Note: Reviewer's comments are in *black italics*. Our replies are in blue. Changes in the manuscript are in red.

RC1: 'Comment on egusphere-2024-479', Anonymous Referee #2, 18 Mar 2024

The pH of aerosols is a crucial parameter that significantly impacts the entire atmospheric chemical process, and it is of utmost importance to accurately assess its value. This article primarily focuses on the issues of averaging methods and temporal resolution that are often overlooked in the process of calculating pH. It is found that these two factors can lead to differences in pH values ranging from 0.5 to 2 units, with the potential to affect the sulfate formation rate by up to two times. This is a meaningful study that provides important insights for our further understanding of the influencing factors of pH. I agree with the publication of this article in ACP. There are a few minor issues that need to be addressed before that.

Response: Thank you very much for the positive evaluation. We have carefully considered your suggestions and have responded to them by point-to-point below.

(1) I did not see how the value of activity of H$^+$ used in calculating pH was obtained. It would be helpful to make this clearer in the article.

Response: The ISORROPIA-II model (version 2.2) was used in GEOS-Chem to calculate the thermodynamic equilibrium processes for the H$^+$−NH$_4^+$−K$^+$−Ca^{2+}−Mg^{2+}−Na$^+$−OH$^-$−SO$_4^{2-}$−NO$_3^-$−Cl$^-$−H$_2$O inorganic aerosol system in this paper. Numerous simplifying assumptions in ISORROPIA-II were taken to increase computational speed and numerical stability without substantially compromising rigor. These include γ_{H^+} was assumed to be equal to unity because the activity coefficient routines were unable to calculate them explicitly (Fountoukis and Nenes, 2007). Then the calculation of pH can be simplified as:

$$\text{pH} = -\log_{10}(a_{H^+}) = -\log_{10}(\gamma_{H^+}\frac{m_{H^+}}{m^\ominus}) = -\log_{10}(\frac{m_{H^+}}{m^\ominus}) - \log_{10}(\gamma_{H^+}) = -\log_{10}(\frac{m_{H^+}}{m^\ominus}) \quad (1)$$

$$m_{H^+} = \frac{x_{H^+}}{x_{\text{water}}} \times 55.509 \quad (2)$$

where a_{H^+} is the activity of H$^+$ (dimensionless), γ_{H^+} is the activity coefficient (dimensionless) of H$^+$, m_{H^+} is the molality (mol kg^{-1} water) of H$^+$, $m^\ominus$ is the standard molality (1 mol kg^{-1} water), and x_{H^+} and x_{water} indicate molar fraction of H$^+$ and aerosol liquid water. 55.509 is the molality of water (Peng et al., 2019).

The calculation of the activity of H$^+$ was neglected in the original paper, and we have made the following additions to the revised manuscript (Section 2.1 Evaluation datasets, **Page 4, Lines 99−105):**

The ISORROPIA-II model (version 2.2) was used in GEOS-Chem to calculate the thermodynamic equilibrium processes for the H$^+$−NH$_4^+$−K$^+$−Ca^{2+}−Mg^{2+}−Na$^+$−OH$^-$−SO$_4^{2-}$−NO$_3^-$−Cl$^-$−H$_2$O inorganic aerosol system (Fountoukis and Nenes, 2007; Pye et al., 2009). The model assumed that γ_{H^+} was always equal

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to unity. The calculation of pH was simplified as Eq. (5)

$$pH = -\log_{10}(\frac{m_{H^+}}{m^\ominus}) \tag{5}$$

$$m_{H^+} = \frac{x_{H^+}}{x_{water}} \times 55.509 \tag{6}$$

where x_{H^+} and x_{water} indicated molar fraction of H^+ and aerosol liquid water, respectively. $m^\ominus$ was the standard molality (1 mol kg^{-1} water), and 55.509 was the molality of water (Peng et al., 2019).

(2) The authors have discussed how averaging methods and temporal resolution can lead to significant differences in pH. It would be more helpful if they could provide more specific recommendations on how to use these.

The primary limitation of existing studies is the opaque methodology employed for pH averaging, often defaulting to the "arithmetic mean" as the sole measure of "average". Therefore, our primary recommendation is to provide detailed information about the averaging approach and temporal resolutions employed in specific studies. Additionally, we suggest that future studies include the original temporal resolution of pH data in supplementary information or publicly available datasets. We provide examples illustrating how to report pH based on the findings of this study.

While $\overline{pH_w^*}$ is more consistent with the central tendency of aerosol pH in the sense of atmospheric chemistry. Thus, calculations involving reaction kinetics necessitate short time steps, and any averaging approach introduces significant uncertainties. Therefore, for subsequent calculations, we recommend utilizing hourly-resolved data rather than longer time-resolved data.

We have made the following additions to the revised manuscript (Section 4 Conclusions, **Page 11, Lines 281−292**):

This technical note underscores the importance of avoiding the default use of the "arithmetic mean" as the sole measure of "average". Additionally, it is also essential to consider the uncertainties introduced by the chosen averaging approach and temporal resolutions, which should be described clearly in future studies to ensure comparability of aerosol pH between models and/or observations. Using this study as an example, pH results for the 2018/2019 winter in the North China Plain were derived at 3-hour resolution through GEOS-Chem simulations. Measures of central tendency included: arithmetic mean ($\overline{pH}$, 4.6), median (pH_{Md}, 4.6), mode (pH_{Mo}, 4.5), the arithmetic mean based on a_{H^+} ($\overline{pH^*}$, 2.6), and the volume-weighted mean based on AWC and a_{H^+} ($\overline{pH_w^*}$, 2.2). For further details, refer to *Code and data availability*.

From an atmospheric chemical perspective, $\overline{pH_w^*}$ may offer a more accurate representation of the central tendency of aerosol pH. However, significant changes in pH can induce shifts in reaction

(3) It seems that the x-axis in Figure 2(d) differs from the other sub-figures.

Thank you for your careful review. We have revised Figure 2 (now Figure 3 in the revised manuscript) accordingly (**Page 9**):
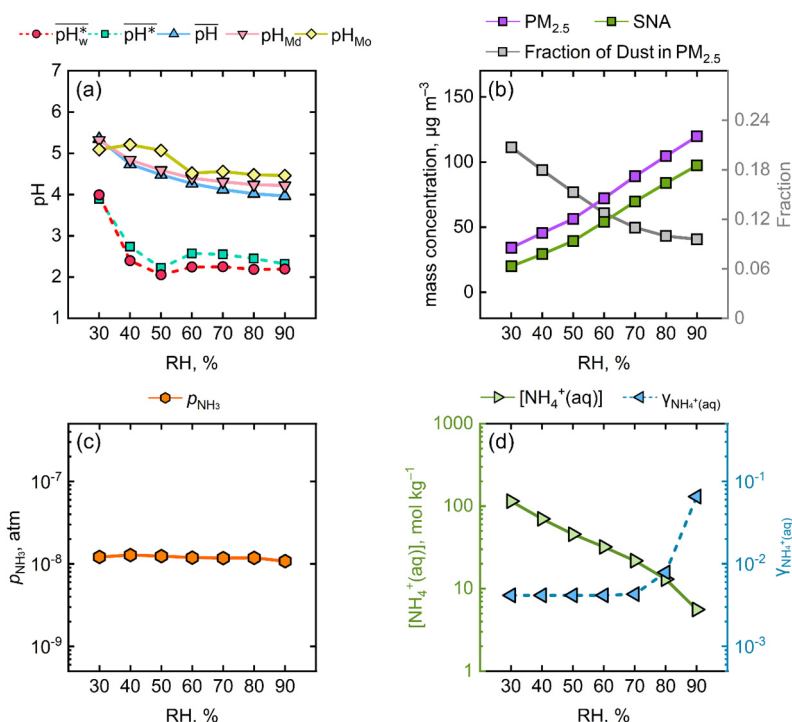
Figure 3. Variations of several chemical and physical parameters as a function of RH. (a) $\overline{\text{pH}_{\text{w}}^{*}}$, $\overline{\text{pH}^{*}}$, $\overline{\text{pH}}$, pH_{Md}, and pH_{Mo}. (b) Fraction of SNA (the summation of sulfate, nitrate, and ammonium) and Dust in PM₂.₅. (c) p_{NH_3}(atm). (d) $\left[\text{NH}_4^{+}(\text{aq})\right]$ (mol kg^{-1}) and $\gamma_{\text{NH}_4^{+}(\text{aq})}$. The range of RH was 25%−95%, and the parameters were averaged at 10% RH intervals.

Reference

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$_2$O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

Peng, X., Vasilakos, P., Nenes, A., Shi, G., Qian, Y., Shi, X., Xiao, Z., Chen, K., Feng, Y., and Russell, A. G.: Detailed Analysis of Estimated pH, Activity Coefficients, and Ion Concentrations between the Three Aerosol Thermodynamic Models, Environ. Sci. Technol., 53, 8903-8913, 10.1021/acs.est.9b00181, 2019.