Response to Reviewer 3

We appreciate the anonymous reviewer for the thoughtful reviews and comments. We have carefully considered the suggestions and revised the manuscript accordingly. The reviewer comments are in blue, our comments are in black, and modifications to the manuscript are in red.

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.

We thank the reviewer for the careful and constructive evaluation and for recognizing the value of the integrated measurement, machine-learning, thermodynamic, and trajectory analysis. We retained the central interpretation of the late-morning nitrate enhancement, but revised the manuscript to state more explicitly where the mechanism is inferred from converging indirect evidence and where direct gas-phase corroboration was not available.

In response to the major suggestions, we clarified the absence of HNO_3/NH_3 and aerosol pH measurements, added robustness checks for SHAP interpretation and the ALWC contrast, softened the subfreezing and phase-state language, and clarified that AMS Dva represents dried residual-particle sizing. We also added the requested figure-caption and reporting clarifications. The detailed manuscript changes are provided under the specific comments below.

Major comment 1

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 -> 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.

We agree. We revised the Results and Conclusions to state that the OH + NO_2 to HNO_3 pathway and subsequent gas-to-particle partitioning are inferred from indirect evidence: nitrate timing, RH tendency, ALWC diagnostics, and AMS dry-residue behavior. The Abstract was also revised consistently to state this mechanism as an inferred, campaign-specific interpretation; the exact Abstract revision is listed under Minor Comment 1.

We also softened the subfreezing interpretation and added a future-work statement recommending simultaneous particle nitrate, gas-phase HNO_3/NH_3, and aerosol pH/phase-state constraints.

Manuscript edits:

1. **Line 250:** "Under strict equilibrium thermodynamics, the concurrent drop in daytime RH would induce immediate particle efflorescence (crystallization), expelling liquid water and shutting down the aqueous volume required for this freshly formed HNO_3 to partition into the aerosol phase. However, our ML and observational analysis strongly suggest that internally mixed urban aerosols persist in a metastable, semi-liquid state well below their theoretical mutual deliquescence RH due to phase hysteresis (Davis et al., 2015; Tang and Munkelwitz, 1993). In this metastable state, the retained ALWC serves as a highly concentrated, high-ionic-strength absorptive reservoir. This allows the newly generated, photochemically produced $HNO_3(g)$ to continuously partition into the particle phase, bridging the gap between gas-phase production and aerosol-phase accumulation, and driving the 10 AM peak despite

drying conditions." **After:** "Decreasing RH can reduce particle water, but internally mixed nitrate-sulfate-organic haze particles may remain aqueous or partially aqueous during drying, depending on RH history and particle composition. Reported urban haze phase-transition ranges include solid-aqueous equilibrium states for urban haze particles at 60-79% RH and 55-77% RH during hydration, with aqueous phases retained during dehydration until about 55% RH and 50% RH, respectively (Sun et al., 2018). During 17 January-16 February 2018, measured RH ranged from 15.2% to 95.9%; haze mornings had a median morning peak RH of 64.3%, followed by a post-peak minimum RH of 43.6% before 11:00. We therefore interpret the morning nitrate enhancement as consistent with RH history, mixed-particle hygroscopicity, and gas-particle partitioning, while treating the literature phase-transition ranges as reference bounds rather than direct ambient phase-state measurements. Under this interpretation, retained ALWC can provide a concentrated absorptive reservoir that allows newly produced $HNO_3(g)$ to partition into the particle phase during drying, linking daytime gas-phase production with aerosol-phase nitrate accumulation. Because HNO_3 and NH_3 were not measured directly, this gas-to-particle partitioning pathway is inferred from the convergence of nitrate timing, RH tendency, ALWC diagnostics, and AMS dry-residue behavior; direct gas-phase corroboration was not available."

2. **Line 328:** "This plateau is primarily indicative of thermodynamic precursor saturation. At subfreezing temperatures, thermodynamic equilibrium shifts so heavily toward the particle phase that nearly all available gas-phase precursors (HNO_3 and NH_3) have likely already partitioned; once the gas-phase reservoir is depleted, further temperature decreases cannot yield more particulate nitrate." **After:** "Under the campaign conditions, this leveling-off is consistent with temperature not being the isolated control in the coldest regime. Although lower temperatures generally favor HNO_3 partitioning into the particle phase, the observed nitrate enhancement did not continue to increase under subfreezing conditions, indicating that the cold-regime response was governed by coupled changes in aerosol water and particle composition rather than by temperature-dependent partitioning alone."
3. **Line 373:** "Instead, the observed morning nitrate peak is more plausibly explained by the phase hysteresis and thermodynamic feedback loop described in Section 3.2.2. As RH begins to decline after sunrise (around 7–8 AM), particles resist immediate crystallization, retaining sufficient aerosol liquid water due to the lowered deliquescence threshold of the nitrate-rich mixture. This metastable aqueous volume allows the freshly generated, photochemically produced HNO_3 to continuously partition into the particle phase. The nitrate peak around 10 AM, therefore, likely reflects this critical transition window—where the retention of ALWC perfectly overlaps with the onset of daytime photochemical precursor production, driving efficient gas-to-particle conversion." **After:** "Instead, the observed morning nitrate peak is more consistent with the RH-history and particle-water interpretation described in Section 3.2.2. As RH begins to decline after sunrise, nitrate-rich mixed particles may retain particle water during part of the drying period, providing a reservoir for newly produced HNO_3 to partition into the particle phase. The nitrate peak around 10 AM therefore likely reflects the coincidence of retained particle water with

daytime photochemical precursor production, although direct gas-phase HNO_3/NH_3 and ambient phase-state measurements were not available."

4. **Line 418 Added:** "Future campaigns should include co-located particle nitrate, gas-phase HNO_3/NH_3, and aerosol pH or phase-state measurements to test the inferred partitioning mechanism."

Major comment 2

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).

We agree. We added the RH-history diagnostic as Figure S18. The diagnostic compares haze and non-haze mornings using pre-drying RH peak, post-peak RH minimum before 11:00, ALWC-based liquid duration during the drying interval, and morning nitrate growth.

This diagnostic addresses campaign-level reproducibility of the RH-history interpretation; broad regional transferability remains outside the scope of the 2018 dataset. The same drying-period structure was also present outside the main haze episode, with positive morning nitrate growth on 27 of 31 non-haze mornings and median non-haze morning nitrate growth of 2.25 μg m^{-3}, compared with 3.94 μg m^{-3} during the 7-11 February haze period. We also added a representativeness sentence noting that the lower 2018 mean PM_1 may reflect interannual differences in meteorological accumulation, regional transport, and/or emissions, so more severe winter haze conditions require separate evaluation.

Manuscript edits:

1. **Line 157 Added:** "The lower 2018 winter mean PM_1 likely reflects interannual differences in meteorological accumulation, regional transport, and/or emissions; these factors cannot be separated

without reanalyzing the 2017 dataset. The 2018 results are therefore treated as a campaign-specific winter case, with more severe winter haze conditions requiring separate evaluation."

2. **Added Figure S18:**

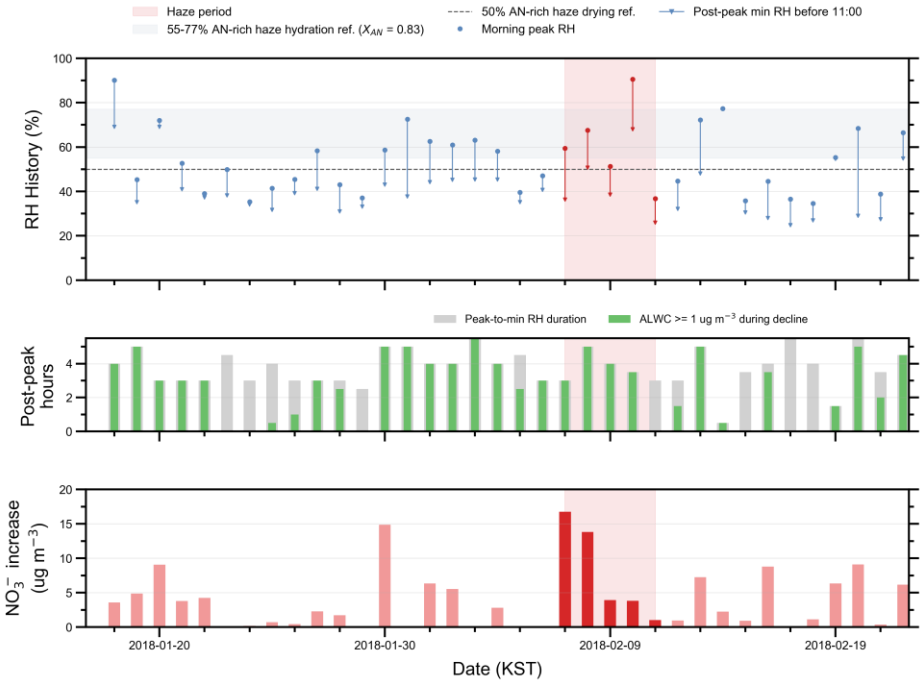


Figure S18. RH-history diagnostic for haze and non-haze mornings. The RH panel compares each day's morning peak RH with the post-peak minimum RH before 11:00; the minimum was required to occur after the peak. The shaded blue band and dashed line show Sun et al. (2018) AN-rich haze reference ranges for hydration and drying retention, used as literature bounds rather than Seoul-specific thresholds. The middle panel shows the peak-to-minimum RH duration and the portion of that drying interval with ISORROPIA-II ALWC >= 1 μg m^{-3}. The bottom panel shows the morning NO_3^- increase, calculated as the 06:00-11:00 peak minus the 03:00-06:00 mean background.

Major comment 3

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.

We agree. We added a Spearman feature-correlation matrix to the Supplement and added a main-text caveat that SHAPRC values are relative predictor rankings within the fitted model.

We also changed “no substantial interactions were found” to “no strong interaction was apparent in the SHAP dependence plots,” which better reflects what Fig. S12 can support.

Manuscript edits:

1. **Line 181:** “These results demonstrate that wintertime nitrate formation is jointly controlled by precursor abundance and meteorological conditions. Our integrated analysis quantitatively resolved the relative contributions of these factors, revealing that NO_2 is the dominant driver, explaining 31.6% of the observed variability in nitrate concentrations. RH (15.9%), solar radiation (14.9%), and temperature (11.6%) were also significant contributors. While precursor availability sets the upper bound for potential formation, meteorological conditions strongly regulate the actual production rate, especially when precursor levels are already high.” **After:** “These results indicate that, during the Seoul winter campaign, PM_1 nitrate variability was linked to measured precursor availability and meteorological conditions. In the XGBoost-SHAP analysis, NO_2 had the largest relative contribution to the model prediction (31.6% ± 0.6%), followed by RH (15.9% ± 0.9%), solar radiation (14.9% ± 0.7%), and temperature (11.6% ± 0.7%). Because meteorological predictors can covary, these percentages are treated as relative predictor rankings within the fitted model; chemical-source or pathway apportionment would require additional mechanistic constraints.”
2. **Line 306:** “No substantial interactions were found between RH and other meteorological variables such as temperature, solar radiation, or boundary layer height (BLH) (Fig. S12), indicating that the nonlinearity in RH's effect is largely intrinsic to RH itself.” **After:** “The SHAP dependence plots did not indicate a strong feature interaction under the observed campaign conditions (Fig. S12).”
3. **Added Figure S19:**

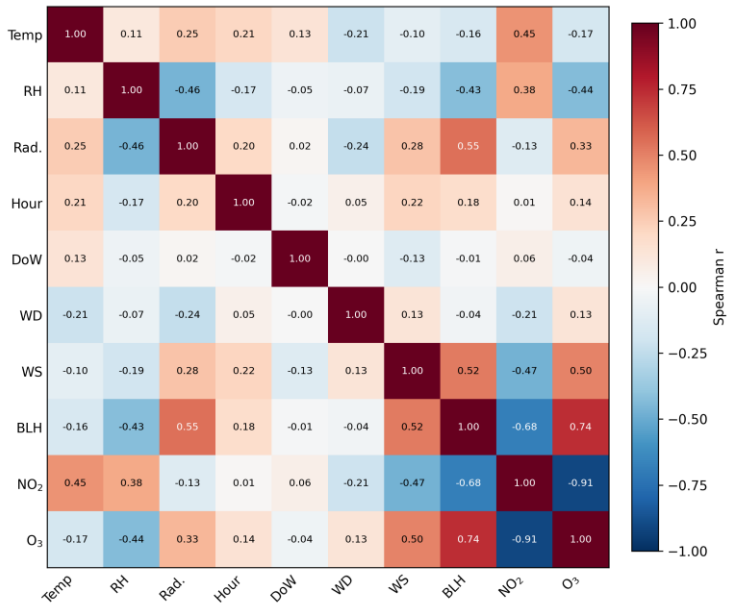


Figure S19. Spearman rank correlation matrix for the complete-case input-feature matrix used in the winter nitrate XGBoost-SHAP model (n = 6,985). Values indicate pairwise Spearman correlation coefficients (r) among temperature (Temp), relative humidity (RH), solar radiation (Rad.), hour of day (Hour), day of week (DoW), wind direction (WD), wind speed (WS), boundary layer height (BLH), NO_2, and O_3. This matrix documents input-feature covariation relevant to interpreting SHAP relative contributions.

Major comment 4

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.

We agree. We revised the manuscript to frame reverse-mode ALWC as a relative diagnostic and completed the requested ±20% ionic-concentration perturbation test with reverse-mode ISORROPIA-II.

For each time point, particle-phase Cl^-, NH_4, NO_3, and Cl were scaled together by 0.8, 1.0, and 1.2, while RH and temperature were unchanged. The same metastable ISORROPIA setting as the manuscript ALWC analysis was used.

The absolute ALWC scale changed, as expected, but the qualitative RH-tendency contrast was preserved. We use this as a robustness check on the Fig. 3a contrast.

Manuscript edits:

1. **Line 270 Added:** "A ±20% perturbation of particle-phase SO_4, NH_4, NO_3, and Cl preserved the decreasing-minus-increasing ALWC contrast in the 50-60% and 60-70% RH bins (Fig. S20)."
2. **Added Figure S20:**

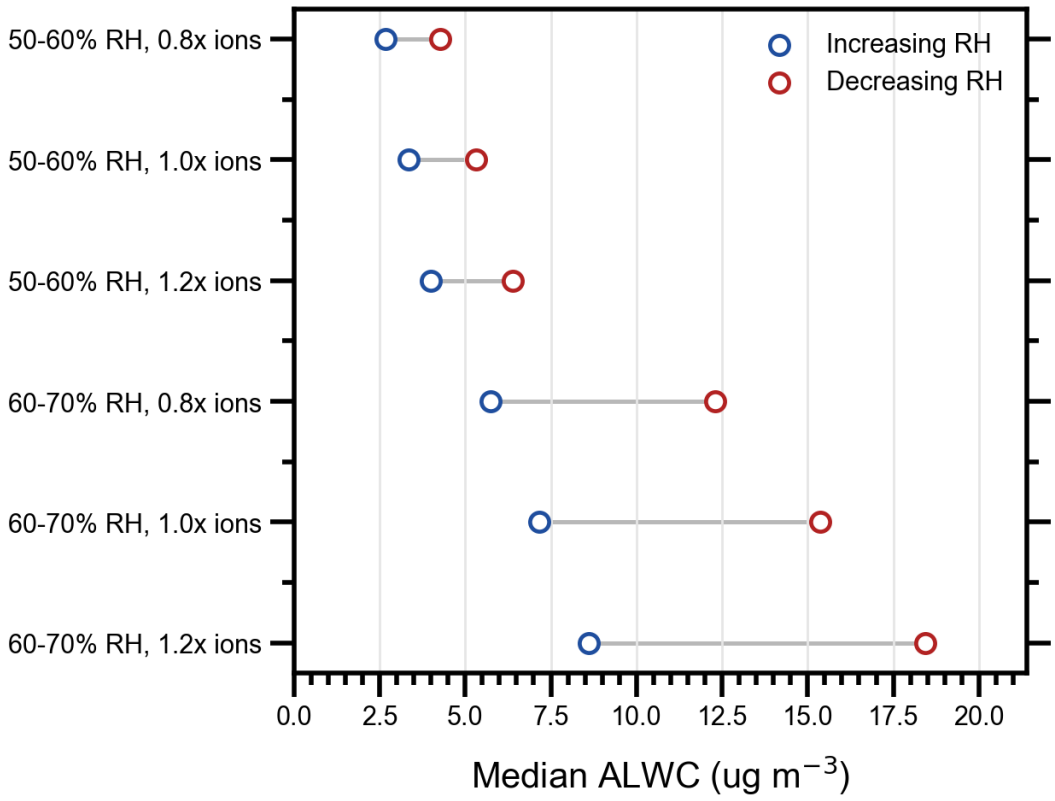


Figure S20. Sensitivity of the RH-tendency ALWC contrast to particle-ion input perturbations. Particle-phase SO_4, NH_4, NO_3, and Cl were scaled together by 0.8, 1.0, and 1.2, while RH and temperature were kept unchanged, and reverse-mode ISORROPIA-II ALWC was recalculated using the same metastable setting as in the manuscript. Points show median ALWC for increasing-RH and decreasing-RH periods; grey lines connect paired medians for the same RH bin and perturbation factor.

Major comment 5

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.

We agree and revised the Dva interpretation more conservatively. The Methods now state that the HR-ToF-AMS sampled through an inlet dryer, so Dva is interpreted as the vacuum aerodynamic diameter of dried non-refractory PM_1 residual particles.

The revised text no longer uses the Dva shift as direct evidence of ambient wet-particle shape, phase state, or partial efflorescence. Instead, it keeps the AMS size distribution as dry-residue evidence and acknowledges that fresh smaller traffic particles, dry-residue morphology or shape factor, and composition/material-density changes could contribute to the observed Dva behavior. The phase-related interpretation is therefore supported mainly by the RH-history and ALWC diagnostics, with Dva treated as a compatible but non-unique dry-residue observation.

Manuscript edits:

1. **Line 80 Added:** "The HR-ToF-AMS sampled through an inlet dryer; particle time-of-flight size distributions therefore represent dried non-refractory PM_1 residual particles."
2. **Line 282:** "Aerosol size distribution microphysics derived from the HR-ToF-AMS further substantiate this morphological transition (Fig. 3). During RH-decreasing periods, the peak vacuum aerodynamic diameter (Dva) of nitrate-containing particles shifted from ~350 nm to ~300 nm. Because the AMS measures Dva, which is highly sensitive to particle morphology and density, this reduction should not be interpreted merely as physical compaction of the dry mass. Rather, it provides strong observational evidence of partial efflorescence. As spherical liquid droplets begin to dehydrate and form semi-solid or crystalline inclusions, their dynamic shape factor (χ) increases (i.e., they become more irregular). An increased shape factor results in higher aerodynamic drag within the AMS aerodynamic lens, causing the particle to be measured at a smaller Dva even if the absolute dry mass is actively increasing (Decarlo et al., 2004; Canagaratna et al., 2007)." **After:** "The HR-ToF-AMS sampled through an inlet dryer; particle time-of-flight size distributions therefore represent dried non-refractory PM_1 residual-particle modes rather than wet ambient droplet morphology (Canagaratna et al., 2007). During the RH-decline period, nitrate-mode Dva shifted from approximately 350 to 300 nm. Dva depends on particle mass,

density, and dynamic shape factor (Canagaratna et al., 2007; DeCarlo et al., 2004), so this shift should not be interpreted as direct evidence of wet ambient particle shape or phase state. Instead, it indicates a change in the dried nitrate-containing residual-particle mode, with possible contributions from material-density changes, dry-residue morphology, and/or smaller fresh particles."

Minor Comment 1

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?

We agree. We revised the Abstract to replace the broad "leverage points" and strong mechanism wording with campaign-specific controls: NO_x availability, RH-history-dependent particle water, aerosol composition, and temperature-dependent partitioning. The revised wording also states that the morning partitioning pathway is inferred from RH tendency and ALWC diagnostics rather than directly measured gas-phase HNO_3/NH_3.

Manuscript edits:

1. **Line 12:** "While NO_2 availability is the primary control, our results reveal critical but underrepresented processes: (1) persistence of nitrate formation during late-morning relative humidity (RH) decline, sustained by metastable semi-liquid particles with retained liquid water that facilitate continuous gas-to-particle partitioning of photochemically produced HNO_3, and (2) temperature threshold effects, where subfreezing conditions suppress further nitrate formation primarily due to thermodynamic precursor saturation, compounded by potential diffusion limitations in highly viscous or solid phases. Contrary to common assumptions, boundary layer height contributes minimally to peak nitrate events. These findings demonstrate the need for air quality models to incorporate RH trends, aerosol phase transitions, and temperature-dependent reactivity to accurately predict nitrate episodes. This study identifies NO_x availability, RH-history windows, aerosol water and composition, and temperature-dependent partitioning as controls for wintertime PM_1 nitrate variability in Seoul." **After: "**NO_2 was the strongest measured gas-phase predictor of PM_1 nitrate variability, and the results point to two campaign-specific process windows: (1) late-morning nitrate enhancement during RH decline, consistent with RH-history-dependent particle water retention and continued HNO_3 partitioning inferred from RH tendency and ALWC diagnostics, and (2) a cold-regime temperature response in which nitrate enhancement leveled off under subfreezing conditions, even though lower temperatures alone would favor particle-phase nitrate, indicating control by coupled aerosol-water and composition changes rather than temperature-dependent partitioning alone. These findings indicate that air-quality models should evaluate RH history,

particle water and composition, NO_x availability, and temperature-dependent partitioning when simulating winter nitrate episodes in Seoul."

Minor Comment 2

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.

We agree. We added a qualitative representativeness sentence noting that the lower 2018 PM_1 may reflect interannual differences in meteorological accumulation, regional transport, and/or emissions, while avoiding assignment to a single cause without reanalyzing the 2017 dataset.

The corresponding manuscript edit is listed under Major Comment 2.2, where the same representativeness issue is addressed.

Minor Comment 3

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.

We agree. We added fold-to-fold uncertainty estimates for the manuscript-reported SHAP relative contributions using the 10-fold cross-validation workflow, while retaining the original SHAPRC baseline values.

Manuscript edits:

Line 181: "These results demonstrate that wintertime nitrate formation is jointly controlled by precursor abundance and meteorological conditions. Our integrated analysis quantitatively resolved the relative contributions of these factors, revealing that NO_2 is the dominant driver, explaining 31.6% of the observed variability in nitrate concentrations. RH (15.9%), solar radiation (14.9%), and temperature (11.6%) were also significant contributors." **After:** "These results indicate that, during the Seoul winter campaign, PM_1 nitrate variability was linked to measured precursor availability and meteorological conditions. In the XGBoost-SHAP analysis, NO_2 had the largest relative contribution to the model prediction (31.6% ± 0.6%), followed by RH (15.9% ± 0.9%), solar radiation (14.9% ± 0.7%), and temperature (11.6% ± 0.7%). Because meteorological predictors can covary, these percentages are treated as relative predictor rankings within the fitted model; chemical-source or pathway apportionment would require additional mechanistic constraints."

Minor Comment 4

Line 188: Please specify whether the reported R values are Pearson or Spearman correlations.

We agree. We revised the text and figure captions to specify whether reported correlations are Pearson or Spearman values.

Manuscript edits:

Line 195: "Strong positive correlation was observed…" **After:** "Strong Spearman positive correlation was observed"

Minor Comment 5

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.

We agree. We added a sentence after the NO_2 model result stating that the strong BLH contribution supports local precursor accumulation under shallow boundary-layer winter stagnation.

Manuscript edits:

Line 220: "This indicates that stagnant atmospheric conditions characterized by a shallow BLH promoted the accumulation of NO_2, thereby increasing the availability of precursors for nitrate formation." **After: "**The large BLH contribution to predicted NO_2 variability supports local precursor accumulation under shallow winter boundary-layer conditions."

Minor Comment 6

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).

We agree. We added the reference value that pure NH_4NO_3 deliquesces at approximately 62% RH near room temperature, and clarified that it is a pure-salt reference.

Manuscript edits:

Line 236: "During periods of increasing RH, nitrate particles undergo water uptake, particularly when RH exceeds ~65%, consistent with the deliquescence point of ammonium nitrate." **After: "**Pure NH_4NO_3 deliquesces at approximately 62% RH near room temperature; this value is cited as a pure-salt reference for comparison with internally mixed particles (Lightstone et al., 2000; Tao et al., 2018)."

Minor Comment 7

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?

We agree. The campaign-mean RH is not the appropriate diagnostic for this question. As shown in the Section 3.2.2 revision under Major Comment 1, we now use an RH-history diagnostic instead: during the campaign, RH ranged from 15.2% to 95.9%, and haze mornings had a median morning peak RH of 64.3%, slightly above the ~62% RH pure-NH_4NO_3 DRH reference, followed by a post-peak minimum RH of 43.6% before 11:00.

This peak-to-minimum behavior is the relevant context for water retention during drying. Because particle phase state was not directly measured, we do not assign a Seoul-specific deliquescence or efflorescence threshold. Instead, the revised interpretation is based on RH history and mixed-particle water retention, with the pure NH_4NO_3 DRH treated only as a reference value rather than as a campaign-average threshold.

Manuscript edits:

Line 296: "In contrast to nitrate, sulfate did not show a significant response to dynamic RH changes (Fig. S17b). This is likely due to the higher deliquescence point of sulfate-containing particles (~80%) compared to ammonium nitrate (Sun et al., 2018). The average RH during the campaign was 47.7 ± 16.3%, and 48.9 ± 14.5% during 7–10 AM—sufficient for nitrate deliquescence but typically below the threshold for sulfate. Consequently, RH-driven phase transitions played a lesser role in modulating sulfate chemistry, as evidenced by the lack of differential RH contributions between increasing and decreasing RH periods (Fig. S17c)." **After:** "Unlike nitrate, sulfate did not exhibit a distinct dependence on RH tendency in the SHAP analysis (Fig. S17c). This contrast is expected because sulfate is nonvolatile in the particle phase, whereas nitrate can vary through coupled aerosol-water changes and HNO_3-pNO_3 partitioning during morning drying. We therefore interpret the nitrate response using RH history and mixed-particle water retention, rather than campaign-average RH or separate pure-salt deliquescence thresholds."

Minor Comment 8

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.

We agree that the stagnation argument should be statistically supported. We added a within-campaign test showing that wind speed during the 7-11 February haze period was significantly lower than during the rest of the 2018 winter campaign (mean 1.38 vs. 1.83 m s^{-1}; $p < 0.001$). This supports the interpretation that stagnant conditions favored local accumulation during the haze episode.

Manuscript edits:

Line 384: "Stagnant atmospheric conditions such as low wind speeds (overall 1.72 ± 1.34 m s^{-1}; haze 1.38 ± 1.12 m s^{-1}) compared to the previous year with more transport contribution (overall 2.34 ± 1.20 m s^{-1}; haze 1.79 ± 0.06 m s^{-1}), likely suppressed effective long-range inflow while enhancing local accumulation (Cheong et al., 2024; Hou et al., 2022; Kim et al., 2022c)." **After:** "During the 2018 winter campaign, wind speed during the 7-11 February haze period was lower than during the remaining campaign (mean 1.38 vs. 1.83 m s^{-1}; $p < 0.001$), supporting local accumulation under stagnant winter conditions. The campaign-mean wind speed was also lower than that reported for the previous winter (overall 1.72 ± 1.34 vs. 2.34 ± 1.20 m s^{-1}), providing interannual context for weaker ventilation (Cheong et al., 2024; Hou et al., 2022; Kim et al., 2022c)."

Minor Comment 9

Figure 1: Adding error bars (e.g., interquartile ranges or ±1σ) on the diurnal averages would help convey the variability around the means.

We agree. We revised Figure 1 to show the interquartile range (IQR) for particulate nitrate. Because Figure 1 contains several variables with different axes, we show the nitrate IQR in the main figure for clarity; the variability of the other diurnal variables is already shown in Fig. S4.

Manuscript edits:

1. **Line 633: Added IQR range to nitrate in Figure 1. Updated Figure 1 caption.**

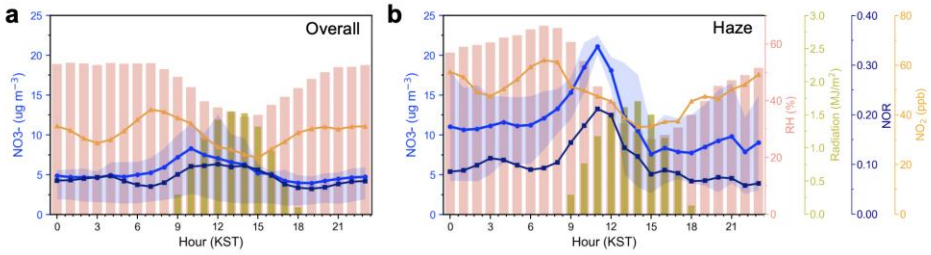


Figure 1: Diurnal variation of nitrate and NO_2 along with nitrogen oxidation ratio (NOR), RH, and solar radiation during winter season. Nitrate peaked around 10 AM, 3 hours after NO_2 peaked at 7 AM. The shaded band around particulate nitrate indicates the interquartile range (IQR); the variability of the other diurnal variables is shown in Fig. S4.

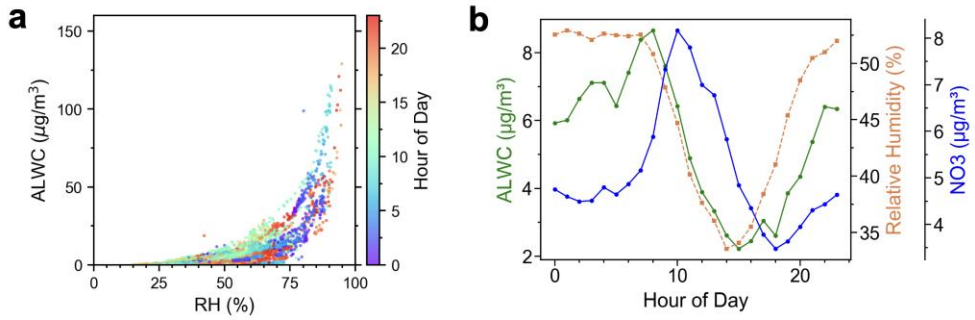
Minor Comment 10

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.

We agree. We removed the linear regression line and equation from Figure 4a, and the caption now describes the ALWC-RH relationship as nonlinear.

Manuscript edits:

Line 669: Removed the fit line from Figure 4's panel a.



Minor Comment 11

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.

We agree. We added the per-season sample sizes to the Figure 5 caption: Summer (n = 7,392) and Winter (n = 8,541).

Manuscript edits:

Line 670 Added: "Sample sizes are Summer (n = 7,392) and Winter (n = 8,541)."""

Minor Comment 12

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.

We agree. We revised the Conclusions to identify the morning RH-history window, the 50-70% RH contrast range used in the ALWC diagnostic, near-freezing/subfreezing temperature behavior around 0 °C, particle composition, and NO_x availability as process windows that models should evaluate during winter nitrate episodes.

Manuscript edits:

Line 411: “These findings highlight the importance of incorporating dynamic aerosol properties—such as RH trends, phase state transitions, and thermodynamic constraints—into chemical transport models and forecasting frameworks. Static parameterizations that overlook these effects may underestimate the conditions conducive to secondary nitrate formation, particularly during wintertime stagnation events. Advancing model treatments of these processes will be essential for improving the accuracy of nitrate predictions and supporting effective pollution mitigation strategies.” **After:** “When evaluating winter nitrate episodes, air-quality models should test sensitivity to morning RH-history, especially the 50-70% RH range where the ALWC contrast was most evident, and to near-freezing or subfreezing temperature regimes around 0 °C. These tests should be considered together with particle composition, NO_x availability, and shallow-boundary-layer conditions, because these coupled process windows can affect when nitrate accumulates during winter stagnation.”

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 NO_3^-, NH_4^+ vs NH_4+) should be standardized.

Thank you for identifying these technical issues. We corrected the duplicate predictor name, punctuation, article usage, reference punctuation, and chemical formatting, and clarified the Text S2 label in the Supplement. For nitrate, 5.19 ± 5.21 μg m^{-3} is reported as mean ± standard deviation; the large standard deviation reflects episodic variability, and all measured nitrate concentrations were above zero. We added the missing closing period to the Tao et al. (2025) reference and checked the reference list for the same punctuation issue. We also checked the manuscript and Supplement for chemical-species formatting and standardized the notation for nitrate, ammonium, sulfate, and related nitrogen species using consistent subscript/superscript formatting (e.g., NO_3^-, NH_4^+, SO_4^{2-}, NO_2, O_3, N_2O_5, HNO_3, and NH_3).

Manuscript edits:

1. **Line 91:** “solar radiation wind speed, wind direction, and solar radiation” **After:** “RH, temperature, wind speed, wind direction, and solar radiation”
2. **Line 196:** “(overall R=0.64; haze period; R=0.56)” **After:** “(overall R=0.64; haze period R=0.56)”
3. **Line 209:** “such as expanded boundary layer” **After:** “such as an expanded boundary layer”
4. **Line 213:** “nitrate showed substantial variability (5.19 ± 5.21 μg m^{-3})” **After:** “nitrate showed substantial variability (5.19 ± 5.21 μg m^{-3}, high standard deviation due to variability, but all nitrate concentrations were above zero)”

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