Response to Reviewer

Anonymous Referee #1

This paper investigated the mechanisms by which sulfuric and nitric acids influence iron (Fe) dissolution at different altitudes through a comparative analysis of aerosol samples collected at ground level in Hangzhou and in the upper mixing layer at Mountain Daming. It reported that there were significant vertical differences in Fe solubility and related aging processes of acidic species. The results are interesting and will help improve our understanding on the biogeochemical cycling of atmospheric Fe. Generally, this manuscript is well structured and written, I will be happy to recommend this manuscript for publication after a minor revision.

Response: We would like to thank the reviewer for their time and the constructive comments on our manuscript. We have carefully considered all the comments and suggestions. Below is our point-by-point response detailing how we will address each issue in the revised manuscript. In the following, paragraphs in ***black*** are reviewer comments; paragraphs in ***blue*** are point to-point responses; paragraphs in ***red*** are revised in the manuscript.

Major Comments

Comment 1: Line 100−105: Only 7 TSP samples per site and 3 sets of MOUDI samples (DMS only, none for HZ) are mentioned. The limitations of this sample size and its potential impact on statistical significance should be more explicitly addressed in the discussion.

Response: We acknowledge the reviewer's concern regarding the sample size. As noted in the original manuscript (Lines 99–101), the sampling campaign was conducted during the summer rainy season, which was frequently interrupted by rain events to prevent wet deposition contamination. Additionally, instrument maintenance prevented the collection of MOUDI samples at the Hangzhou site.

In the revised manuscript, we add a dedicated statement in the ***Discussion*** section to explicitly address this limitation.

Page 17, line 404−409:

"Although the number of samples collected in this study is limited and does not allow assessment of long-term variability or climatological trends, our study focus on different mechanism of acid processing at the two altitudes. These field campaign provided a valuable observational dataset for testing and improving model representations of Fe dissolution. To further strength these findings, future work should incorporate long-term, vertically resolved observations to better characterize Fe solubility profiles throughout the lower troposphere."

Comment 2: Brief summary on air pollution conditions during the sampling period should be supplemented.

Response: We agree that providing a context for the air pollution levels is beneficial. We have added a brief summary of the air quality conditions in the ***Section 3.1***.

Page 6, line 179−184:

"Figure 1a shows the time series of TSP mass concentrations at Mt. Daming and in Hangzhou during the sampling period. The mean concentrations of aerosol particles reached 41 ± 17 μg m^{-3} at Mt. Daming and 86 ± 28 μg m^{-3} in Hangzhou, respectively. The loading of TSP in the upper mixing layer (Mt. Daming) was much lower than that at the ground-level (Hangzhou), indicating relatively clean conditions. In addition, relative humidity at Mt. Daming (88.1 ± 5.8%) was much higher than in the urban environment (70.5 ± 9.3%), confirming that the mountain site was consistently influenced by a more humid atmosphere (Table S1 in the Supplement).

Comment 3: Line 156-161: For aerosol pH calculation, only size-resolved aerosols were considered, what about the TSP samples? In addition, 2025 NH_3 data was used to estimate 2021 levels at DMS, while acknowledged, may introduce uncertainty. I suggest the author implement a sensitivity analysis or further discussion on the potential impact of this assumption on pH calculation.

Response: We thank the reviewer for these valuable comments. We answer these questions in the following:

(1) Calculation of TSP pH

Since concurrent ambient gas-phase NH_3 measurements were not available for the TSP samples during the campaign, we adopted an iteration-based method to estimate its concentration (Zhang et al., 2022; Fang et al., 2017; Sun et al., 2018). This method involves the following steps: (i) The input for ISORROPIA II is initialized as the sum of measured aerosol ammonium ($NH_4^+{}_{(p)}$]) and an estimated gas-phase component (i.e., [TNH_4] = [$NH_4^+{}_{(p)}$] + [$NH_{3(g)}$]). (ii) The gas-phase NH_3 ($NH_{3(g)}$) output from the initial run is added to the original aerosol data to update the total ammonia input for the subsequent run. (iii) This process is repeated until the variance of NH_4^+ output mass concentrations (L) fall below a 0.01 threshold. As shown in the following equation:

$$\text{Input } [NH_4^+{}_{(p)} + NH_{3(g)}]_{n+1} = NH_4^+{}_{(p)} + [NH_{3(g)}]_n \quad \text{(E1)}$$

$$L = ([NH_4^+{}_{(p)}]_{n+1} - [NH_4^+{}_{(p)}]_n) / [NH_4^+{}_{(p)}]_n \quad \text{(E2)}$$

Using this method, we performed iterations ($n > 5$), however we failed to achieve convergence. As an alternate approach, Hennigan et al., (2015) concluded that if there is no gas-phase data to constrain the thermodynamic models, the use of aerosol concentrations as input in forward-mode calculations may yield a more accurate representation of aerosol pH. Followed his suggestion, we performed ISORROPIA II using aerosol mass concentrations without gas-phase as the model inputs and set the mode with forward. The simulation indicates that the mean aerosol pH at the upper mixing layer (Mt. Daming) is 2.4 ± 2.3, which is significantly lower than that at ground level (Hangzhou, 4.7 ± 2.2) (Figure S11). This higher acidity corresponds to the greater acidification capacity and elevated Fe solubility ($\%\text{Fe}_\text{S}$) observed in the upper mixing layer. We have incorporated this figure and analysis into Figure S11 in the ***Supplement*** and *Section 4.2* of the ***Discussion***, respectively.

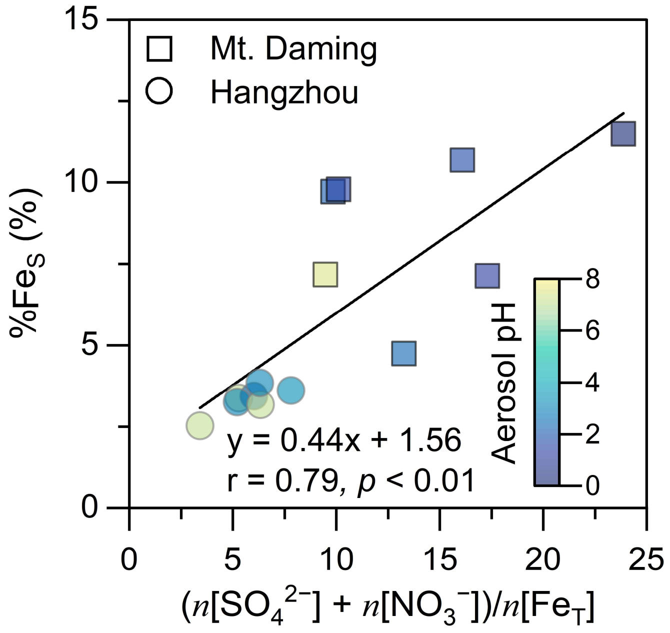

Figure S11. Correlations between $\%\text{Fe}_\text{S}$ and the corresponding molar ratio of $(n[\text{SO}_4^{2-}] + n[\text{NO}_3^-])/n[\text{Fe}_\text{T}]$ at Mt. Daming and Hangzhou. Linear regression lines are shown for each site. Data points (solid circles and squares) are colored according to aerosol pH.

Page 13, lines 327−331:

"…The ISORROPIA II thermodynamic model, operated in forward mode, was used to simulate aerosol pH for TSP. The mean aerosol pH at Mt. Daming was 2.4 ± 2.3, substantially lower than that at Hangzhou (4.7 ± 2.2) (Fig. S11), indicating markedly stronger aerosol acidity in the upper mixing layer. This enhanced acidity helps explain the higher acidification potential of aerosols aloft and the correspondingly elevated $\%\text{Fe}_\text{S}$ observed in this layer (Fig. 6a)."

References

[1] 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.org10.1029/2021jd036070, 2022.

[2] Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environ. Sci. Technol., 51, 2611−2620, https://doi.org10.1021/acs.est.6b06151, 2017.

[3] Sun, P., Nie, W., Chi, X., Xie, Y., Huang, X., Xu, Z., Qi, X., Xu, Z., Wang, L., Wang, T., Zhang, Q., and Ding, A.: Two years of online measurement of fine particulate nitrate in the western Yangtze River Delta: influences of thermodynamics and N_2O_5 hydrolysis, Atmos. Chem. Phys., 18, 17177-17190, https://doi.org10.5194/acp-18-17177-2018, 2018.

(2) Sensitivity Analysis of NH_3 Data

To evaluate the sensitivity of pH to the assumed NH_3 level in size-resolved aerosols, we conducted a sensitivity analysis by varying NH_3 concentrations over an order of magnitude while holding all other parameters constant (Figure S3). The results showed that two times (4 ppb) change in NH_3 can increase pH with 0.2 unit and a ten-fold (20 ppb) change in NH_3 induces approximately a 1-unit change in aerosol pH—consistent with previous modeling studies (Guo et al., 2017; Weber et al., 2016). Given the relatively clean background environment at our mountain sampling site, the NH_3 emissions is expected to exhibit minimal variation over the short sampling period, thus, the assumed NH_3 concentration is likely conservative and within reasonable bounds. Therefore, while we acknowledge the potential uncertainty due to the 2025 NH_3 measurements, we believe the simulated aerosol pH values are sufficiently representative for investigating proton-promoted processes such as Fe dissolution.

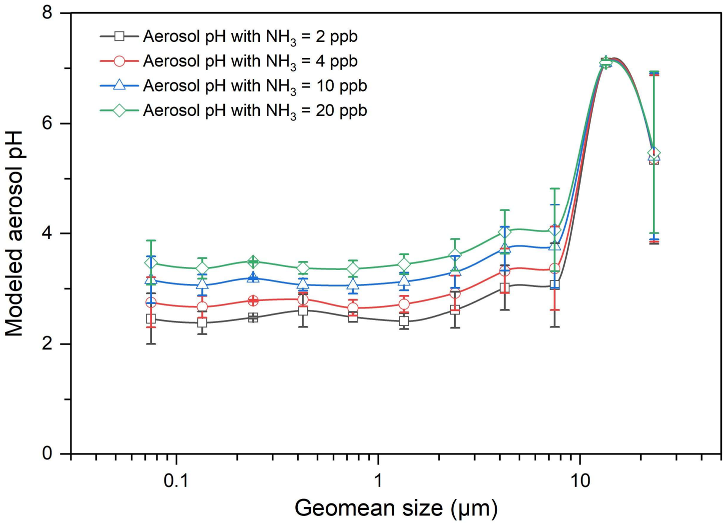

Figure S3. Modeled aerosol pH for the Mt. Daming across different particle size bins under varying NH_3 concentrations (2, 4, 10, and 20 ppb), simulated using the ISORROPIA II model. The lowest NH_3 concentration (~2 ppb) represents the average level observed during the 2025 field campaign. The pH was calculated based on measured inorganic composition and assumed thermodynamic equilibrium under metastable conditions. Error bars represent the standard deviation of pH values within each size bin ($n = 3$).

The sensitivity analysis of aerosol pH induced by varying NH_3 concentration was conducted in the Figure S3 and Texts S1 in the ***Supplement***.

Page 6, lines 174−176:

"Moreover, sensitivity analysis further supported that a small change in NH_3, leading to a bit pH variation (see Text S1 and Fig. S3 in the Supplement). Thus, the 2025 NH_3 data can be as an alteration to represent ambient NH_3 levels in Mt. Daming."

References

[1] Guo, H., Weber, R. J., & Nenes, A. (2017). High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production. Scientific Reports, 7(1), 12109. https://doi.org/10.1038/s41598-017-11704-0

[2] Weber, R. J., Guo, H., Russell, A. G., & Nenes, A. (2016). High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. Nature Geoscience, 9(4), 282−285. https://doi.org/10.1038/ngeo2665.

Comment 4: Figure 2e: In consideration of the deviation, single peak pattern may be more suitable for size distributions of total Fe rather than bimodal pattern.

Response: We agree with the reviewer's comment. Given the large standard deviations (error bars), describing it strictly as "bimodal" might overstate the separation. We have revised it in the manuscript.

Page 7, lines 206−208:

"The size distribution of Fe_T was dominated by supermicron particles, with a pronounced peak in the 3.2–5.6 μm size range (Fig. 2e)."

Comment 5: Line 287–289. The concentrations of oxalate were estimated by empirical relationship with sulfate, resulting in associated uncertainty. Therefore, the result "organic acids played a limited role in Fe dissolution" should be more conservative. In addition, what about the potential synergistic effect between organic and inorganic acids on Fe dissolution?

Response: We thank the reviewer for this constructive comment. We acknowledge that the empirical estimation of oxalate concentrations introduces inherent uncertainties. We have revised the manuscript to adopt a more conservative tone regarding the role of organic acids and have expanded our discussion on the potential synergistic effects between organic and inorganic acids (**Page 12, lines 311–316**). However, our conclusion that organic acids play a relatively limited role in Fe dissolution should be understood in the context of the following two aspects:

(1) **Particle size dependence**

Previous studies have shown that ligand-promoted dissolution by organic acids, such as oxalate, is most effective in fine particles, where oxalate can act synergistically with protons to enhance Fe solubility. For example, Zhang et al. (2021) reported a significant correlation between Fe solubility and the oxalate-to-Fe ratio in fine particles ($r = 0.34$, $p < 0.01$), but no such relationship in coarse particles ($r = 0.04$, $p > 0.05$). Moreover, Shi et al. (2022) also showed that the contribution of organics (e.g., oxalate) to Fe solubility was more significant in the fine particles (D_p <1 μm). These findings suggest that organic ligands may enhance Fe dissolution in fine aerosols but exert a much weaker influence in coarse particles. As our analysis is based on total suspended particles (TSP), which are dominated by coarse-mode, the contribution of organic-acid-driven dissolution is expected to be comparatively small.

References

[1] 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.org10.1029/2021jd036070, 2022.

[2] Shi, J., Guan, Y., Gao, H., Yao, X., Wang, R., and Zhang, D.: Aerosol Iron Solubility Specification in the Global Marine Atmosphere with Machine Learning, Environ. Sci. Technol., 56, 16453−16461, https://doi.org10.1021/acs.est.2c05266, 2022.

(2) **Relative Concentration Levels**

Although organic acids can contribute to Fe mobilization, their concentrations are generally much lower than those of strong inorganic acids such as sulfuric and nitric acids. For instance, Deshmukh et al. (2023) reported oxalate-to-sulfate and oxalate-to-nitrate mass ratios of approximately 1:25 and 1:4 in fine particles (D_p <1 μm), and ~1:16 and ~1:18 in coarse particles (D_p >1 μm), respectively. In our original manuscript, oxalate concentrations in TSP were estimated following an empirical relationship ($[C_2O_4^{2-}] = 0.05 \times [SO_4^{2-}] - 0.273$) proposed by Yu et al. (2005), yielding oxalate-to-(sulfate + nitrate) ratios of ~6% at the mountain site and ~5% at Hangzhou. These low relative loadings suggest that even with synergistic effects, the total capacity for ligand-promoted dissolution remains small. Consistent with this interpretation, our recent work (Li et al., 2025) showed that oxalate—similar to Ca^{2+}—is predominantly associated with coarse-mode particles, with peak concentrations in the 3.2–5.6 μm size range, in agreement with Deshmukh et al. (2023). Given that coarse particles generally exhibit lower surface-area-to-mass ratios and slower dissolution kinetics, the effectiveness of oxalate-driven ligand-promoted dissolution in TSP is expected to be reduced.

Overall, while we recognize the uncertainties associated with the indirect estimation of oxalate and the potential for synergistic acid effects, our results suggest that, for bulk

TSP in urban and mountain environments, inorganic acids dominate Fe dissolution, with organic acids playing a secondary or modulating role rather than a primary driver. We have revised the manuscript accordingly to reflect this more conservative interpretation.

Page 12, lines 311–316:

"Field-based evidence indicates that ligand-promoted pathways involving organic acids can enhance Fe dissolution more efficiently in fine particles (Shi et al., 2022; Zhang et al., 2022). In our study, however, the analysis is based on bulk TSP samples, and oxalic acid concentrations in both the ground-level (Hangzhou) and the upper mixing layer (Mt. Daming) were relatively low (Text S3 in the Supplement*)*. Under these conditions, Fe dissolution is likely dominated by inorganic acids, and the contribution of organic acids is therefore expected to be limited. Accordingly, we focus primarily on the proton-promoted dissolution pathway."

References

[1] Deshmukh, D. K., Kawamura, K., Kobayashi, M., & Gowda, D. (2023). Changes in the Size Distributions of Oxalic Acid and Related Polar Compounds Over Northern Japan During Spring. Journal of Geophysical Research: Atmospheres, 128(11), e2022JD038461. https://doi.org/10.1029/2022jd038461

[2] Yu, J. Z., Huang, X. F., Xu, J., & Hu, M. (2005). When Aerosol Sulfate Goes Up, So Does Oxalate-Implication for the Formation Mechanisms of Oxalate. Environmental Science & Technology, 39(1), 128–133. https://doi.org/10.1021/es049559f

[3] Li, W. J., Ito, A., Wang, G. C., et al. (2025). Aqueous-phase secondary organic aerosol formation on mineral dust, National Science Review, nwaf221, https://doi.org/10.1093/nsr/nwaf221

Minor Comments

Comment 1: The relevant work of Tang et al. (2025, AMT) and Chen et al. (2024, EST) might be considered for citation in this manuscript.

Response: We thank the reviewer for pointing out these relevant studies. We have now added citations of Tang et al. (2025, AMT) and Chen et al. (2024, EST) and incorporated them into our revised manuscript.

Comment 2: Line 185 "…or 10–18…", "or" should be replaced with "and".

Response: Corrected. Please refer to **Page 7, line 202**.