Authors' response to comments made by anonymous reviewer #1:

This study examines the role of NH_3 emissions in global aerosol chemical composition and acidity. The study uses the EMAC model with three different emissions scenarios to quantify effects on size-resolved inorganic aerosol composition and pH. The study observes a link between NH_3 emissions and pH, with complex effects that vary regionally. The study is the first, to my knowledge, to examine predictions of aerosol pH and the sensitivity of pH to different emissions scenarios on a global scale. The study highlights some current model limitations that contribute to challenges predicting pH. The manuscript is very well written and nicely organized. The scope is certainly a fit for ACP and I believe it will be of interest to a broad audience once a number of issues are addressed.

We thank the reviewer for the thoughtful and positive comments on our manuscript. We greatly appreciate the constructive feedback provided, which has helped us improve the clarity and overall quality of the manuscript. Below, we provide a point-by-point response (in black) to all the issues raised (in red).

Specific Comments:

1. A significant issue with the manuscript is the predictions of pH in arid regions of the globe. Thermodynamic equilibrium models, including ISORROPIA, are challenged to represent aerosol pH when relative humidity is low (e.g., see the extensive discussion in Pye et al. (2020)). The manuscript contains significant discussion of results in dry, arid regions – e.g., the Middle East, and over desert regions. The physical interpretation of these results is ambiguous unless the predictions of ALWC and aerosol pH in these regions are more closely scrutinized. The associated discussions likely need substantial revision, or at least more discussion about the potential problems of such predictions under low RH conditions.

We thank the reviewer for highlighting the limitations of thermodynamic equilibrium models under low relative humidity (RH) conditions. We fully acknowledge that predicting aerosol pH in arid regions remains a significant challenge, as discussed in Pye et al. (2020). Discrepancies among thermodynamic models tend to grow as RH decreases, primarily due to differences in the assumptions about activity coefficients. For instance, ISORROPIA assumes constant mean activity coefficients and a unity activity coefficient for H^+, which results in relatively invariant and often lower pH predictions under dry conditions. In contrast, models such as E-AIM incorporate RH-dependent variations in single-ion activity coefficients for both solutes and solvents, potentially leading to more dynamic pH behavior as RH changes. Additionally, the choice between stable and metastable phase state assumptions introduces further uncertainty. Under low RH (e.g., <35%), the metastable assumption allows for supersaturated solutions, enabling pH calculations even at low aerosol liquid water content (ALWC), often resulting in low pH values. Conversely, the stable state permits salt crystallization, and in cases where the aerosol becomes fully solid, pH may no longer be defined. To assess the sensitivity of our results to this assumption, we conducted a simulation using the metastable assumption (Meta case; see Table 1), with results presented in Table 9 and Figure 7. We have revised the relevant discussion sections (especially section 2.2.1) to better reflect these uncertainties and to avoid overinterpreting pH predictions in arid regions.

2. The title and the abstract are misleading because the different emission scenarios vary SO_2 and NO_x emissions at the same time as NH_3. Therefore, interpreting the results is more complex than a typical modeling sensitivity analysis where one factor is varied while all other factors are held constant. In the case of pH, it is not straightforward to attribute the observed changes to the differences in NH_3 because the precursors for aerosol sulfate and nitrate also changed simultaneously. With the emissions in SO_2, NO_x, and NH_3 changing in different directions (some regions, these go up, in other regions, they go down, and not always together), the results were quite complex and not easy to interpret. For example, a conclusion of the study succinctly stated in Line 707 is: "pH changes closely correspond to variations in NH_3 emissions", however, the study is not really able to derive the quantitative relationship in each region because of the concurrent changes in SO_2 and NO_x. Ultimately, I think the authors need to do more to facilitate interpretation of the results and isolate the effects of individual species on the observed changes in pH, though this is not easy.

We sincerely thank the reviewer for this insightful comment. We acknowledge that the emission scenarios used in our study involve simultaneous changes in SO_2 and NO_x emissions, while NH_3 emissions are not directly varied but are instead represented using three different emission inventories: two bottom-up inventories (CAMS and CEDS_GBD) and one top-down inventory (Luo et al., 2022). This approach allows us to explore the sensitivity of aerosol pH to plausible variations in NH_3 emissions as reflected by different inventory methodologies, rather than through isolated perturbation experiments. We agree that the co-variation of SO_2, NO_x, and NH_3 across these inventories adds complexity to the interpretation of pH changes, and we have revised the manuscript to clearly articulate this point. The title has been revised to "*The influence of ammonia emission inventories on the size-resolved global atmospheric aerosol composition and acidity*" to more accurately reflect the study. Furthermore, we have expanded the discussion in Section 7 to more explicitly address the interactions among NH_3, SO_2, and NO_x, and we have revised the abstract and conclusion to better reflect the complexity of interpreting pH responses under varying emission inputs and avoid over-attributing pH changes to NH_3 alone.

3. The authors acknowledge that the size-resolved pH predictions do not follow the expected trend in many cases, as pH does not systematically decrease with decreasing particle diameter for the different size bins in many locations. Only when NH_3 emissions are eliminated does the model predict more acidic smaller particles. The model errors in predictions of NH_3/NH_4^+ partitioning suggest there are associated errors in the predictions of aerosol pH. Much more discussion of this point is warranted.

Indeed, our model does not consistently reproduce the expected trend of decreasing pH with decreasing particle size across all regions. This trend is only clearly observed in the no-NH_3 scenario, where smaller particles are predicted to be more acidic than those in the coarse mode. To further investigate this issue, we compared the simulated SNA composition and NH_3/NH_4^+ partitioning ratios with available observational data. This comparison revealed discrepancies that can contribute to positive biases in pH predictions of submicron particles, particularly an overestimation of NH_3 partitioning into the aerosol phase and an underestimation of acidic components such as sulfate and nitrate, especially over Europe. We have incorporated a more detailed discussion of these findings in Section 6, emphasizing the implications of partitioning errors on size-resolved pH predictions. We highlight the need for caution when interpreting pH trends in regions with high ammonium content in fine aerosol modes, where model uncertainties in gas-particle partitioning can significantly influence the predicted acidity.

4. A comparison of stable and metastable mode results from thermodynamic models has been done before. However, it has never been done for global simulations, so the present results are quite important because of their scale. I encourage the authors to expand on this discussion and to consider moving Fig. S4 to the main manuscript.

We thank the reviewer for this valuable suggestion. Karydis et al. (2021) conducted a global-scale comparison of stable and metastable state assumptions and found that the stable-state assumption leads to global average pH values approximately 0.5 units higher than those under metastable conditions. Our study builds on this by providing additional insights into size-resolved pH differences and their regional variability. Our results corroborate the global-scale findings of Karydis et al. (2021) but also reveal that discrepancies between stable and metastable assumptions can be substantially larger, exceeding 2 pH units, in regions with high concentrations of crustal cations and persistently low RH, such as South Asia and the Middle East. Moreover, our analysis highlights how these differences vary across aerosol size modes, offering a more detailed understanding of the thermodynamic behavior of aerosols under varying environmental conditions. In response to the reviewer's recommendation, we have moved Figure S4 to the main manuscript as Figure 7, and we have expanded the discussion in Section 6 to more thoroughly examine the implications of phase state assumptions for interpreting aerosol acidity, particularly in arid and dust-influenced regions.

5. Section 2.2.2: it is really not accurate to frame the discussion around H^+ and H_2O, only. Other particle components can affect the aerosol pH by affecting the H^+ activity coefficient. Although ISORROPIA assumes an H^+ activity coefficient of unity, other models that solve for γ_{H+} would have an effect on pH from other aerosol components.

We agree that it is not fully accurate to frame the discussion of aerosol pH solely in terms of H^+ and H_2O. As correctly noted, other aerosol components, such as sulfate, nitrate, and organics, can significantly influence the ionic strength of the aerosol solution and, consequently, the activity coefficient of H^+. While ISORROPIA assumes a constant H^+ activity coefficient of unity, this simplification limits its ability to capture composition-dependent effects on pH, particularly under low relative humidity (RH) conditions where ionic strength can vary substantially. In our study, following ISORROPIA's framework, pH is approximated based on free-H^+ molality under the assumption of $\gamma_H{}^+ = 1$. Accordingly, our discussion in Section 2.2.2 focuses on variations in free-H^+ concentration as the primary driver of pH changes. We have revised Section 2.2.1 to explicitly acknowledge this limitation and to clarify that our pH estimates do not account for composition-dependent variations in activity coefficients. We also highlight that this simplification may contribute to discrepancies when comparing with models that include a more detailed thermodynamic treatment.

6. Table 7: why is the SE-USA case from Pye et al. (2020) not included in this comparison? Aerosol pH in this region has been studied extensively and should provide a good point of comparison for the present study.

We appreciate the reviewer's suggestion to include the SE-USA case from Pye et al. (2020) as a point of comparison. We agree that this region has been extensively studied and offers valuable insights into the aerosol pH behavior. However, the observational period in Pye et al. (2020) (June 6 – July 14, 2013) does not overlap with our simulation period (2009–2012), which limits the direct comparability of the datasets. Nevertheless, we now refer to the findings from that study in section 4.2 to provide additional context and to support the interpretation of our results in the southeastern U.S. region.

7. For the comparison to the field-derived pH in Xi'an shown in Table 7, the authors are encouraged to consult Guo et al. (2017), who provide a different estimate of aerosol pH in Xi'an. It is not reasonable to request the present manuscript to arbitrate this disagreement, however, the authors should be aware of different pH estimates for this region.

Similar to our response to Comment 6, the observational period in Guo et al. (2017), which focuses on winter 2013, falls outside our simulation period (2009–2012). Nonetheless, we recognize the importance of acknowledging alternative pH estimates for Xi'an. To reflect this, we have added a reference to Guo et al. (2017) in section 4.2, noting the differences in observational periods and highlighting the variability in reported pH values for this region. While our study does not attempt to reconcile these differences, we agree it is important to be aware of them when interpreting model–observation comparisons.

8. Overall comment: reconsider the number of sig figs used in many cases. E.g., in Section 5.3 reporting NH_3 emissions to 0.01 Tg and reporting NH_3 lifetimes to the 0.01 day do not likely reflect uncertainties in these values.

We agree with the reviewer's suggestion regarding numerical precision. We have revised the number of significant figures in Tables 2, 8, and S1, and throughout the related text. Emissions and deposition are now reported to 0.1 Tg yr^{-1}, burdens to 0.1 Tg, and lifetimes to 0.1 days.

9. Lines 72 – 74: this sentence needs revision – what does "excess NH_3 released to the atmosphere" really mean.

Due to reductions in SO_2 and NO_x emissions, the atmospheric formation of H_2SO_4 and HNO_3 has declined. Consequently, less NH_3 is required to neutralize these acids. At the same time, NH_3 emissions have remained stable or slightly increased, resulting in a relative surplus of NH_3 in the atmosphere. We have revised the sentence to clarify this point.

10. Color scale of Fig. 1 was quite difficult to determine the magnitude of the changes in many regions.

We have reconfigured the data intervals and the corresponding color bar to enhance visual clarity and improve the distinction between different regional patterns and gradients.

11. Line 411 and 430 (and elsewhere): best not to use phrases like this…global pH values show that sulfuric acid is rarely fully neutralized. See also Guo et al. (2017).

We have revised this terminology throughout the manuscript to use more appropriate language.

12. Paragraph lines 549 – 555: I do not follow the discussion in this paragraph.

We believe that part of the discrepancy in size-resolved pH calculations between models may arise from differences in how particle size distributions and gas-particle partitioning are treated. For example, the EMAC model uses a lognormal size distribution and applies ISORROPIA separately to each size mode to calculate gas-aerosol partitioning. In contrast, other studies (e.g., Kakavas et al., 2021) employ sectional approaches, where gas-aerosol partitioning is first performed on the bulk aerosol phase, and the resulting condensed mass is then distributed across size bins based on the available surface area. These fundamental differences in modeling assumptions can lead to variations in the predicted distribution of aerosol components across size ranges, which in turn affects the calculated size-resolved pH. To clarify this point, we have revised the text to better explain how differences in size distribution and partitioning methods may contribute to the observed discrepancies.

13. Line 562: the effect of NH_3 emissions on SNA formation has been studied for decades. Also, I would not categorize the effect of NH_3 emissions on pH as the "subject of debate," but rather understudied.

Thank you for the helpful suggestion. We agree that the role of NH_3 emissions in SNA formation has been extensively studied over the past decades. Additionally, we acknowledge that describing the effect of NH_3 on aerosol pH as a "subject of debate" may be misleading. A more accurate characterization is that this topic remains understudied, particularly in terms of its size-resolved and region-specific impacts in global modeling frameworks. Accordingly, we have revised the sentence in revised manuscript to better reflect the current state of knowledge.

14. Line 704: this is not true in terrestrial regions where highly acidic (e.g., pH < 2) particles are observed or predicted.

We apologize for the confusion. The original statement was intended to compare high-latitude marine aerosols to those over remote ocean regions, not to terrestrial regions. We have revised the text to clarify that high-latitude marine aerosols are more acidic compared to aerosols over remote oceanic regions.

Technical Corrections:

1. Line 67: trend should be plural.

Thank you for pointing this out. We have corrected the typo.

2. *Line 133: should 'of' be added after 'number'?*

Thank you for the suggestion. We have added "of" after "number" to improve clarity.

3. *Table 2 header: 'cases' is repeated.*

We have removed the repeated word.

4. *Line 653: do the authors mean 'marine aerosol' instead of 'oceanic'?*

Yes, "marine aerosol" is more accurate in this context. We have revised the text accordingly.

References

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific Reports, 7, 12109, 10.1038/s41598-017-11704-0, 2017a.

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, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmos. Chem. Phys., 20, 4809-4888, 10.5194/acp-20-4809-2020, 2020.