1. General Comments

This manuscript presents a thoughtful, methodologically integrated investigation of wintertime particulate nitrate formation in Seoul, combining high time-resolution HR-ToF-AMS measurements with explainable machine learning (XGBoost-SHAP), thermodynamic equilibrium modelling (ISORROPIA-Ⅱ), and HYSPLIT back-trajectory analysis. The persistence of elevated particulate nitrate in East Asian megacities despite substantial reductions in NO_x and NH_3 emissions is a science- and policy-relevant problem, and the authors' framing of the question is timely.

The most original contribution of this work, in my view, is the proposed mechanistic explanation for the late-morning (~10 AM) nitrate peak. Rather than attributing this peak to either daytime photochemistry alone or to downward mixing from a nitrate-rich nocturnal residual layer, the authors argue that **internally mixed urban aerosols persist in a metastable, semi-liquid state during periods of declining RH**, and that this retained aerosol liquid water enables continuous gas-to-particle partitioning of photochemically produced HNO_3. The convergence of three independent lines of evidence in support of this hypothesis—ML-derived feature attributions, ISORROPIA-II ALWC estimates, and AMS-derived size-distribution and shape-factor inferences—is compelling and represents a meaningful methodological advance.

In summary, this is a well-structured and scientifically valuable manuscript supported by clear evidence. While the core findings are persuasive, the study could be further strengthened through targeted clarifications and robustness checks. These enhancements should be feasible using the authors' existing datasets and tools.

2. Major Comments

2.1. More transparent treatment of the gas-phase measurement gap

The central mechanistic claim of this work—that photochemically produced $HNO_3(g)$ continuously partitions into metastable semi-liquid aerosols during the morning RH-decline period—rests fundamentally on assumed gas–particle partitioning dynamics. Direct measurements of HNO_3(g) and NH_3(g) were not available for this campaign. The authors acknowledge this in Section 2.4 (lines 131–132), but I think the implications would benefit from being treated more explicitly in the results discussion as well.

Suggestions:

(a) In Section 3.2.2 (in particular around lines 236–246), please add a sentence or two acknowledging that the $OH + NO_2 \rightarrow HNO_3$ pathway is invoked without direct gas-phase corroboration, and that the proposed mechanism is therefore inferred from the convergence of indirect evidence.

(b) The "thermodynamic precursor saturation" hypothesis offered to explain the subfreezing temperature plateau (lines 308–311) is reasonable but cannot be independently verified without information on residual gas-phase reservoirs. I would suggest softening "primarily indicative of" to "consistent with" or similar phrasing to better reflect this.

(c) The Conclusions (Section 4) would be a natural place to add a brief future-work paragraph noting that direct verification of this mechanism would benefit from coupled gas-phase HNO_3/NH_3 measurements in future campaigns.

2.2. Generalizability beyond a single haze event

Much of the detailed mechanistic analysis is anchored on the 8–9 February 2018 haze event (lines 70–72, 158–163). I would encourage the authors to provide some indication that the proposed mechanism is not unique to this single episode.

Suggestions:

(a) Using the existing campaign dataset, please verify whether the same RH-trend dependence (e.g., the ALWC contrast in Fig. 3a, or the diurnal nitrate pattern in Fig. S4) is reproducible during non-haze periods or weaker pollution episodes within the same campaign. A supplementary figure showing this consistency would substantially strengthen confidence in the generality of the mechanism. This should be feasible with the data already analyzed.

(b) The 2018 winter mean PM_1 (20.5 μg m^{-3}) was considerably lower than that of the previous winter (32.6 μg m^{-3} in 2017; Kim et al., 2022c). Please add a brief paragraph qualitatively discussing how this concentration difference might affect the generality of the proposed mechanism (a re-analysis of the 2017 data is not requested—a thoughtful discussion will suffice).

2.3. Multicollinearity in the SHAP-based interpretation

XGBoost is reasonably robust to feature correlation in terms of predictive performance, but SHAP attributions can be more difficult to interpret when input variables are strongly collinear. In a wintertime urban dataset, RH, temperature, solar radiation, and BLH all share pronounced diurnal cycles and are mutually correlated. Consequently, the reported relative contributions (NO_2: 31.6%, RH: 15.9%, solar radiation: 14.9%, temperature: 11.6%) should be interpreted with appropriate caution.

Suggestions:

(a) Please provide a pairwise correlation matrix (Pearson and/or Spearman) for the input features as a supplementary table. This is a minor analytical addition.
(b) Please add a brief caveat in the main text along the lines of: "given the inherent collinearity among meteorological variables, the reported SHAPRC values should be interpreted as relative rankings rather than as fully independent contributions."
(c) The statement at lines 285–287 that "no substantial interactions were found" between RH and other meteorological variables appears to rest primarily on Fig. S12. I would suggest softening this to something like "no strong interaction was apparent in the SHAP dependence plots," which more accurately reflects what the figure can support.

2.4. A brief robustness check for the central ALWC contrast

Figure 3a—showing higher ISORROPIA-II ALWC during the decreasing-RH period than the increasing-RH period at the same RH—is one of the paper's most important findings. Given that reverse-mode ISORROPIA-II is known to be sensitive to measurement noise (as the authors note at lines 139–142), a modest robustness check would strengthen this result.

Suggestions (either of the following would be sufficient):

(a) A simple sensitivity test in which the input ionic concentrations are perturbed by ±20%, demonstrating that the qualitative ALWC contrast between the increasing- and decreasing-RH periods is preserved. This should be quick to run with the existing analysis pipeline and could be presented as a supplementary figure.

(b) Alternatively, a brief paragraph explicitly framing the reverse-mode ALWC values as relative rather than absolute, and noting that the conclusions depend on the *contrast* between the two periods rather than on absolute ALWC magnitudes.

2.5. Brief acknowledgement of alternative interpretations for the Dva shift

The interpretation that the morning shift in peak Dva from ~350 nm to ~300 nm reflects an increase in dynamic shape factor due to partial efflorescence (lines 260–268) is creative and consistent with the broader narrative. However, alternative explanations are also possible—for instance, an increased contribution of fresh, smaller traffic-emitted particles during the morning rush hour, or changes in particle material density driven by compositional shifts (Dva in AMS depends on both density and shape factor).

Suggestion: It would be helpful to add two or three sentences in the relevant paragraph briefly acknowledging these alternative possibilities and explaining why the phase-transition interpretation is the most consistent with the full set of observations. No additional analysis is requested—a brief textual acknowledgement should be sufficient.

3. Minor Comments

- **Line 21 (Abstract):** The phrase "leverage points for mitigation strategies" is somewhat vague. Could the authors specify what these leverage points are—for example, humidity-aware emission control timing, or prioritization of NO_x reduction during specific meteorological windows?

- **Line 152:** A brief explanation of why 2018 winter PM_1 was lower than that of 2017 (meteorological factors, emission changes, or both) would help the reader assess the representativeness of the analyzed haze event.
- **Lines 175–178:** The reported quantitative contributions (31.6%, 15.9%, etc.) should be accompanied by uncertainty estimates derived from the 10-fold cross-validation (e.g., standard deviations). These should be readily available from the existing analysis.
- **Line 188:** Please specify whether the reported R values are Pearson or Spearman correlations.
- **Line 207:** The finding that BLH explains over 53% of NO_2 variability is striking and deserves a brief dedicated comment. It strongly supports the local accumulation hypothesis.
- **Line 225:** When stating "consistent with the deliquescence point of ammonium nitrate," please cite a specific value (the DRH of NH_4NO_3 is approximately 62% at 25°C).
- **Line 277:** The campaign-mean RH of 47.7% is well below the DRH of pure NH_4NO_3. The statement that this is "sufficient for nitrate deliquescence" therefore requires brief clarification—is this relying on efflorescence hysteresis, on mixed-salt MDRH lowering, or on both? A single sentence would suffice.
- **Lines 358–359:** A simple t-test (or non-parametric equivalent) on the wind speed comparison (1.72 vs 2.34 m s^{-1}) would lend statistical support to the stagnation argument.
- **Figure 1:** Adding error bars (e.g., interquartile ranges or ±1σ) on the diurnal averages would help convey the variability around the means.
- **Figure 4a:** The linear regression line ($y = 0.47x - 16.44$) fitted to clearly nonlinear data is potentially misleading. Please consider replacing it with a nonlinear fit or removing the fit line altogether.
- **Figure 5b:** The seasonal contrast in the RH–nitrate response is striking. Indicating the per-season sample sizes in the figure or its caption would help readers assess the robustness of the comparison.

- **Section 4 (Conclusions):** A more specific recommendation—for example, identifying the RH window or temperature range that air quality models should prioritize for improvement—would strengthen the policy and modelling impact of the paper. One or two added sentences would suffice.

4. Technical Corrections

- **Line 90:** "solar radiation wind speed, wind direction, and solar radiation" — "solar radiation" appears twice; missing comma after the first occurrence.
- **Line 188:** "(overall R=0.64; haze period; R=0.56)" — inconsistent semicolon usage.
- **Line 198:** "such as expanded boundary layer" → please add the article: "such as an expanded boundary layer."
- **Line 202:** Reported nitrate concentration of 5.19 ± 5.21 μg m^{-3} implies a coefficient of variation greater than 100%. Please verify the values.
- **Line 222:** "details in Text S2" — please ensure that Text S2 is appropriately labelled and locatable in the supplementary material.
- **Line 537:** The Tao et al., 2025 reference is missing a closing period.
- **Throughout:** Minor inconsistencies in subscript and superscript formatting for chemical species (e.g., NO_3^- vs NO3-, NH_4^+ vs NH4+) should be standardized.