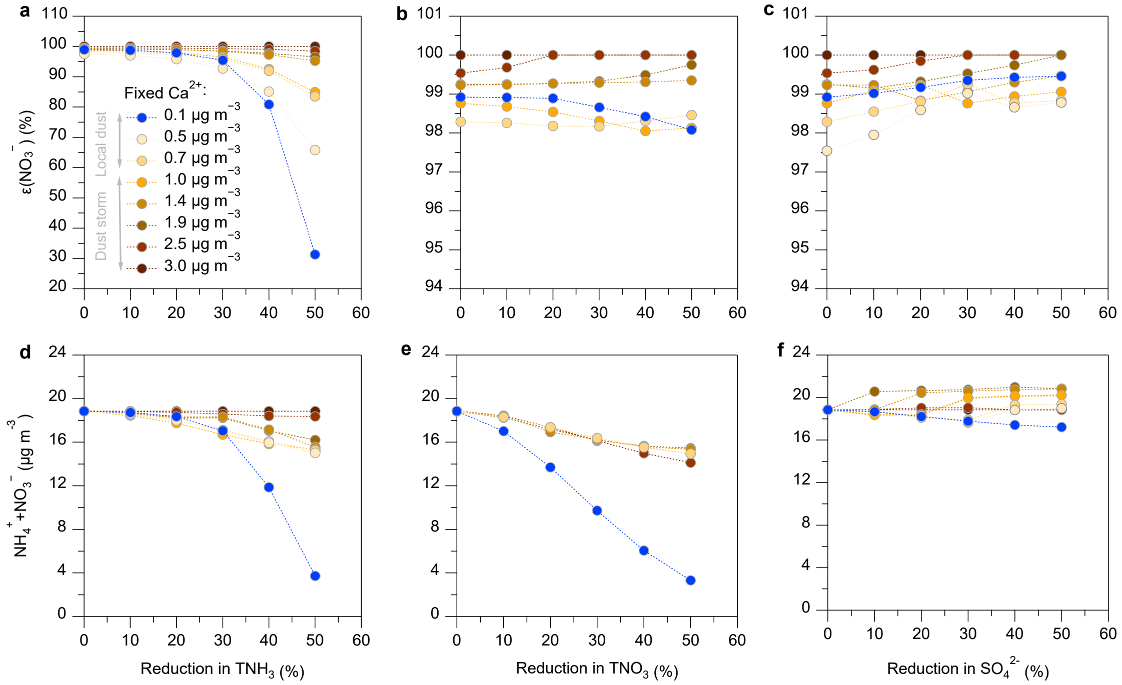

Figure 9. Sensitivity analysis based on the thermodynamic model ISORROPIA-II simulated the impact of reducing TNH_x ($TNH_x = NH_3 + NH_4^+$), TNO_3 ($TNO_3 = HNO_3 + NO_3^-$), and SO_4^{2-} by 0-50% during dust events of varying intensities on $\varepsilon(NO_3^-)$ and $NH_4^+ + NO_3^-$.

References

Guo, H., Nenes, A., and Weber, R. J.: The underappreciated role of nonvolatile cations in aerosol ammonium-sulfate molar ratios, Atmos. Chem. Phys., 18, 17307-17323, https://doi.org/10.5194/acp-2017-737, 2018.

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NOx promote the conversion of SO2 to sulfate in heavy pollution days, Sci. Rep., 4, 4172, https://doi.org/10.1038/srep04172, 2014.

Laskin, A., Wietsma, T. W., Krueger, B. J., and Grassian, V. H.: Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCSEM/EDX, ESEM, and ICP-MS study, J. Geophys. Res. Atmos., 110, https://doi.org/10.1029/2004JD005206, 2005.

Li, W., Qi, Y., Liu, Y., Wu, G., Zhang, Y., Shi, J., Qu, W., Sheng, L., Wang, W., Zhang, D., and Zhou, Y.: Daytime and nighttime aerosol soluble iron formation in clean and slightly polluted moist air in a coastal city in eastern China, Atmos. Chem. Phys., 24, 6495-6508, https://doi.org/10.5194/acp-24-6495-2024, 2024.

Li, W. J. and Shao, L. Y.: Observation of nitrate coatings on atmospheric mineral dust particles, Atmos. Chem. Phys., 9, 1863-1871, https://doi.org/10.5194/acp-9-1863-2009, 2009.

Liu, L., Li, W., Lin, Q., Wang, Y., Zhang, J., Zhu, Y., Yuan, Q., Zhou, S., Zhang, D., Baldo, C., and Shi, Z.: Size-dependent aerosol iron solubility in an urban atmosphere, npj Clim. Atmos. Sci., 5, 53, https://doi.org/10.1038/s41612-022-00277-z, 2022.

Rumsey, I. C., Cowen, K. A., Walker, J. T., Kelly, T. J., Hanft, E. A., Mishoe, K., Rogers, C., Proost, R., Beachley, G. M., Lear, G., Frelink, T., and Otjes, R. P.: An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds, Atmos. Chem. Phys., 14, 5639-5658, https://doi.org/10.5194/acp-14-5639-2014, 2014.

Tobo, Y., Zhang, D., Matsuki, A., and Iwasaka, Y.: Asian dust particles converted into aqueous droplets under remote marine atmospheric conditions, Proc. Natl. Acad. Sci. U.S.A., 107, 17905-17910, https://doi.org/10.1073/pnas.1008235107, 2010.

Trebs, I., Meixner, F. X., Slanina, J., Otjes, R., Jongejan, P., and Andreae, M. O.: Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmos. Chem. Phys., 4, 967-987, https://doi.org/10.5194/acp-4-967-2004, 2004.

Vasilakos, P., Russell, A., Weber, R., and Nenes, A.: Understanding nitrate formation in a world with less sulfate, Atmos. Chem. Phys., 18, 12765-12775, https://doi.org/10.5194/acp-18-12765-2018, 2018.

Wang, T., Liu, Y., Cheng, H., Wang, Z., Fu, H., Chen, J., and Zhang, L.: Significant formation of sulfate aerosols contributed by the heterogeneous drivers of dust surface, Atmos. Chem. Phys., 22, 13467-13493, https://doi.org/10.5194/acp-22-13467-2022, 2022.

Weber, R. J., Guo, H., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nat. Geosci., 9, 282-285, https://doi.org/10.1038/ngeo2665, 2016.

Zhang, H., Li, R., Dong, S., Wang, F., Zhu, Y., Meng, H., Huang, C., Ren, Y., Wang, X., Hu, X., Li, T., Peng, C., Zhang, G., Xue, L., Wang, X., and Tang, M.: Abundance and Fractional Solubility of Aerosol Iron During Winter at a Coastal City in Northern China: Similarities and Contrasts Between Fine and Coarse Particles, J. Geophys. Res. Atmos., 127, e2021JD036070, https://doi.org/10.1029/2021JD036070, 2022.

Zhang, S., Li, D., Ge, S., Wu, C., Xu, X., Liu, X., Li, R., Zhang, F., and Wang, G.: Elucidating the Mechanism on the Transition-Metal Ion-Synergetic-Catalyzed Oxidation of SO2 with Implications for Sulfate Formation in Beijing Haze, Environ. Sci. Technol., 58, 2912-2921, https://doi.org/10.1021/acs.est.3c08411, 2024.

Zhi, M., Wang, G., Xu, L., Li, K., Nie, W., Niu, H., Shao, L., Liu, Z., Yi, Z., Wang, Y., Shi, Z., Ito, A., Zhai, S., and Li, W.: How Acid Iron Dissolution in Aged Dust Particles Responds to the Buffering Capacity of Carbonate Minerals during Asian Dust Storms, Environ. Sci. Technol., https://doi.org/10.1021/acs.est.4c12370, 2025.