Comments by Anonymous Referee #1

General Comments:

This study investigates the driving factors of ammonium nitrate activity using comprehensive simulations and global ambient observations, comparing three widely used thermodynamic models (ISORROPIA, E-AIM, and AIOMFAC) to clarify the impacts of meteorological conditions and chemical profiles.

The manuscript is acceptable for publication following the implementation of the following key revisions:

Responses:

We thank the reviewer for the comments. Please find our point-to-point responses below.

Specific comments:

1. *How does this study interpret the activity coefficient of ammonium nitrate (NH_4NO_3)? Aerosols are complex systems, and the individual activity coefficients of NH_4^+ and NO_3^- are objectively existing concepts. How is the activity coefficient of NH_4NO_3 defined to clarify its differences from those of other compounds such as sodium nitrate ($NaNO_3$) and ammonium sulfate ($(NH_4)_2SO_4$)? Additionally, why does the study use γ_{AN} in some places and its square in others?*

Responses:

We thank the reviewer for the comment. The mean activity coefficients of neutral electrolytes is typically defined as (Zünd, 2007):

$$\gamma_{\pm} = \left[\gamma_{+}^{\nu^{+}} \cdot \gamma_{-}^{\nu^{-}}\right]^{1/(\nu^{+}+\nu^{-})} \qquad \text{(R1)}$$

This concept is introduced as an important complement of the activity coefficients of individual cations and anions (γ_+ or γ_-), as only $\gamma_{\pm}$ can be directly measured. This is due to that any real solution must be electrically balanced. The γ_+ or γ_- cannot be measured, but is derived or calculated based on the measured $\gamma_{\pm}$ values under different conditions.

Following this convention, here the "activity coefficient of ammonium nitrate" (γ_{AN}) represents the mean ionic activity coefficient of the dissociated ion pair NH_4^+ and NO_3^-, which is defined as:

$$\gamma_{\mathrm{AN}} = \sqrt{\gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{NO_3^-}}}. \qquad \text{(R2a)}$$

Or equivalently,

$$\gamma^2{}_{\mathrm{AN}} = \gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{NO_3^-}} \qquad \text{(R2b)}$$

Similarly, the activity coefficient of sodium nitrate ($NaNO_3$) and ammonium sulfate ($(NH_4)_2SO_4$) would be defined as $\gamma_{\mathrm{SN}} = \sqrt{\gamma_{\mathrm{Na^+}}\gamma_{\mathrm{NO_3^-}}}$ and $\gamma_{\mathrm{AS}} = [\gamma_{\mathrm{NH_4^+}}.\gamma_{\mathrm{SO_4^{2-}}}{}^2]^{1/3}$, respectively. In a mixed solution of $NaNO_3$ and NH_4NO_3, for example, the $\gamma_{\mathrm{NO_3^-}}$ is the same, and their difference would be caused by the cation, or $\gamma^2{}_{\mathrm{AN}}/\gamma^2{}_{\mathrm{SN}} = \gamma_{\mathrm{NH_4^+}}/\gamma_{\mathrm{Na^+}}$.

For the three thermodynamic models of concern, ISORROPIA can only output the mean activity coefficient $\gamma_{\pm}$, while E-AIM and AIOMFAC can estimate individual cation and anion activity coefficient. As shown in Eq. R2b, the γ_{AN}^2 is adopted for consistency and easy comparison among the three models. In comparison, the γ_{AN} is used only for definition, or when referring to "the activity coefficient of ammonium nitrate".

We've further clarified this point in the revised manuscript as (see the last paragraph in Introduction):

"Our previous studies have revealed that the mean activity coefficient of ammonium nitrate, $\gamma_{AN} = \sqrt{\gamma_{NH_4^+}\gamma_{NO_3^-}}$, is a key parameter influencing the gas-particle partitioning of nitrate (see SI Text S1) (Zheng et al., 2022). Note that for easy comparison with individual ions and among different thermodynamic models, the square form of γ_{AN}, or $\gamma^2{}_{AN} = \gamma_{NH_4^+}\gamma_{NO_3^-}$, is adopted in following discussions (Zheng et al., 2022)."

2. *I understand that the authors did not decouple meteorological factors and chemical composition in the study design. However, the expression in lines 14–16 of the abstract may need further refinement to more clearly convey the interdependence and relative contributions of these two types of factors, thus avoiding potential ambiguity for readers regarding the study's core findings on γ_{AN}.*

Responses:

We thank the reviewer for the comment. We've further refined the statement into:

"For all three models and all chemicals profile tested, the γ_{AN}^2 correlates positively with relative humidity (RH) and temperature, and RH generally contributes larger variations ~~under typical scenarios~~. In comparison, the effect of chemical composition on γ_{AN}^2 is more complex and is strongly modulated by RH, with differed dependence pattern observed at varying RH levels."

3. *The title mentions the "impact on nitrate pollutions", yet the relevant description in the abstract is overly brief. It is recommended to supplement a concise statement explaining how discrepancies in ammonium nitrate activity coefficients among thermodynamic models affect the prediction, assessment, or mitigation of nitrate pollution. This will help readers quickly grasp the real-world relevance of the research beyond theoretical parameter analysis.*

Responses:

We thank the reviewer for the comment. We've added relevant statement in the revised abstract as:

"The activity coefficient of NH_4NO_3, γ_{AN}, is one key parameter controlling the gas-particle partitioning of nitrate, with lower γ_{AN} typically favoring particle-phase partitioning of nitrate. However, the γ_{AN} dependence on meteorological condition and chemical profile remains uncertain."

In addition, we've clarified this point in the manuscript as (see Line 71-76 in the revised manuscript):

"Our previous studies have revealed that the mean activity coefficient of ammonium nitrate, $\gamma_{AN} = \sqrt{\gamma_{NH_4^+}\gamma_{NO_3^-}}$, is a key parameter influencing the gas-particle partitioning of nitrate, with lower γ_{AN} typically favoring higher particle-phase partitioning of nitrate (see SI Text S1)(Zheng et al., 2022). This can be interpreted in that, the lower activity coefficient would reduce the activity of nitrate at given concentrations, while it's the activity that matters in the gas-particle equilibrium. Therefore, at given gas-phase concentrations, the equilibrium activity is fixed, while the actual particle-phase concentration would increase with decreased activity coefficient γ. Note that for easy comparison with individual ions and among different thermodynamic models, the square form of γ_{AN}, or $\gamma^2{}_{AN} = \gamma_{NH_4^+}\gamma_{NO_3^-}$, is adopted in following discussions (Zheng et al., 2022)."

4. *It is recommended that 2–3 sentences be added in the Introduction to summarize the comparisons of the three thermodynamic models (ISORROPIA, E-AIM, and AIOMFAC) regarding pH and hydrogen ion activity. This supplementation will help better highlight the research gap in the comparative analysis of γ_{AN} and clarify the necessity of the current study.*

Responses:

We thank the reviewer for the comment. Below has been added into Introduction line 79-83.

"Previous studies on thermodynamic model comparison and performance evaluations on non-ideality characterizations focused primarily on acidity (i.e., the activity coefficient of H^+) (Liu et al., 2017; Peng et al., 2019; Song et al., 2018; Yao et al., 2006; Zheng et al., 2022). These studies have shown that ISORROPIA, E-AIM, and AIOMFAC can yield systematically different predictions of aerosol pH under identical chemical and meteorological conditions, partially due to differences in their estimation of ion activity coefficients including γ_{H+} and γ^2_{AN}. Despite these documented discrepancies in acidity-related diagnostics, a comparable inter-model evaluation of the ammonium nitrate activity coefficient and its sensitivity to chemical and meteorological drivers remains scarce."

5. *The statement "AIOMFAC consistently underestimates..." in line 147 is overly absolute.*

Responses:

We thank the reviewer for the comment. We've revised accordingly as (see Line 163 in revised manuscript):

"Although ISORROPIA align relatively well with E-AIM considering the generally smaller γ^2_{AN} differences, the f_{p,NO_3^-} could still differ by $\sim \pm 0.1$. In comparison, AIOMFAC tends to underestimates γ^2_{AN} and consequently overestimates f_{p,NO_3^-} as compared with the other two models."