Response to Reviewer 2

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 comment

Many Asian regions have high concentrations of fine particle nitrate in cool seasons. There is significant interest in understanding the sources and processes that affect these aerosols to provide insights on how to lower PM2.5. The goal of this paper is to "investigate the atmospheric drivers of particulate nitrate formation in wintertime Seoul". The approach focusses on measurements between January 17 and February 16, 2018, in Seoul, Korea, a period that includes episodes of high PM_1 concentration (>40 ug/m3). ML was used to interpret the measurement data. Aerosol liquid water content (ALWC) was predicted by ISORROPIA in reverse mode.

Measurement data included: AMS PM_1 data, including nitrate (pNO_3); BC was reported but did not see info on the measurement method; gas phase O_3 and NO_2; various meteorological data (T, RH, wind speed/direction, solar strength).

There are major limitations in assessing drivers of PM_1 nitrate given this data set due to it's limited extent. This is especially true for attempting to link sources and processes (NO_x emissions and subsequent chemistry) to PM_1 nitrate concentration since there are many processes involved and species in addition to nitrate that can also be formed, such as various organo-nitrates (ie, gas phase PAN and related products, and particle organonitrates), and nitric acid. The ML analysis may identify from the limited set of variables certain links to nitrate, such as RH, T, etc, but the explanation provided in this manuscript for the cause for the link are not novel and not justified in some cases. Finally, the conclusion that various parameters, such as RH trends, phase state transitions, and thermodynamic constraints, need to be considered is nothing new. Most researchers addressing the question of what explains PM_1 nitrate would run a full thermodynamic analysis that incorporates these various aspects parameters, that means having measurements of key gas phase species, such as ammonia and nitric acie. Finally, some of the discussion on water uptake (efflorescence/deliquescence) and interpretation of AMS data to infer wet aerosol morphology is also questionable. I do not recommend publishing this paper.

We thank the reviewer for the detailed critique. We agree that this dataset cannot close a full nitrate-formation budget. The revised manuscript therefore no longer presents the ML result as a direct NO_x-to-nitrate source calculation, a gas-particle thermodynamic closure, or proof of ambient particle phase transitions. It is framed as an observation-constrained interpretation of measured PM_1 particle-nitrate variability in Seoul.

The specific revisions address the technical issues raised here: RH is discussed through RH history rather than campaign-average RH; ISORROPIA-II is limited to relative ALWC and bounded temperature sensitivity; AMS

Dva is limited to dried residual particle evidence because the instrument sampled through an inlet dryer; and the missing BC measurement method has been added.

Within this revised scope, we would also like to state what we believe the study still contributes. We agree that a full gas-particle thermodynamic budget would require co-located HNO_3 and NH_3 measurements, which were not part of this campaign's instrument suite and cannot be obtained retroactively. Rather than overstate a closure we cannot perform, we combine high-time-resolution HR-ToF-AMS composition with explainable machine learning, reverse-mode ISORROPIA-II aerosol-water diagnostics, RH-history classification, and back-trajectory analysis to characterize a specific, reproducible wintertime process window in Seoul: the persistence of PM_1 nitrate enhancement during the late-morning RH-decline period. As detailed in our response to Comment 2, a bounded forward-mode ISORROPIA-II diagnostic further indicates that during the high-nitrate haze periods central to our findings, nitrate is predominantly particle-phase, so the unmeasured gas-phase HNO_3 is a comparatively small fraction of total nitrate in exactly the regime of interest. We therefore believe the revised manuscript provides a measurement-grounded, appropriately bounded contribution, and we have removed the statements that previously exceeded what the data support.

Comment 1

There are major limitations in assessing drivers of PM_1 nitrate given this data set due to it's limited extent. This is especially true for attempting to link sources and processes (NO_x emissions and subsequent chemistry) to PM_1 nitrate concentration since there are many processes involved and species in addition to nitrate that can also be formed, such as various organo-nitrates (ie, gas phase PAN and related products, and particle organonitrates), and nitric acid. The ML analysis may identify from the limited set of variables certain links to nitrate, such as RH, T, etc, but the explanation provided in this manuscript for the cause for the link are not novel and not justified in some cases.

We agree that the original NO_2 language could be read as source attribution. We revised it to describe NO_2 as a reactive-nitrogen proxy and statistical predictor of observed PM_1 nitrate variability, not as a mass-balance source fraction.

As response-side support, the campaign-regime diagnostic shows that the top nitrate decile occurred at higher median NO_2 (0.057 ppm versus 0.024 ppm outside the top decile), higher RH (59.8% versus 43.2%), lower O_3 (0.007 ppm versus 0.022 ppm), and shallower BLH (241 m versus 523 m). Spearman correlations with nitrate were positive for NO_2 ($r = 0.727$) and RH ($r = 0.476$), negative for O_3 ($r = -0.613$) and BLH ($r = -0.473$), and near zero for solar radiation ($r = 0.029$). These values support interpreting NO_2 as a measured winter reactive-nitrogen proxy within stagnant, humid conditions, while PAN and particle organic nitrates are identified as unmeasured reservoirs whose contributions cannot be quantified from this dataset and are not expected to dominate this low-O3, weak-solar winter regime.

The novelty framing was also revised. RH effects, nitrate partitioning, and aerosol water uptake are now treated as established processes applied to the Seoul winter field case. We also softened the concluding transferability statement so that broader applicability is presented as a future evaluation need rather than as a direct conclusion from this campaign. At the same time, reframing the scope does not remove the study's specific contribution. Within this Seoul winter campaign, the convergence of XGBoost-SHAP predictor attribution, reverse-mode ISORROPIA-II aerosol-water diagnostics, and HR-ToF-AMS evidence resolves a specific and previously underexamined process window—the persistence of PM_1 nitrate enhancement through the late-morning RH-decline period—that is not explained by daytime photochemistry or nocturnal residual-layer mixing alone. We present this as an observation-grounded finding rather than a transferable mechanism, but it is a substantive result that the narrowed scope sharpens rather than removes.

Manuscript edits:

1. **Line 193:** "NO_2, the primary precursor of nitrate, was identified as the most significant contributor, accounting for 31.6% of nitrate formation during winter (Fig. 2a)." **After:** "NO_2 showed the largest SHAP relative contribution (31.6%) to predicted PM_1 nitrate variability, indicating that NO_2 was the strongest statistical predictor in this winter dataset (Fig. 2a), and the remaining SHAP attribution was distributed among meteorological and temporal predictors."
2. **Line 202:** "The observed association between NO_2 and nitrate, supported by strong correlations and consistent diurnal patterns, confirms NO_2 as a key precursor and highlights its central role in wintertime nitrate formation." **After:** "These winter observations indicate that measured NO_2 availability was closely linked to PM_1 inorganic nitrate variability. VOC-derived reactive-nitrogen reservoirs, including PAN and particle organic nitrates, were not measured, so their contributions cannot be quantified here. However, prior ground-based studies suggest that, because these reservoirs are photochemically driven, their influence may be more relevant during photochemically active seasons with limited wet removal, such as spring and autumn in urban Seoul (Lee et al., 2013)."
3. **Line 416:** "While this study focuses on Seoul during winter and summer, the mechanisms identified here—particularly those related to phase-dependent chemistry—are likely relevant across a range of urban settings." **After:** "While this study focuses on Seoul during winter and summer, the process interpretations discussed here—particularly those related to RH history, particle water, and temperature-dependent partitioning—should be treated as campaign-specific constraints. 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."

Comment 1b

Finally, the conclusion that various parameters, such as RH trends, phase state transitions, and thermodynamic constraints, need to be considered is nothing new. Most researchers addressing the question of what explains PM_1 nitrate would run a full thermodynamic analysis that incorporates these various aspects parameters, that means having measurements of key gas phase species, such as ammonia and nitric acid.

We agree. We revised the manuscript to treat RH trends, particle phase behavior, and thermodynamic constraints as established concepts used to interpret the Seoul winter observations.

We also clarified that reverse-mode ISORROPIA-II is used as a relative ALWC diagnostic, while forward-mode calculations are presented as bounded sensitivity tests based on prescribed reservoir assumptions.

The detailed low-temperature and phase-state wording is revised under the specific temperature comments below, where the response includes aerosol water, particle composition, OA influence, and the cold low-ALWC diagnostic.

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."
2. **Line 62:** "The results provide insights that can inform model development and support effective mitigation strategies for wintertime nitrate pollution in East Asian megacities" **After:** "The results

provide campaign-specific constraints for evaluating wintertime nitrate variability in Seoul and related East Asian urban environments."

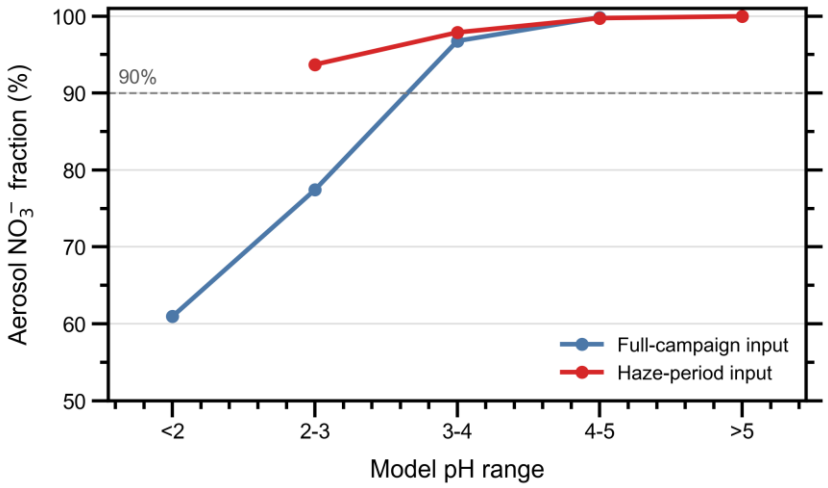
Comment 2

Considering just pNO_3 and HNO_3, since this is the focus of the paper, these species can change concentrations back and forth (ie, partition) due to changes in ambient conditions, such as T, RH, other aerosol species concentrations, all of which affect ALWC and pH. ALWC can be estimated from measured aerosol composition, which is what has been done in this paper. But factors that affect pH are not considered, and pH strongly affects HNO_3/pNO_3 partitioning (this is discussed at times in the paper). A thermodynamic equilibrium model can predict this partitioning and pH and is really required for a more in-depth analysis. Because partitioning back and forth between the gas and particle phase can be fast (10s of minutes), just discussing changes in observed pNO_3 severely limits the interpretation since there is a missing component, gas phase HNO_3.

We agree. The revised manuscript treats aerosol pH, total inorganic nitrate closure, and the ambient HNO_3/pNO_3 split as measurement boundaries because gas-phase HNO_3 and NH_3 were not measured. Observed pNO_3 is retained as the directly measured PM_1 particle-nitrate target.

We also revised the ALWC discussion to treat particle nitrate and water as coupled thermodynamic variables.

As a response-only check for the pH and partitioning issue, we performed a bounded forward-mode ISORROPIA-II diagnostic using representative full-campaign and haze-period particle-composition inputs. Because forward mode requires gas-plus-particle precursor inputs, and HNO_3 and NH_3 were not measured, we prescribed a small reservoir ensemble: NH_3 at 1x, 1.5x, and 2x the representative NH_4 level; HNO_3-equivalent nitrate at the representative particle NO_3 level plus 0, 2, and 5 $\mu g\ m^{-3}$; RH at 35%, 50%, and 65%; and temperature from -10 to 5 °C. The HNO_3 range was included because KORUS-AQ work found South Korean aerosol formation to be sensitive to HNO_3, especially in polluted regions (Ibikunle et al., 2024). The diagnostic is included in the response to show the expected pH-dependent partitioning behavior, but is not added to the manuscript or used as an ambient reconstruction of HNO_3, NH_3, or pH.



Response Figure 1. Forward-mode ISORROPIA-II pH-partitioning diagnostic included with the response. Points show prescribed NH_3/HNO_3 reservoir scenarios for representative full-campaign and haze-period particle-composition inputs; the reservoir ensemble is not measured campaign pH or reconstructed ambient HNO_3/NH_3.

Within these bounded scenarios, the modeled aerosol NO_3^- fraction increased with scenario-output pH, and haze-period inputs showed predominantly particle-phase nitrate across the tested pH ranges. Because the high-nitrate haze periods are the focus of our key findings, this indicates that the measured pNO_3 captures the large majority of total nitrate in precisely the regime of interest, so the unmeasured gas-phase HNO_3 represents a comparatively small fraction of total nitrate where our interpretation is concentrated.

The revised manuscript states this measurement need directly: pH effects, HNO_3/pNO_3 repartitioning, and nitrate-ALWC feedback require co-located particle nitrate, gas-phase HNO_3/NH_3, and aerosol pH measurements.

Manuscript edits:

1. **Line 135 Added:** "Reverse-mode ISORROPIA-II calculations were therefore used as a relative ALWC diagnostic based on measured particle composition, ambient temperature, and RH."
2. **Line 267:** "The diurnal cycle of ALWC largely follows RH, but with additional modulation by particulate NO_3^- (Fig. 4b)." **After:** "Because the reverse-mode ISORROPIA-II calculation uses measured particle-phase inorganic composition, including nitrate, the ALWC estimate includes water associated with particulate nitrate. We therefore interpret the ALWC-NO_3 relationship as composition-water coupling, not as an independent one-way effect of ALWC on nitrate."
3. **Line 276:** "This creates a thermodynamic positive feedback loop: the initial photochemical nitrate formation lowers the mutual deliquescence relative humidity (MDRH) of the aerosol mixture." **After:** "This pattern is consistent with composition-dependent water retention: increasing nitrate fraction can lower the effective RH required for particle water retention in a mixed aerosol."

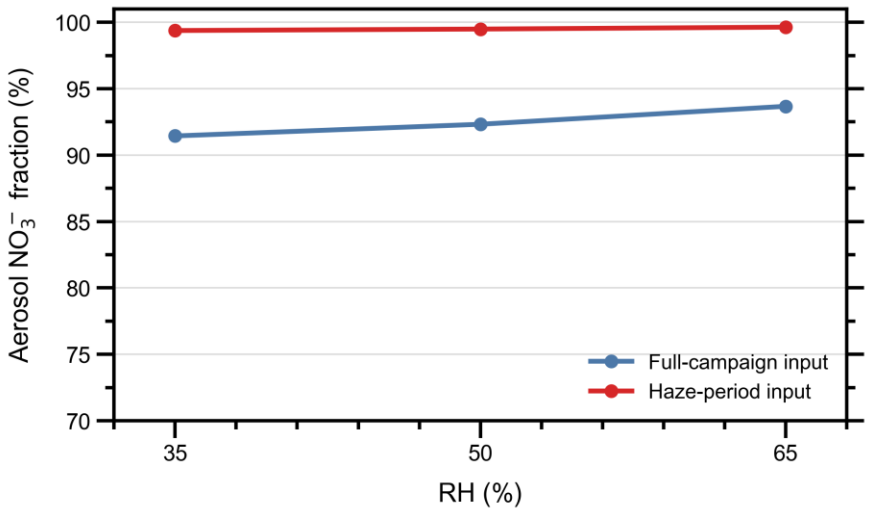
4. **Line 279:** "Operating in tandem with potential phase hysteresis, this sustained aqueous volume allows continuous HNO_3 partitioning, preventing immediate crystallization and driving the 10 AM peak." **After:** "Together with possible RH-history hysteresis, this retained particle water can support continued HNO_3 partitioning during the observed morning nitrate increase."
5. **Line 289:** "The continued accumulation of nitrate mass across size bins during this period (Fig. S3b) demonstrates that even as this morphological shift occurs, the particles retain sufficient ALWC in a metastable state to facilitate continuous HNO_3 gas-to-particle partitioning." **After:** "The continued accumulation of nitrate mass across size bins during this period (Fig. S3b) is consistent with particle-water retention inferred from the ALWC diagnostics, but does not directly determine ambient particle phase state."
6. **Line 293 Added:** "Within this framework, aerosol pH, total inorganic nitrate closure, HNO_3/pNO_3 partitioning, and possible N_2O_5-related production are treated as coupled factors influencing nitrate enhancement, without apportioning their individual pathway contributions."

Comment 3

Here is a specific example for this. Line 211-213 states: "The positive correlation between relative humidity (RH) and particulate nitrate is well established, primarily due to the enhancement of heterogeneous and aqueous-phase pathways such as N_2O_5 hydrolysis under high-RH conditions (Liu et al., 2020)". (Also, see discussion that go to the end of the paragraph, line 229.). This statement is highly qualified and not informative. For example, instead of concluding that this observation is linked to N_2O_5 hydrolysis, much of the RH affect could be due to a change in HNO_3/pNO_3 partitioning, which is a complex function of RH, T, and particle composition, ie pH, none of which are discussed. There is no way to know if N_2O_5 hydrolysis had any effect at all, so the statement is speculation.

We agree. We revised the RH discussion so it no longer assigns the RH-nitrate relationship mainly to N_2O_5 hydrolysis. RH is now treated as a coupled control on aerosol liquid water, HNO_3 partitioning, and possible heterogeneous chemistry.

As noted in Comment 2, the forward-mode ISORROPIA-II sensitivity tests are bounded by prescribed NH_3/HNO_3 reservoirs and are not reconstructions of ambient partitioning. Within the same response-only scenario framework, the RH-dependent cases support the narrower revised statement that RH can affect HNO_3/pNO_3 partitioning through particle water, while pathway apportionment remains outside the present observation set.



Response Figure 2. RH-dependent subset of the bounded ISORROPIA-II sensitivity framework described in Comment 2. Lines show median particle nitrate fraction across prescribed NH_3/HNO_3 reservoir and temperature scenarios at each RH step. The diagnostic is a sensitivity check, not a measured ambient HNO_3/pNO_3 partitioning reconstruction.

Manuscript edits:

1. **Line 223:** "The positive correlation between relative humidity (RH) and particulate nitrate is well established, primarily due to the enhancement of heterogeneous and aqueous-phase pathways such as N_2O_5 hydrolysis under high-RH conditions" **After:** "The positive correlation between RH and particulate nitrate reflects coupled effects of aerosol liquid water, HNO_3 partitioning, and heterogeneous or aqueous pathways such as N_2O_5 hydrolysis under high-RH conditions"

Comment 4

Line 186 to 187 states; "NO_2, the primary precursor of nitrate, was identified as the most significant contributor, accounting for 31.6% nitrate formation during winter (Fig. 2a)." What was the other source of the pNO_3?

We agree that the original wording could be read as a source fraction. The 31.6% value is now reported as a SHAP relative contribution for the XGBoost prediction of observed PM_1 nitrate variability.

The remaining SHAP contribution is distributed among other model predictors, and the campaign-regime check supports interpreting NO_2 as a precursor-availability proxy for the observed PM_1 nitrate target.

Manuscript edits:

1. **Line 193:** "NO_2, the primary precursor of nitrate, was identified as the most significant contributor, accounting for 31.6% of nitrate formation during winter (Fig. 2a)." **After:** "NO_2 showed the largest SHAP relative contribution (31.6%) to predicted PM_1 nitrate variability, indicating that NO_2 was the

strongest statistical predictor in this winter dataset (Fig. 2a), and the remaining SHAP attribution was distributed among meteorological and temporal predictors."

Comment 5

Line 238-240 states: "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." What is the expected RH for efflorescence and does the ambient measured RH every reach these values? There are publications on water uptake of ambient aerosols, which may provide some insights. How does particle mixing state effect this. In summary, is the actual ambient particle efflorescence RH known – or is this all speculation.

Thank you. We revised this paragraph to remove the sharp equilibrium-efflorescence claim. The manuscript no longer states that the daytime RH decrease would necessarily cause immediate particle crystallization.

Because particle phase state was not measured in Seoul, the cited urban-haze particle measurements provide literature context for mixed-particle RH-history behavior and reference ranges for interpreting the campaign RH record (Sun et al., 2018). We do not infer a Seoul-specific deliquescence or efflorescence threshold from these literature values.

The response diagnostic below reports the campaign RH context relevant to the reviewer's peak-RH point. During the campaign, RH ranged from 15.2% to 95.9%; haze mornings had a median peak RH of 64.3%, followed by a post-peak minimum RH of 43.6% before 11:00, with a median morning NO_3^- increase of 7.0 μg m^{-3}. We therefore describe the morning nitrate behavior as consistent with RH history, mixed-particle hygroscopicity, and gas-particle partitioning, while stating that the actual Seoul PM_1 efflorescence RH was not directly measured.

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."

2. **Supplementary Line 128:** "This RH decline is closely associated with aerosol phase transitions such as efflorescence and water evaporation." **After:** "This RH decline is closely associated with changes in particle water and possible RH-history-dependent phase behavior."
3. **Added Figure S18:**

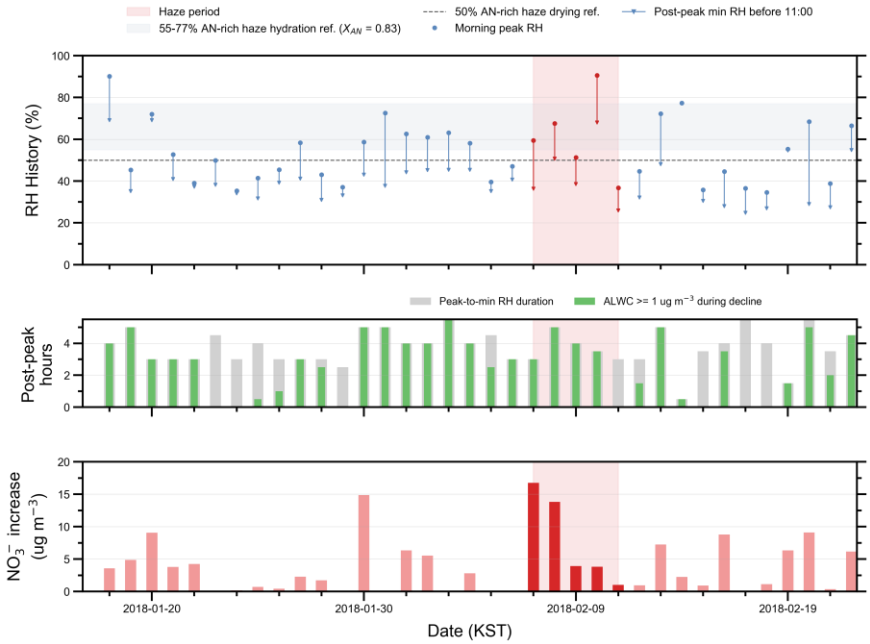


Figure S18. RH-history diagnostic for haze and non-haze mornings. The RH panel compares each day's morning peak RH with the post-peak minimum RH before 11:00; the minimum was required to occur after the peak. The shaded blue band and dashed line show Sun et al. (2018) AN-rich haze reference ranges for 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.

Comment 6

Typically, the AMS is operated with a dryer at the AMS inlet - so it measures properties of dried particles. Was that the case for this study? If so, how can AMS data then be used to infer the behavior (eg, shape) of a wet ambient particle?

The AMS did sample through an inlet dryer. We therefore revised the wording so that AMS size distributions are interpreted as dried non-refractory PM_1 residual particles, not wet ambient droplet morphology.

We removed the interpretation of the AMS Dva shift as evidence for ambient wet-particle shape, phase state, or partial efflorescence. The revised text treats the Dva shift as an observed change in the dried nitrate-containing residual-particle mode. Because Dva depends on particle mass, density, and dynamic shape factor (Canagaratna et al., 2007; DeCarlo et al., 2004), material-density changes, dry-residue morphology, and/or smaller fresh particles are listed as possible contributors without assigning a single cause.

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."

Comment 7

Line 267 and on. Sulfate's behavior is in part different from pNO_3 because it is nonvolatile, it does not shift between particle and gas phases. There is confusion on particle water uptake and loss (hysteresis behavior), which is demonstrate by the following line (line 265-267) that states: 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." First this implies sulfate and nitrate are externally mixed, is this reasonable? What is the effect of internal mixing of the salts and also OA aerosol on deliquescence? Second, avg RH is not what matters, peak RH matters, since once above the deliquescence point the particle will remain wet as long as the RH does not drop below the efflorescence point. Since RH time series are not given, this is hard to interpret. (There is average data in Fig S4, which seems to show the RH does not go below the efflorescence RH of ammonium sulfate or ammonium nitrate). Furthermore, internally mixed particles do not strictly follow the sharp changes in water uptake/loss of pure salts.The following line is not supported by the data and is unclear: Line 289-290 states: "Together, these results provide, for the first time, field-based evidence that RH impacts on nitrate formation are dynamic and modulated by aerosol phase transitions, not merely RH magnitude."

Thank you. We replaced the pure-salt and campaign-average-RH wording with a mixed-particle RH-history interpretation. The revised text no longer treats sulfate and nitrate as externally mixed salts with separate sharp deliquescence thresholds.

The RH-history diagnostic reported in Comment 5 provides the campaign peak-RH and post-peak RH context relevant to this comment. We also removed "for the first time" and reframed the section conclusion so that it refers to RH history and mixed-particle water retention, not a directly measured phase transition.

We also revised the corresponding Conclusions paragraph so that it no longer attributes the RH effect mainly to N_2O_5 hydrolysis or treats phase transitions as directly measured.

Manuscript edits:

1. **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."

2. **Line 309:** "Together, these results provide, for the first time, field-based evidence that RH impacts on nitrate formation are dynamic and modulated by aerosol phase transitions, not merely RH magnitude." **After:** "Together, these results indicate that the RH-nitrate relationship during the campaign reflected RH history and mixed-particle water retention rather than instantaneous RH magnitude 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 397:** "We find that elevated NO_2, high RH, sufficient solar radiation, and temperatures above the freezing point contribute to enhanced nitrate formation, consistent with established understanding. However, the results further reveal that the temporal dynamics of RH—specifically, whether it is increasing or decreasing—play a critical role in modulating aerosol phase transitions and subsequent heterogeneous reactivity. Periods of rising RH, particularly beyond the deliquescence point of ammonium nitrate, favor aqueous-phase reactions such as N_2O_5 hydrolysis. Importantly, even during RH decline, particles often remain in a metastable semi-liquid state with elevated ionic strength, sustaining the partitioning of secondary inorganic species. This explains persistent early morning nitrate production under conditions traditionally considered less favorable." **After:** "The RH-dependent results indicate that nitrate accumulation during the campaign was influenced by RH tendency and RH history, not by instantaneous RH magnitude alone. During the morning RH decline, retained water in nitrate-rich mixed particles may provide a reservoir for HNO_3 partitioning into the particle phase. This interpretation is consistent with the observed RH-history and ALWC diagnostics, but the available measurements do not directly determine ambient particle phase state or apportion individual chemical pathways."

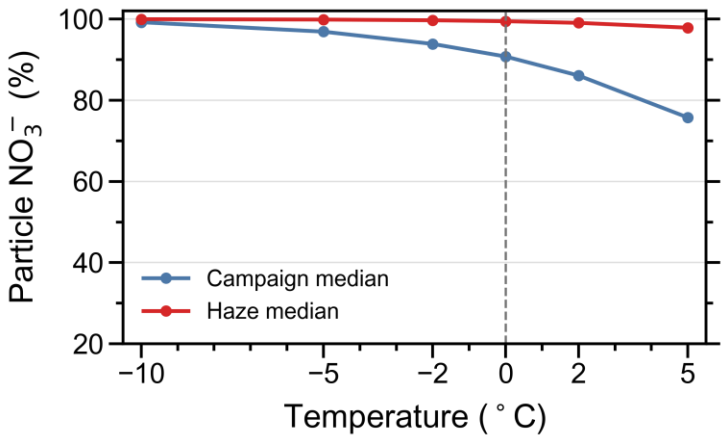
Comment 8

The authors could use thermodynamic parameters, like Henry's law constants, or sensitivity analysis with a thermodynamic model, to support the following statement (which is likely not true): Lines 309-311: "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."

We agree. We replaced the precursor-depletion statement because HNO_3 and NH_3 were not measured and the proposed reservoir-depletion explanation was not supported by the available observations. As a response-side check, we performed a forward-mode ISORROPIA-II temperature-sensitivity diagnostic using prescribed NH_3/HNO_3 reservoirs.

In the prescribed-reservoir sensitivity test, lower temperature increased the modeled particle-phase nitrate fraction. This result supports the revision: thermodynamic partitioning alone does not explain the measured winter behavior. In the campaign data, temperature and nitrate were positively associated (Spearman R = 0.43, n = 8541), and the association remained positive within subfreezing observations (Spearman R = 0.29, n = 5986). Median nitrate was lower at T < 0 °C than at T >= 0 °C (2.32 versus 5.57 µg m^{-3}). We therefore revised the cold-temperature interpretation as a field-regime response involving aerosol water, particle composition, and possible kinetic or phase-state constraints; the low-temperature diagnostic and revised wording are addressed in Comment 9.

This response-side diagnostic documents the bounded thermodynamic check and explains why the manuscript no longer uses thermodynamic precursor saturation to interpret the subfreezing plateau.



Response Figure 4. Forward-mode ISORROPIA-II temperature-sensitivity diagnostic for representative campaign-median and haze-median particle-composition cases. Lines show the median modeled particle NO_3 fraction across the prescribed

scenario ensemble at each temperature. The dashed line marks 0 °C. The diagnostic is a bounded thermodynamic sensitivity test, not a reconstruction of measured ambient HNO_3/NH_3 partitioning.

Manuscript edits:

1. **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."
2. **Line 402:** "Temperature also exerts a nuanced influence. While lower temperatures enhance gas-to-particle partitioning of nitric acid, the effect plateaus under subfreezing conditions. This threshold is primarily driven by thermodynamic precursor saturation, where available gas-phase precursors are nearly depleted, and is likely compounded by kinetic limitations as aerosols transition into highly viscous or solid phases that constrain diffusion." **After:** "Temperature also exerts a nuanced influence. Although lower temperatures generally favor HNO_3 partitioning into particles, nitrate enhancement leveled off under the coldest campaign conditions—opposite to the direction expected from temperature-dependent partitioning alone. We therefore interpret the subfreezing behavior as a coupled cold-regime response governed by aerosol water and particle composition, with possible kinetic or phase-state constraints."

Comment 9

Line 312 to 314 states, .. "at subfreezing temperatures, aerosols can transition into highly viscous semi-solid or glassy states, which restrict bulk diffusion and suppress heterogeneous reactivity (Meng et al., 2024; Shiraiwa et al., 2011)." At what T does this happen, and is it likely for the T's and RH of this study?

We agree. We revised this statement to treat viscosity as a possible regime-dependent constraint, not as a transition at one fixed subfreezing temperature.

The RH-history and ALWC diagnostic shown in Comment 5 addresses the RH part of this question: haze mornings often moved from high morning RH to lower post-peak RH while retaining ALWC during part of the drying interval. We therefore use RH history and particle water as campaign context, not as direct phase-state measurements. For the temperature part, the revised text separates established physical dependencies from the

campaign observations: lower temperature, lower particle water, and less-volatile organic material favor higher organic-aerosol viscosity and lower diffusivity; in this campaign, subfreezing periods had low ALWC while retaining appreciable OA. Independent wintertime Seoul thermodenuder measurements provide relevant context by showing that Seoul OA can include both primary and secondary low-volatility material (Kim et al., 2026)

Manuscript edits:

Line 332: "Secondarily, this plateau may also be compounded by kinetic phase-state limitations: at subfreezing temperatures, aerosols can transition into highly viscous semi-solid or glassy states, which restrict bulk diffusion and suppress heterogeneous reactivity" **After:** "Rather than a transition at a fixed subfreezing temperature, the possible phase-state limitation is treated as a regime-dependent constraint. Organic-aerosol viscosity generally increases as temperature and particle water decrease, and lower-volatility organic material, including primary and secondary low-volatility OA reported in wintertime Seoul thermodenuder measurements, can further promote semisolid or glassy behavior; such high-viscosity matrices reduce molecular diffusion, gas uptake, and heterogeneous reactivity (Kim et al., 2026; Koop et al., 2011; Meng et al., 2024; Renbaum-Wolff et al., 2013; Shiraiwa et al., 2011). During the campaign, subfreezing periods had low ALWC (median 1.51 μg m^{-3}) while retaining appreciable OA (median 6.71 μg m^{-3}); at T < -10 °C, ALWC remained low (median 1.39 μg m^{-3}) and nitrate was reduced (median 1.79 μg m^{-3}). These observations are consistent with a cold, low-water, organic-influenced regime in which viscosity-limited uptake or multiphase production may contribute to weak nitrate enhancement, although particle phase state was not directly measured."

Comment 10

The following line appears to be speculation, (what data supports it): Line 318… "Therefore, while low temperatures generally enhance nitrate formation through thermodynamic favorability, extremely low temperatures introduce phase-related limitations that partially counteract this effect. These findings clarify why a positive temperature–nitrate relationship is observed overall, despite the apparent suppression of reactivity under very cold conditions." I would suggest the situation is much more complicated than that. Example, have you considered temperature effects on activity coefficients – just to name one.

We agree. The original sentence over-interpreted the positive temperature-nitrate relationship by presenting it as a simple balance between thermodynamic favorability and phase-state limitation. Activity coefficients are part of the thermodynamic partitioning problem, but they vary with particle composition, ionic strength, aerosol water, and temperature; the present observation-ML framework does not isolate those terms or the residual HNO_3/NH_3 gas reservoirs.

Accordingly, we removed the causal balancing statement. The revised text keeps the seasonal thermodynamic comparison, but interprets the winter temperature response as a campaign-level association coupled with aerosol water, particle composition, and unresolved thermodynamic factors.

Manuscript edits:

Line 346: "Therefore, while low temperatures generally enhance nitrate formation through thermodynamic favorability, extremely low temperatures introduce phase-related limitations that partially counteract this effect. These findings clarify why a positive temperature-nitrate relationship is observed overall, despite the apparent suppression of reactivity under very cold conditions." **After:** "Taken together, the positive winter temperature-nitrate relationship should be interpreted as a campaign-level association, not as an isolated temperature dependence. It reflects the covariance of temperature with gas-particle partitioning, aerosol water, particle composition, and other thermodynamic factors that were not independently resolved in this observation-based analysis."

Comment 11

Define NOR, NO_x oxidation ratio.

We added the definition at first use. NOR was calculated from molar concentrations.

Manuscript edits:

Line 177 Added: "The nitrogen oxidation ratio (NOR) was calculated as NOR = $[NO_3^-]$ / ($[NO_3^-]$ + $[NO_2]$) using molar concentrations."

Comment 12

BC was reported but did not see info on the measurement method.

Thank you. We added the missing Methods description. BC was measured every minute with a multi-angle absorption photometer (MAAP; Thermo Fisher Scientific), and the text now states that BC was used with AMS non-refractory species to characterize PM_1 composition.

Manuscript edits:

Line 81 Added: "Black carbon (BC) was measured every minute using a multi-angle absorption photometer (MAAP; Thermo Fisher Scientific) and was used with AMS non-refractory species to characterize PM_1 composition."

References

Canagaratna, M. r., Jayne, J. t., Jimenez, J. l., Allan, J. d., Alfarra, M. r., Zhang, Q., Onasch, T. b., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. r., Trimborn, A. m., Northway, M. j., DeCarlo, P. f., Kolb, C. e., Davidovits, P., and Worsnop, D. r.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, Mass Spectrometry Reviews, 26, 185–222, https://doi.org/10.1002/mas.20115, 2007.

Davis, R. D., Lance, S., Gordon, J. A., Ushijima, S. B., and Tolbert, M. A.: Contact efflorescence as a pathway for crystallization of atmospherically relevant particles, Proc. Natl. Acad. Sci. U.S.A., 112, 15815–15820, https://doi.org/10.1073/pnas.1522860113, 2015.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory, Aerosol Science and Technology, 38, 1185–1205, https://doi.org/10.1080/027868290903907, 2004.

Ibikunle, I., Beyersdorf, A., Campuzano-Jost, P., Corr, C., Crounse, J. D., Dibb, J., Diskin, G., Huey, G., Jimenez, J.-L., Kim, M. J., Nault, B. A., Scheuer, E., Teng, A., Wennberg, P. O., Anderson, B., Crawford, J., Weber, R., and Nenes, A.: Fine Particle pH and Sensitivity to NH3 and HNO3 over South Korea During KORUS-AQ, CHIMIA, 78, 762–770, https://doi.org/10.2533/chimia.2024.762, 2024.

Kim, H., Jeong, J., Moon, J., and Kang, H. G.: Source-resolved volatility and oxidation state decoupling in wintertime organic aerosols in Seoul, Atmospheric Chemistry and Physics, 26, 1145–1161, https://doi.org/10.5194/acp-26-1145-2026, 2026.

Koop, T., Bookhold, J., Shiraiwa, M., and Pöschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13, 19238–19255, https://doi.org/10.1039/C1CP22617G, 2011.

Lee, J.-B., Yoon, J.-S., Jung, K., Eom, S.-W., Chae, Y.-Z., Cho, S.-J., Kim, S.-D., Sohn, J. R., and Kim, K.-H.: Peroxyacetyl nitrate (PAN) in the urban atmosphere, Chemosphere, 93, 1796–1803, https://doi.org/10.1016/j.chemosphere.2013.06.019, 2013.

Meng, X., Wu, Z., Chen, J., Qiu, Y., Zong, T., Song, M., Lee, J., and Hu, M.: Particle phase state and aerosol liquid water greatly impact secondary aerosol formation: insights into phase transition and its role in haze events, Atmospheric Chemistry and Physics, 24, 2399–2414, https://doi.org/10.5194/acp-24-2399-2024, 2024.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity, Proceedings of the National Academy of Sciences, 110, 8014–8019, https://doi.org/10.1073/pnas.1219548110, 2013.

Shiraiwa, M., Ammann, M., Koop, T., and Pöschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles, Proceedings of the National Academy of Sciences, 108, 11003–11008, https://doi.org/10.1073/pnas.1103045108, 2011.

Sun, J., Liu, L., Xu, L., Wang, Y., Wu, Z., Hu, M., Shi, Z., Li, Y., Zhang, X., Chen, J., and Li, W.: Key Role of Nitrate in Phase Transitions of Urban Particles: Implications of Important Reactive Surfaces for Secondary Aerosol Formation, Journal of Geophysical Research: Atmospheres, 123, 1234–1243, https://doi.org/10.1002/2017JD027264, 2018.

Tang, I. N. and Munkelwitz, H. R.: Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols, Atmospheric Environment. Part A. General Topics, 27, 467–473, https://doi.org/10.1016/0960-1686(93)90204-C, 1993.