Comments by Anonymous Referee #2

General Comments:

Ammonium nitrate (AN) is an important inorganic aerosol, impacting air quality and climate. However, the activity coefficient of AN that shapes the gas-particle partitioning has not been well examined. This paper investigated the dependence of the activity coefficient of AN on meteorological conditions and chemical composition by using three commonly used thermodynamic models. The critical role of RH or ionic strength was demonstrated through well-designed aerosol proxies and real ambient aerosols. The findings have important implications for improving the prediction of ammonium nitrate aerosols. Overall, the paper is well written and fits the scope of ACP. The paper can be recommended for publication after addressing the following comments.

Responses:

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

Specific comments:

1. *Abstract: I would suggest the authors add 1-2 sentences to conclude the impact of uncertainties of the activity coefficient of AN on nitrate pollutions, given that the impact on nitrate pollutions has been highlighted in the title.*

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 70-77 in the revised manuscript): "Our previous studies have revealed that the mean activity coefficient of ammonium nitrate, $\gamma_{AN} = \sqrt{\gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{NO_3^-}}}$, is a key parameter influencing the gas-particle partitioning of nitrate, with lower γ_{AN} typically favors 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 ${\gamma^2}_{\mathrm{AN}} = \gamma_{\mathrm{NH_4^+}}\gamma_{\mathrm{NO_3^-}}$, is adopted in following discussions (Zheng et al., 2022)."

2. *Lines 50-60: It is unclear how the different methods of calculating activity coefficients for three models would introduce intrinsic differences in activity coefficients. More discussions on this aspect would help understand the different performances of the models.*

Responses:

We thank the reviewer for the comment. To address this concern, we have revised line 53-61 as below:

"The ISORROPIA employs an extended Debye-Hückel form ("Bromley's formula"), in which non-ideality is parameterized through empirical ion-pair terms. While computationally efficient, this approach assumes simplified binary ion interactions and is known to become less accurate at elevated ionic strengths of above ~6 mol kg^{-1}(Bromley, 1973; Nenes et al., 1998). The E-AIM calculated γ for individual ions based on the Pitzer–Simonson–Clegg formula, which accounted for long-range electrostatic interactions via Debye-Hückel effect and short-range binary/ternary ion–ion interactions through a Margules expansion(Clegg et al., 1992; Pitzer and Simonson, 1986), with parameters from empirical data (Carslaw et al., 1995; Clegg et al., 1998b; Friese and Ebel, 2010). This structure enables E-AIM to better capture non-ideal behavior in highly concentrated electrolyte solutions. AIOMFAC combines a Pitzer-like electrolyte model with a modified UNIFAC approach, representing long-, middle-, and short-range organic–inorganic interactions, allowing for explicit treatment of more organic–inorganic interactions (Zuend et al., 2010; Zünd, 2007). E-AIM and ISORROPIA ……"

3. *Lines 118-119: The amount of species in µg/m3 can be provided to have a straightforward connection with ambient conditions.*

Responses:

We thank the reviewer for the comment. Now it has been revised as below in line 132-134: "The total amount of anions is set to 1 µmol m^{-3}, corresponding to approximately 62–96 µg m^{-3} depending on anion composition (e.g., NO_3^- versus SO_4^{2-}), $NH_{3,\,tot}$ is fixed at 2 µmol m^{-3} (34 µg m^{-3}), ensuring an excess relative to anions."

4. *Line 155: As shown in Fig. S3, chloride is present in ISORROPIA, but not in EAIM. Why? How would chloride influence the calculations of activity coefficients?*

Responses:

We thank the reviewer for the comment. The presence of trace chloride in ISORROPIA originates from the internal structure of the model rather than from the input aerosol composition. For the Na^+-NH_3-H_2SO_4-HNO_3-H_2O system, ISORROPIA automatically invokes the ISRP3F subroutine, which is formulated for sodium–ammonium–nitrate–sulfate–chloride aerosol systems (Fountoukis and Nenes, 2007; Nenes et al., 1998). In this subroutine, Cl^- is treated as a potential aqueous species and the equilibrium equations are solved using a bisection method by scanning a range of very low [Cl^-(aq)] values to ensure numerical robustness. As a result, trace amounts of chloride may appear in the output even when no chloride is specified in the input.

The predicted chloride concentrations (10^{-5} µmol m^{-3}) are several orders of magnitude smaller than the dominant anions NO_3^- and SO_4^{2-} (10^{-1} µmol m^{-3}) (see Fig. S3), contributing negligibly to ionic strength. Consequently, their influence on the calculated activity coefficients is insignificant and does not affect the conclusions of this study. In contrast, E-AIM strictly solves the equilibrium based on the specified input species, and chloride is absent when it is not in the input.

5. *Lines 186-187: Is the dependence on RH and T similar for other conditions with different fractions of nitrate?*

Responses:

We thank the reviewer for the comment. To examine the robustness of the RH and *T* dependence under different nitrate fractions, we have added additional cases with f_{NO3-} = 0.6 and 0.9, which are presented in Fig. S7 of the Supplement. The results show that the overall dependence on RH and temperature remains qualitatively similar across the different nitrate fractions.

We've also clarified this point in the abstract as:

"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~~."

6. *Section 3.2.2: Have the authors examined the dependence of γ_{AN}^2 on sulfate concentrations? The presence of other soluble ions can largely mediate the calculation of activity coefficients.*

Responses:

We thank the reviewer for the comment. The dependence of γ_{AN}^2 on sulfate is implicitly examined in the chemical profile tests. In our setup, the total amount of anions (i.e., $[NO_3^-(p)+2[SO_4^{2-}(p)]$) is fixed at 1 μmol m^{-3}, and the nitrate fraction within the anion pool is defined as:

$$f_{NO_3^-}\left(\frac{\mu eq}{\mu eq}\right)=\frac{[NO_3^-(p)]}{[\mathrm{Anions}(p)]}=\frac{[NO_3^-(p)]}{[NO_3^-(p)]+2[SO_4^{2-}(p)]}$$

Therefore, when $f_{NO_3^-}$ is varied, the sulfate fraction changes accordingly. As a result, the influence of sulfate on γ_{AN}^2 is inherently embedded in the analysis through the varying anion composition.

7. *Lines 371-372: The underestimation may also arise from the uncertainties of measured f_{pNO3}. The authors should provide more discussion on this aspect and offer additional insights on how to narrow the discrepancies between measurements and models.*

Responses:

We thank the reviewer for the comment. We've revised the manuscript accordingly as (see line 286-298 in the revised manuscript):

"However, none of them are in good alignment with observational $f_pNO_3^-$, and larger underestimation is often seen in lower ambient $f_pNO_3^-$ range (see Fig. S10). This may also be partially attributed to the uncertainties of measured f_{pNO3}, including sampling artifacts associated with semi-volatile ammonium nitrate, potential volatilization losses during filter-based measurements, temporal mismatches between gas-phase HNO_3 and particulate NO_3^- observations, etc. These effects can be particularly pronounced under low total nitrate (NO_3^- + HNO_3) conditions, where small absolute errors in nitrate or nitric acid measurements may translate into large uncertainties in $f_pNO_3^-$ (Guo et al., 2016; Tao and Murphy, 2019). Future studies should therefore focus on narrowing these discrepancies through coordinated improvements in both measurement and model. On the measurement side, the use of online or semi-continuous techniques, together with collocated and time-resolved observations of gas-phase HNO_3 and particulate NO_3^-, would help reduce uncertainties associated with sampling artifacts and temporal mismatches. On the modeling side, the variability of $f_pNO_3^-$, especially at low nitrate levels, may be better captured by considering potential kinetic limitations and by improving the parameterization of activity coefficients in inorganic-organic mixed aerosol system. Observation-constrained modeling, together with sensitivity analyses, can further reduce discrepancies in $f_pNO_3^-$ between modeled and observed values.”