Reply to comments on "Chlorine enhances nocturnal heterogeneous uptake of NO_2 in coastal atmosphere under sea-land breeze circulation" by Lin et al.

We would like to sincerely thank the editor and reviewers for their time and constructive comments, which have helped us further improve our manuscript. We have carefully considered all feedback and implemented revisions accordingly. All comments have been addressed point-by-point below.

Short summary of major revision in the manuscript:

1. We expanded the rationale for using Cl_{total} as a proxy of the chlorine involved in heterogeneous NO_2 uptake and performed additional random forest analyses using particulate Cl^- and gaseous HCl separately as predictor variables.
2. We clarified the calculation of kNO_2 and added a sensitivity analysis using different HONO emission factors.
3. We adjusted the HONO deposition velocity to 3.2 cm s^{-1}, within the observational range reported in the literature. We also evaluated different γN_2O_5 parameterization schemes and adopted the BT09 scheme, which explicitly accounts for aerosol chloride, nitrate, and liquid water, for the final simulations.
4. We revised the language throughout the manuscript to improve accuracy and avoid overstating the strength of the results and mechanistic evidence.

Response to Reviewer #1:

General comment

This manuscript investigates the enhancement of nocturnal heterogeneous NO_2 uptake by chlorine in the coastal atmosphere of Xiamen under sea-land breeze circulation. The study addresses an important and timely topic in atmospheric multiphase chemistry, particularly the role of sea-salt-derived chlorine in reactive nitrogen cycling. The authors combine comprehensive field observations, machine-learning analysis, and a multiphase chemical box model to show that sea-land breeze periods are associated with elevated chlorine levels, enhanced NO_2 uptake rates, and increased formation of HONO and particulate nitrate. The manuscript is generally well organized, the scientific question is clearly motivated, and the results provide valuable observational evidence connecting laboratory-identified chlorine effects with real coastal atmospheric conditions. Overall, I find the work suitable for publication in ACP. The dataset is valuable, the analysis is relevant to coastal air quality and nocturnal chemistry, and the conclusions are broadly supported by the observations and modeling. I recommend publication after the authors address the following comments.

Response: We are grateful for your thoughtful comments on the manuscript and we have made careful revisions accordingly. A brief summary of major revisions made to the entire manuscript is provided above. Our point-to-point responses to each comment are as follows (reviewer's comments are in black font, our responses are in blue font and our revisions in the manuscript are italic font).

Specific comment

1. In Section "2.3 Machine learning technique", the use of Cl_{total} as a chlorine proxy

should be explained more clearly. Since Cl_{total} includes both particulate Cl^- and gaseous HCl, please clarify whether the enhancement is mainly related to sea-salt chloride, chloride depletion, or their combined effect.

Response: Thank you for this comment. We agree that the original description did not clearly distinguish the mechanistic role of particulate chloride from the definition of Cl_{total}. We have therefore clarified in Section 2.3 that Cl_{total} is defined as the sum of particulate Cl^- and gaseous HCl. However, this definition does not imply that gaseous HCl directly enhances NO_2 uptake. Rather, particle-surface Cl^- is proposed to facilitate the heterogeneous uptake process. During NO_2 uptake, the generated H^+ can react with particulate Cl^- to form HCl, which is subsequently released into the gas phase. Consequently, measured particulate Cl^- represents the residual chloride after depletion, whereas HCl accounts for part of the chloride removed from the particle phase. Cl_{total} therefore combines residual sea-salt chloride and its depleted fraction and serves as a proxy of the chlorine involved in the uptake process.

To examine whether the random forest (RF) results depended on combining these two chlorine components, we conducted additional simulations using particulate Cl^- and HCl separately as predictor variables (**Figs. S10-S11**). Both variables ranked third in their respective models, with r^2 values of 0.90 for Cl^- and 0.89 for HCl, whereas Cl_{total} ranked first in the combined model, which yielded an r^2 of 0.91. These results indicate that both residual particulate chloride and its conversion to HCl contain information related to the uptake process, while their combination provides a more representative proxy.

We have revised the corresponding content in the Section 2.3 (**line 166-175**) and Section 3.2 (**line 308-318**) sections accordingly, as shown below:

"Cl_{total} was defined as the sum of particulate Cl^- and gaseous HCl. Particle-surface Cl^- can facilitate heterogeneous NO_2 uptake, however, H^+ produced during this process can protonate particulate Cl^- to form HCl, which subsequently partitions into the gas phase. Consequently, the measured Cl^- represents the residual concentration after chloride depletion and may underestimate the amount of particle-phase chloride present before and during NO_2 uptake. Adding gaseous HCl to the residual Cl^- partly accounts for this depleted fraction, therefore, Cl_{total} was used as a proxy for the particle-phase chloride involved in the uptake process, rather than assuming that gaseous HCl directly promotes NO_2 uptake. To evaluate whether the inferred chlorine dependence was sensitive to this proxy, two additional RF models were constructed by replacing Cl_{total} with either Cl^- or gaseous HCl." (line 166-175)

*"The RF models using Cl_{total} reproduced the calculated kNO_2 well during both SLB and non-SLB periods, with R^2 values of 0.91 and 0.87, respectively (**Figs. S10c-10d**). To evaluate the robustness of the Cl_{total} proxy, RF models were also constructed using residual particulate Cl^- or gaseous HCl separately. Both models retained good predictive performance on SLB days, with R^2 values of 0.90 and 0.89, respectively, compared with 0.91 for the Cl_{total}-based model (**Fig. S10**). When considered separately, Cl^- and HCl both ranked third after RH and SA (**Fig. S11**). In comparison, Cl_{total} ranked first and produced a modest improvement in model performance (**Fig. 3a**). These results indicate that the chlorine-related signal is captured partly by residual particulate Cl^-*

and partly by gaseous HCl formed through chloride depletion. Combining the two species therefore provides a more representative process-based proxy for the particulate chloride involved in NO_2 uptake." (line 308-318)

2. Please briefly discuss how general these findings may be. The observations were conducted at one coastal urban site in autumn/winter, so it would be useful to comment on whether similar chlorine-enhanced NO_2 uptake is expected in other seasons or other coastal regions.

Response: Thank you for this important comment. We have revised the Conclusion (**line 443-449**) to clarify the scope and potential generality of our findings. We now state that chlorine-enhanced NO_2 uptake may also occur in other coastal environments where chloride-rich sea-salt aerosols, high RH, and sufficient NO_2 coexist. However, its magnitude is expected to vary with season and region because of differences in sea-salt loading, aerosol water content and composition, and NO_2 abundance. We have therefore clarified that the quantitative contribution reported in this study is specific to the observation site and period, and that multi-season and multi-site observations are required to evaluate its broader relevance. The modifications in the revised manuscript are as follows:

"Although the observations were limited to one coastal urban site in autumn and winter, chlorine-enhanced NO_2 uptake may also occur in other coastal environments where chloride-rich sea-salt aerosols, high RH, and sufficient NO_2 coexist. Its magnitude is expected to vary seasonally and regionally with sea-salt loading, aerosol water content, aerosol composition, and NO_2 abundance. Therefore, the quantitative contribution derived here should be considered site- and period-specific, and multi-season observations at other coastal sites are needed to assess its broader relevance." (line 443-449)

Technical corrections

1. Line 26: Use proper scientific notation: 9.70×10^{-6} s^{-1}.

Response: We have corrected it in the revised manuscript.

2. Line 63: "These findings suggests" should be "These findings suggest".

Response: We have corrected it in the revised manuscript.

3. Line 87: The degree symbol "24.61°N, 118.06°E" should be 24.61° N, 118.06° E.

Response: We have corrected it in the revised manuscript.

4. Line 130: "set as a lower limit" could be revised to "used as a lower-limit estimate".

Response: We have corrected it in the revised manuscript.

5. Line 163: "Only nighttime data was trained in model" should be "Only nighttime data were used to train the model".

Response: We have corrected it in the revised manuscript.

6. Line 169: “accesses the interaction effects” should be “assess the interaction effects”.
Response: We have corrected it in the revised manuscript.

7. Line 172: Add the subsection number.
Response: We have corrected it in the revised manuscript.

8. Line 173: “Table. S1” should be “Table S1”; same for “Table. S2”.
Response: We have corrected it in the revised manuscript.

9. Line 226: “defining as” should be “defined as”.
Response: We have corrected it in the revised manuscript.

10. Line 316: “Fig. S9 show” should be “Fig. S9 shows”.
Response: We have corrected it in the revised manuscript.

11. Line 319: “muti-fold” should be “multi-fold”.
Response: We have corrected it in the revised manuscript.

12. Line 331: “Enhanced NO_2 uptake promote” should be “Enhanced NO_2 uptake promotes”.
Response: We have corrected it in the revised manuscript.

13. Line 340: “Fig. 10” should be “Fig. S10”.
Response: We have corrected it in the revised manuscript.

14. Line 397: “facilitate kNO_2” should be “increase kNO_2” or “facilitate NO_2 uptake”.
Response: We have corrected it in the revised manuscript.

15. Line 404: Replace the comma before “Future investigations” with a period.
Response: We have corrected it in the revised manuscript.

Response to Reviewer #2:

Short summary of major revision in the manuscript:

1. We expanded the rationale for using Cl_{total} as a proxy of the chlorine involved in heterogeneous NO_2 uptake and performed additional random forest analyses using particulate Cl^- and gaseous HCl separately as predictor variables.
2. We clarified the calculation of kNO_2 and added a sensitivity analysis using different HONO emission factors.
3. We adjusted the HONO deposition velocity to 3.2 cm s^{-1}, within the observational range reported in the literature. We also evaluated different γN_2O_5 parameterization schemes and adopted the BT09 scheme, which explicitly accounts for aerosol chloride, nitrate, and liquid water, for the final simulations.
4. We revised the language throughout the manuscript to improve accuracy and avoid overstating the strength of the results and mechanistic evidence.

General comments:

The manuscript "Chlorine enhances nocturnal heterogeneous uptake of NO_2 in coastal atmosphere under sea-land breeze circulation" investigates the role of chlorine in nocturnal reactive nitrogen cycling during the sea-land breeze (SLB) events using field observations, machine learning, and a chemical box model. It provides valuable observational evidence on the relationship between chloride concentrations and the heterogeneous reaction rate constant of NO_2 (kNO_2), with potentially important implications for coastal atmospheric chemistry. However, the key finding regarding chloride-enhanced NO_2 uptake is not well supported by the current results. There are several methodological issues in the data analysis and model setup, as well as overinterpretations of the results. Major revisions are required before the manuscript can be considered for publication in *Atmospheric Chemistry and Physics*.

Response: We are grateful for your thoughtful comments on the manuscript and we have made careful revisions accordingly. A brief summary of major revisions made to the entire manuscript is provided above. Our point-to-point responses to each comment are as follows (reviewer's comments are in black font, our responses are in blue font and our revisions in the manuscript are italic font).

Major comments

1. The relationship between Cl_{total} and kNO_2

The key evidence in the manuscript for the chloride-enhanced NO_2 uptake is that Cl_{total} (defined as the sum of gaseous HCl and particulate Cl^-) shows the highest factor importance for predicting kNO_2 in the random forest model (Fig. 3). However, gaseous HCl is itself a product of the heterogeneous reaction of NO_2, as shown by R2-R3 (lines 248-250) and discussed in relation to Fig. 2 (lines 238-244). This means that gaseous HCl is a dependent variable of the NO_2 heterogeneous reaction, so higher gaseous HCl concentrations are expected to be correlated with enhanced NO_2 heterogeneous reaction, regardless of whether chloride is mechanistically promoting the reaction. The random

forest model identifies statistical associations, but not causal relationships. Yet the authors used the random forest model results to draw a mechanistic conclusion about the role of chlorine. Moreover, as indicated in the manuscript (lines 241-247), chloride depletion could occur, and once particulate Cl^- is converted to HCl and partitioned into the gas phase, it no longer participates in or affects the aerosol surface properties relevant to NO_2 uptake. To put it simply, why do the authors conclude the role of chloride based on Cl_{total}? This is a fundamental question that the authors need to address. The authors should also clarify and justify the design of the random forest input variables and discuss how including a reaction product as a predictor affects the interpretation of the factor importance.

Response: Thank you for raising this fundamental concern. We agree that the original manuscript did not adequately distinguish between particulate Cl^- involved in aerosol chemistry and gaseous HCl formed during chloride depletion. In the heterogeneous uptake of NO_2, HONO and HNO_3 are formed; the resulting aerosol acidity can subsequently drive the acid displacement of particulate Cl^-, releasing HCl into the gas phase. Thus, HCl is not a direct product of NO_2 hydrolysis but can be formed as a secondary consequence of the uptake process. Its concentration may therefore covary with kNO_2 even after Cl^- has been removed from the particle phase. Our use of Cl_{total} was intended to account for this gas-particle redistribution of chlorine. Specifically, Cl_{total} was calculated as the sum of particulate Cl^- and gaseous HCl. Particle-surface Cl^- is the species potentially involved in enhancing NO_2 uptake, whereas gaseous HCl does not contribute directly to aerosol-surface reactivity. However, measurements of particulate Cl^- alone represent only the residual chloride remaining after acid displacement and may therefore underestimate the amount of chloride present before or during the uptake process. Therefore, Cl_{total} was used as a proxy for the particle-phase chloride involved in the uptake process, rather than assuming that gaseous HCl directly promotes NO_2 uptake.

We also agree that including HCl in Cl_{total} may strengthen its statistical relationship with kNO_2, because HCl can be formed following NO_2 uptake. To evaluate whether the importance of Cl_{total} was driven solely by gaseous HCl, we performed additional RF analyses using particulate Cl^- and HCl separately as predictor variables (**Figs. R1-R2**). Particulate Cl^- and HCl both ranked third in their respective models, with r^2 values of 0.90 and 0.89, respectively, whereas Cl_{total} ranked first in the original model, which yielded an r^2 of 0.91. In the separate model, particulate Cl^- remained an important predictor of kNO_2 after HCl was excluded, showing that the chlorine-related association was not driven solely by HCl. Cl_{total} combines the residual particulate Cl^- with the fraction converted to gaseous HCl during chloride depletion. Its higher importance therefore supports its use as a more complete proxy for the particulate chloride involved in the uptake process.

Accordingly, we have revised Section 2.3 (**line 166-175**) and 3.2 (**line 308-327**) to clarify the definition of Cl_{total} and added separate RF models using particulate Cl^- and gaseous HCl to support the rationale for using Cl_{total} as a proxy for the particle-phase chloride involved in uptake process. In addition, we also moderated the mechanistic interpretation of the chlorine-related results. The corresponding revisions in the revised

manuscript are as follows:

"Cl_{total} was defined as the sum of particulate Cl^- and gaseous HCl. Particle-surface Cl^- can facilitate heterogeneous NO_2 uptake; however, H^+ produced during this process can protonate particulate Cl^- to form HCl, which subsequently partitions into the gas phase. Consequently, the measured Cl^- represents the residual concentration after chloride depletion and may underestimate the amount of particle-phase chloride present before and during NO_2 uptake. Adding gaseous HCl to the residual Cl^- partly accounts for this depleted fraction; therefore, Cl_{total} was used as a proxy for the particle-phase chloride involved in the uptake process, rather than assuming that gaseous HCl directly promotes NO_2 uptake. To evaluate whether the inferred chlorine dependence was sensitive to this proxy, two additional RF models were constructed by replacing Cl_{total} with either Cl^- or gaseous HCl." (line 166-175)

*"The RF models using Cl_{total} reproduced the calculated kNO_2 well during both SLB and non-SLB periods, with R^2 values of 0.91 and 0.87, respectively (**Figs. S10c-10d**). To evaluate the robustness of the Cl_{total} proxy, RF models were also constructed using residual particulate Cl^- or gaseous HCl separately. Both models retained good predictive performance on SLB days, with R^2 values of 0.90 and 0.89, respectively, compared with 0.91 for the Cl_{total}-based model (**Fig. S10**). When considered separately, Cl^- and HCl both ranked third after RH and SA (**Fig. S11**). In comparison, Cl_{total} ranked first and produced a modest improvement in model performance (**Fig. 3a**). These results indicate that the chlorine-related signal is captured partly by residual particulate Cl^- and partly by gaseous HCl formed through chloride depletion. Combining the two species therefore provides a more representative process-based proxy for the particulate chloride involved in NO_2 uptake. Notably, the role of Cl_{total} and RH diminished substantially on non-SLB days (**Fig. 3b**), underscoring the profound modulation of these two influencing factors by the SLB circulation. **Fig 3c-3e** further elucidate the specific impacts of these primary drivers on nocturnal kNO_2 under SLB conditions. Specifically, Cl_{total} exhibits a positive correlation with kNO_2 (**Fig. 3c**). This phenomenon is likely attributable to the preferential partitioning of chloride ions at the gas-aqueous interface of aerosols (Zhang et al., 2025a; Shen et al., 2025; Wang et al., 2025a). The surface-bound Cl^- can attract gaseous NO_2 molecules (R4) to form interfacial intermediates $[Cl\text{-}NO_2]^-$, thereby facilitating the overall NO_2 uptake process. Subsequent interaction analysis was consistent with the mechanisms proposed in laboratory studies (R4-R5) and suggest that similar processes may operate in the coastal boundary layer." (line 308-327)*

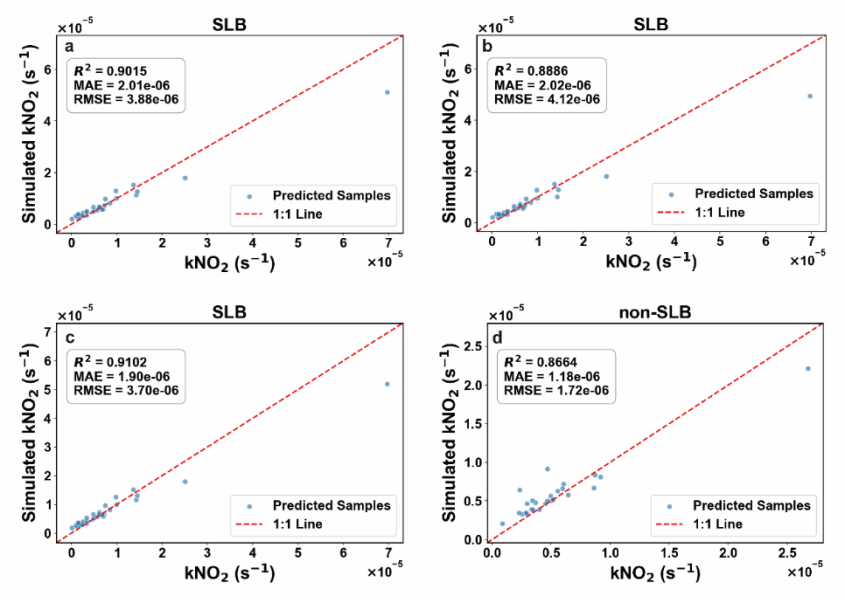

Figure R1. Performance of the random forest (RF) models. Simulated versus calculated kNO_2 for the SLB models using (a) Cl^-, (b) gaseous HCl, and (c) Cl_{total} as the chlorine-related predictor, and (d) for the non-SLB model using Cl_{total}. The red dashed lines indicate the 1:1 relationship.

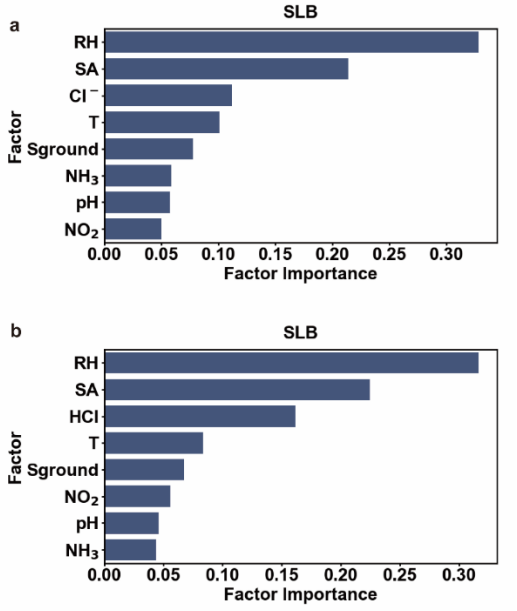

Figure R2. RF feature importance on SLB days when Cl_{total} was replaced by (a) Cl^- or (b) gaseous HCl, while the remaining predictor variables were unchanged.

2. Concerns regarding kNO_2 calculation

(1) The text states that kNO_2 is calculated with the $HONO_{corr}/NO_2$ ratio (lines 147 & 269), but Eq.5 (line 149) calculates kNO_2 using the difference in $HONO_{corr}$ between two time points divided by the mean concentrations of NO_2 over the time interval, multiplied by the time interval. These two calculations are not mathematically

equivalent, especially when NO_2 concentrations change over the time interval, which could happen in field observations. The authors should reconcile the text and equation.
(2) For $HONO_{corr}$ calculation, Eq.1 (line 127) combines quantities with inconsistent units – $HONO_t$ and $E_{vehicle,t}$ are concentrations, while $P_{NO+OH,t}$ is defined as a formation rate (Eq.2, line 133). The time step used to convert the rate into concentration should be specified.
(3) For $E_{vehicle,t}$, a single fixed "lower-limit" emission factor of 0.005 is applied for the entire campaign. Given the site's proximity to major traffic arteries, this is likely to be oversimplified without temporal dependence. The authors could consider whether the emission factor can be estimated from observations (e.g., using approaches such as those in Xu et al., *AE*, 2015) or at least conduct a sensitivity analysis. Because the choice of emission factor further affects the calculation of $HONO_{corr}$, kNO_2, and the subsequent evaluation of the contribution of heterogeneous NO_2 on reactive nitrogen cycling with chemical box models (Section 3.3), a clear clarification on this choice and sensitivity analysis might be needed.
Response: Thank you for carefully examining the calculation of kNO_2. We agree that the original description of the calculation procedure and units was insufficiently clear. We have substantially revised manuscript to address the three concerns as follows.

(**1**) We have reconciled the text with eq 5 by clarifying that kNO_2 was calculated from the change in $HONO_{corr}$ over a selected interval, normalized by the mean NO_2 concentration and the duration of that interval, rather than directly from the $HONO_{corr}/NO_2$. The corresponding descriptions in the Results have also been revised for consistency.

(**2**) We have revised eq 2 and its accompanying description to clarify that the instantaneous HONO formation rate from the homogeneous NO + OH reaction was integrated over the 1 h observational interval (3600 s) and converted to the same concentration unit as the observed HONO. Thus, all terms in eq 1 are now consistently expressed as concentrations.

(**3**) We agree that a fixed HONO/NO*x* emission factor cannot fully represent the temporal variability of vehicle emissions. Xu et al. (2015) derived emission ratios from selected fresh traffic plumes (Xu et al., 2015). Because our observations represent mixed coastal urban air masses influenced by traffic, ship emissions, and secondary HONO formation, the dataset was not designed to isolate fresh vehicle plumes throughout the campaign. We therefore retained 0.005 as the conservative base-case emission factor and conducted sensitivity calculations using emission factors of 0.005, 0.008, and 0.012. The corresponding mean $HONO_{corr}$ concentrations were 0.58, 0.53, and 0.51 ppb, and the mean kNO_2 values were 9.70×10^{-6}, 1.01×10^{-5}, and 1.03×10^{-5} s^{-1}, respectively. Relative to the base case, the maximum changes in $HONO_{corr}$ and kNO_2 were 12.1% and 6.2%, respectively. These results, presented in **Fig. R3**, indicate that the calculated kNO_2 was only weakly sensitive to the assumed emission factor within the tested range.

Accordingly, we revised Section 2.2 (**line 132-134 and line 145-154**) to clarify the equations, calculation intervals, and units used for $HONO_{corr}$ and kNO_2, and added an emission-factor sensitivity analysis in Section 3.2 (**line 292-295**) to quantify its

influence on the calculated results. The corresponding revisions in the revised manuscript are as follows:

"$P_{NO+OH,t}$ is calculated as follows:

$$P_{NO+OH,t} = k_{NO+OH} \times [NO] \times [OH] \times 3600 \quad (2)$$

where k_{NO+OH} (cm^3 $molecules^{-1}$ s^{-1}) is calculated in the Master Chemical Mechanism 3.3.1 (MCM v3.3.1 https://mcm.york.ac.uk/MCM/), 3600 s represents the 1 hour integration interval, and the concentration of OH radicals is estimated based on the steady-state balance of H_2SO_4" (line 132-134)

"In line with previous studies (Zhang et al., 2025b; Zhang et al., 2020; Zhang et al., 2024), the heterogeneous conversion of NO_2 to form HONOcorr at night is considered a pseudo-first-order reaction. The reaction rate constant (k_{NO2}, s^{-1}) is calculated based on the conversion of NO_2 during a given period (from t_1 to t_2) as follows:

$$kNO_2 = \frac{HONO_{corr,t_2} - HONO_{corr,t_1}}{\overline{NO_2}(t_2 - t_1)} \quad (5)$$

where $\overline{NO_2}$ is the mean concentration of NO_2 between t_1 and t_2.

"To evaluate the sensitivity of the results to the assumed emission factor, the calculation of $HONO_{corr}$ and k_{NO2} (Fig. S3) were calculated using emission factors of 0.005, 0.008 and 0.012 (Xu et al., 2015), while the observational inputs, analysis periods and calculation procedures held constant." (line 145-154)

"Across the tested emission factors, the mean $HONO_{corr}$ decreased from 0.58 to 0.51 ppb on SLB days, whereas kNO_2 varied by no more than 6.2%, indicating limited sensitivity of the derived rate constant to the assumed emission factor (Fig. S3)." (line 292-295)

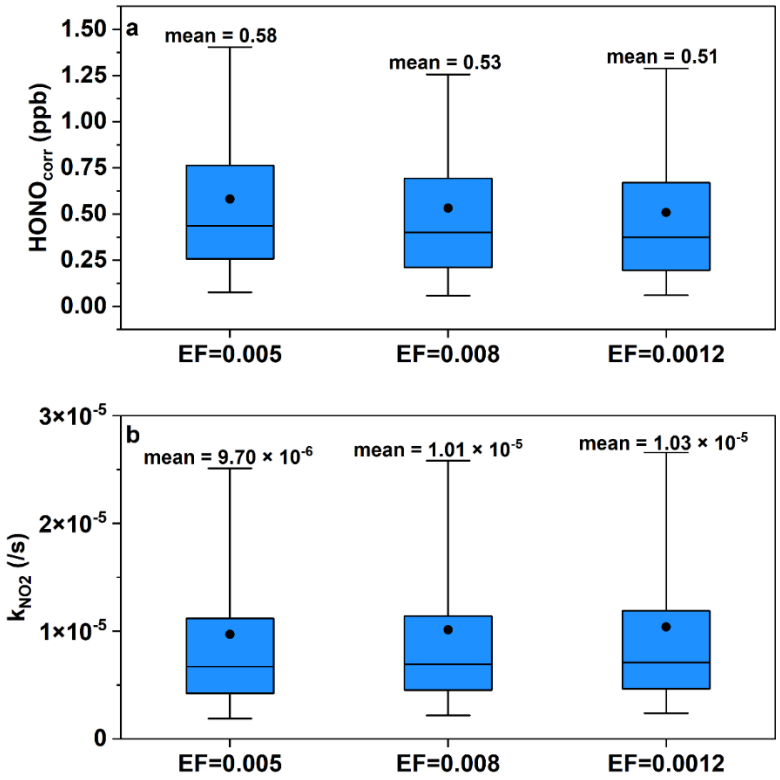

Figure R3. Calculated $HONO_{corr}$ and kNO_2 under different emission factor levels during nighttime on SLB days. (a) $HONO_{corr}$ and (b) kNO_2 calculated using emission factors of 0.005, 0.008, and 0.0012.

Reference: Xu, Z., Wang, T., Wu, J., Xue, L., Chan, J., Zha, Q., Zhou, S., Louie, P. K. K., and Luk, C. W. Y.: Nitrous acid (HONO) in a polluted subtropical atmosphere: Seasonal variability, direct vehicle emissions and heterogeneous production at ground surface, Atmospheric Environment. 106, 100-109, https://doi.org/10.1016/j.atmosenv.2015.01.061, 2015.

3. Concerns regarding the multiphase chemical box model

(1) For model setup, the authors should specify whether the calculated mean kNO_2 on SLB days is applied to scenarios (3) and (4), or whether specific kNO_2 values derived on SLB and non-SLB days are applied to the respective scenarios (lines 178-179). In addition, the authors should compare the HONO deposition velocity used in the box model (4 cm/s, Table S1) with values reported in the cited literature (0.6-3.2 cm/s, Zhang et al., 2003) and justify their choice of this parameter, as it directly affects the simulated HONO concentrations and budgets.

(2) In the model results section, the authors should report the absolute improvement in simulated HONO concentrations and NO_3^- production rates compared to the scenarios excluding NO_2 uptake mechanisms, in addition to the reported improvement in r (lines 336 339). In addition, the authors state that "This massive overestimation implies that the actual difference in kNO_2 between SLB and non-SLB days is likely greater than

1.44-fold, underscoring the amplified importance of NO_2 uptake on SLB days." (lines 342-344). If SLB-derived kNO_2 values were applied to scenario (4) (see comment (1) above), the authors should consider whether the overestimation exceeding the calculated kNO_2 difference between SLB days and non-SLB days could arise from differences in boundary layer height (BLH) and aerosol surface area (Sa), which could influence the simulated HONO concentrations and NO_3^- production rates. This would improve the discussions beyond simply attributing this excess overestimation to amplified importance of NO_2 uptake.

(3) In evaluating the NO_3^- formation enhancement by NO_2 uptake mechanism, the authors compare the simulated NO_3^- production rate against the observed concentrations (Fig. 4b). However, the production rate and concentration are different quantities. This comparison needs to be explained in more detail. In addition, when quantitatively comparing the contribution of NO_2 uptake and N_2O_5 uptake (lines 359-377), the applicability and uncertainties of the sulfate-based N_2O_5 uptake coefficient (γN_2O_5) parameterization (Table S2) should be discussed.

Response: Thank you for these constructive comments. We have revised the model description, model-observation evaluation, and sensitivity analysis as follows.

(**1**) We have clarified that condition-specific kNO_2 values were used in the model. Specifically, the mean kNO_2 derived for SLB days was applied to the SLB simulation in scenario (3), whereas the mean value derived independently for non-SLB days was applied to the non-SLB simulation in scenario (4). Scenarios (5) and (6) used the 25th and 75th percentiles of the SLB-specific kNO_2, respectively.

We agree that the previously used HONO deposition velocity of 4.0 cm/s exceeded the range reported in the cited literature (Zhang et al., 2003). We therefore compared simulations using deposition velocities of 3.2 and 4.0 cm/s, which produced comparable model-observation agreement (see in **Fig. R4**). A value of 3.2 cm/s, corresponding to the upper limit of the literature-reported observational range, was adopted for the revised simulations. All subsequent model results and HONO budgets were updated accordingly.

(**2**) In addition to the correlation coefficient, we now report absolute error metrics for the simulated HONO concentrations. Incorporating NO_2 uptake increased r from 0.57 to 0.94 and reduced the MAE from 0.58 to 0.11 ppb and the RMSE from 0.64 to 0.13 ppb. Thus, the absolute reductions in MAE and RMSE were 0.47 and 0.51 ppb, corresponding to decreases of approximately 81% and 80%, respectively (**Fig. 4a**). For NO_3^-, incorporating NO_2 uptake increased the mean simulated net NO_3^- formation rate by 2.14 $\mu g/m^3/h$ and strengthened the temporal consistency between the simulated net formation rate and observed concentration, increasing r from 0.04 ($p > 0.05$) to 0.64 ($p < 0.001$, **Fig. 4b**). This improvement indicates that the added mechanism better represented the observed temporal variability in NO_3^- during SLB periods.

We further clarify that scenario (4) used the non-SLB-specific mean kNO_2, rather than the SLB-derived value. Nevertheless, the simulation with NO_2 uptake still overpredicted HONO and nitrate under non-SLB conditions. In response to the reviewer's concern, we revised and qualified the original interpretation by explicitly considering uncertainties in BLH, deposition, dilution and other loss processes. We now

clarify that the model bias cannot be attributed solely to kNO_2. Nevertheless, it suggests that the effective contrast in NO_2 uptake impacts between SLB and non-SLB conditions may exceed that inferred from the observation-derived mean kNO_2 values, which differed by a factor of 1.44.

(**3**) We agree that the simulated NO_3^- production rate and observed NO_3^- concentration are different quantities and should not be compared directly in magnitude. We have clarified that Fig. 4b evaluates their temporal covariation only. The simulated net formation rate represents the modeled tendency for NO_3^- accumulation, and the comparison tests whether periods of enhanced simulated formation correspond to elevated observed NO_3^- concentrations. It is therefore not interpreted as a direct quantitative comparison between production rate and concentration.

We also evaluated the uncertainty associated with the γN_2O_5 parameterization by comparing the EJ05, BT09, and GRI09 schemes (**Fig. R5** and **Table R1**). The BT09 scheme was adopted for the final simulations because it explicitly accounts for the effects of aerosol liquid water, particulate nitrate, and chloride and is therefore more appropriate for the chloride- and nitrate-containing aerosols observed at this coastal site. Across the three schemes, the mean γN_2O_5 ranged from 0.011 to 0.013, and the mean simulated N_2O_5 uptake rate during nighttime ranged from 2.61 to 2.78 $\mu g/m^3/h$. The contributions of NO_2 and N_2O_5 uptake to nocturnal nitrate formation varied only from 46.4% to 47.9% and from 50.0% to 51.6%, respectively, indicating that their comparable contributions were not sensitive to the choice of γN_2O_5 parameterization.

Accordingly, we have revised Section 2.4 (**line 190-195**), Section 3.3 (**line 367-381** and **line 396-402**), and Supplementary Material (**Tables S1-S2**), to clarify the condition-specific application of kNO_2, revise the HONO deposition velocity, report additional model-performance metrics, qualify the interpretation of the non-SLB overprediction, explain the nitrate rate–concentration comparison, and evaluate the sensitivity to different γN_2O_5 parameterizations. The corresponding revisions in manuscript are presented below:

"Six simulation scenarios were conducted: simulations without heterogeneous NO_2 uptake for (1) SLB and (2) non-SLB days; simulations with NO_2 uptake for (3) SLB and (4) non-SLB days, using the mean kNO_2 derived from SLB days for the SLB simulation and that derived from non-SLB days for the non-SLB simulation, respectively; and two additional sensitivity simulations for SLB days using the (5) 25th and (6) 75th percentiles of the kNO_2 distribution derived from SLB days." (line190-195)

"Incorporating NO_2 uptake mechanism substantially improved the simulated diurnal HONO profile during SLB periods: r increased from 0.57 to 0.94, while mean absolute error (MAE) and root mean square error (RMSE) decreased from 0.58 to 0.11 ppb and from 0.64 to 0.13 ppb, respectively (Fig. 4a). For NO_3^-, incorporating NO_2 uptake increased the mean simulated net NO_3^- formation rate by 2.14 $\mu g/m^3/h$ and strengthened the temporal consistency between the simulated net formation rate and observed concentration, increasing r from 0.04 ($p > 0.05$) to 0.64 ($p < 0.001$, Fig. 4b). This improvement indicates that the added mechanism better represented the observed temporal variability in NO_3^- during SLB periods. Additionally, the NO_2 uptake could robustly explain the enhancements in both atmospheric reactive nitrogen species on

SLB days across various kNO_2 quantiles (Fig. S13). Conversely, applying the current calculated kNO_2 to non-SLB days overpredicted HONO and NO_3^- levels (Fig. S14). Given uncertainties in BLH, deposition, dilution and other loss processes, this bias cannot be attributed solely to kNO_2. Nevertheless, it suggests that the effective difference in NO_2 uptake impacts between SLB and non-SLB conditions may exceed that inferred from the observation-derived mean kNO_2 values, which differed by a factor of 1.44." (line367-381)

"Fig. 4f shows that NO_2 uptake contributed 46.4% to nocturnal NO_3^- formation, which was almost comparable to that of N_2O_5 uptake (51.6%). These values were obtained using the BT09 parameterization of γN_2O_5 (Bertram and Thornton, 2009b). Additional simulations using the EJ05 and GRI09 schemes yielded contributions of 47.0–47.9% for NO_2 uptake and 50.0–50.9% for N_2O_5 uptake (Fig. S16 and Table S5), indicating that their comparable importance was insensitive to the choice of γN_2O_5 parameterization (Evans and Jacob, 2005; Hallquist et al., 2003; Griffiths et al., 2009)." (line396-402)

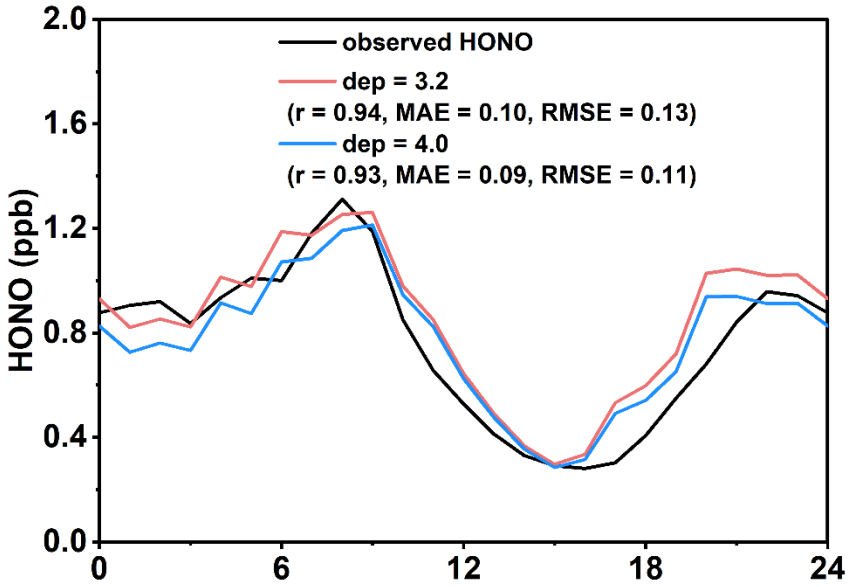

Figure R4. Sensitivity of the simulated diurnal HONO concentration to the assumed dry-deposition velocity. The black line represents observed HONO, and the red and blue lines represent simulations using deposition velocities of 3.2 and 4.0 cm/s, respectively.

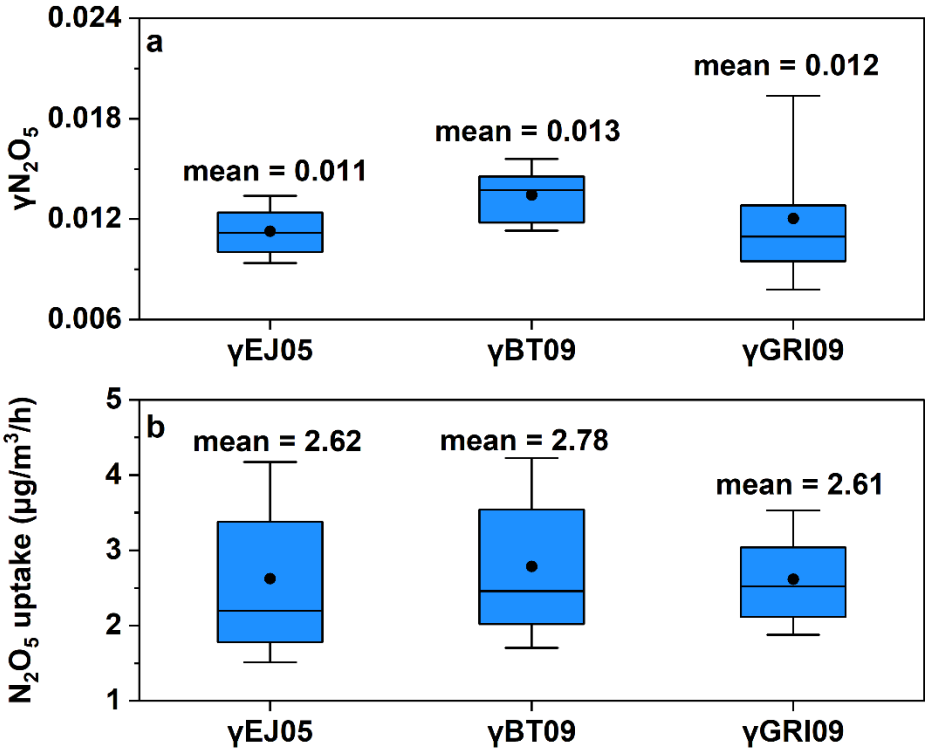

Figure R5. γN_2O_5 and simulated heterogeneous uptake rates of N_2O_5 derived under different parameterization schemes. (a) γN_2O_5 and (b) simulated N_2O_5 uptake rates.

Table R1. Contributions of NO_2 and N_2O_5 uptake to nocturnal NO_3^- formation under different γN_2O_5 parameterization schemes.

Parameterization	NO_2 uptake	N_2O_5 uptake
BT09	46.4% ± 9.8%	51.6% ± 9.7%
EJ05	47.9% ± 10.4%	50.0% ± 10.4%
GRI09	47.0% ± 7.1%	50.9% ± 6.9%

Reference: Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, Atmos. Chem. Phys., 3, 2067-2082, https://doi.org/10.5194/acp-3-2067-2003, 2003.

Minor comments

1. In Fig. 1, the distribution of the observed parameters is fitted with a normal distribution and mean values are used to describe their characteristics. Most species are not normally distributed but show skewness. It would be better to describe the skewed data with median and percentiles.

Response: Thank you for this suggestion. We agree that several observed species exhibit skewed distributions and therefore should not be characterized solely by their mean values. We have revised **Fig. 1** to additionally show the median values, while the boxes represent the 25th–75th percentiles and the mean values are retained as separate

markers. Comparisons based on the medians showed the same directional differences between SLB and non-SLB days as those based on the means. We therefore retained the means to maintain consistency with the mean-based enhancement ratios and subsequent model analyses, but no longer rely on the means alone to describe the observed distributions. The **Fig. 1** caption has also been revised to clearly define the median, mean, and percentile ranges. These additions do not change the interpretation of the differences between SLB and non-SLB conditions.

2. In Fig. 2, the range of observed $HONO_{corr}$ on SLB is substantially higher than on non-SLB days, although there are few data points above 1.5ppb on SLB days. This difference in data range can affect the Pearson r on SLB days relative to non-SLB days. When comparing the overlapped $HONO_{corr}$ range (<1.5ppb), the two groups of data points do not appear to show a substantial difference in data scattering. The author should discuss how the choice of the ranges for correlations may affect their interpretations.

Response: Thank you for this important comment. We agree that the broader $HONO_{corr}$ range on SLB days may affect the Pearson correlation coefficients and their direct comparison with those on non-SLB days. To evaluate this effect, we added a correlation analysis restricted to the common $HONO_{corr}$ range below 1.5 ppb (**Fig. R6**). Within this overlapping range, $HONO_{corr}$ remained significantly correlated with NO_3^- on SLB days ($r = 0.63$, $p < 0.001$, **Fig. R6a**), although the coefficient was close to that on non-SLB days ($r = 0.56$). This indicates that the wider $HONO_{corr}$ range partly contributed to the higher full-range correlation on SLB days, while the positive relationship persisted within the common concentration range. The corresponding analysis for HCl also showed a significant correlation on SLB days ($r = 0.47$, $p < 0.001$, Fig. **Fig. R6b**), which remained appreciably higher than that on non-SLB days ($r = 0.16$). Thus, the association between $HONO_{corr}$ and HCl during SLB periods was still evident after controlling for the difference in $HONO_{corr}$ range. Observations above 1.5 ppb were retained in the full-range analysis because they represent the elevated $HONO_{corr}$ levels that occurred under SLB conditions. The revised manuscript now presents the full-range and overlapping-range results together, allowing the influence of the concentration range to be distinguished from the relationships observed within the common range.

Accordingly, we have added correlation analyses within the overlapping $HONO_{corr}$ range to the main text (**line 249-254** and **line 257-262**) to more systematically compare the relationships of $HONO_{corr}$ with NO_3^- and HCl under SLB and non-SLB conditions. The corresponding revisions are shown below:

"The $HONO_{corr}$ concentrations under the two conditions overlapped mainly below 1.5 ppb. Within this overlapping range, the correlation on SLB days remained significant ($r = 0.63$, $p < 0.001$, Fig. S7a) but was close to that on non-SLB days ($r = 0.56$), indicating that the wider concentration range partly contributed to the higher full-range correlation on SLB days, while the positive relationship between $HONO_{corr}$ and NO_3^- persisted within the overlapping range." (line 249-254)

"Figs. 2c-2d show that the full-range correlation between $HONO_{corr}$ and gaseous HCl was stronger on SLB days than on non-SLB days ($r = 0.58$ versus 0.16). Within the

overlapping $HONO_{corr}$ range below 1.5 ppb, the correlation on SLB days decreased to ($r = 0.47$) but remained significant ($p < 0.001$, Fig. S7b) and appreciably higher than that on non-SLB days. This result indicates that the stronger HCl-$HONO_{corr}$ relationship during SLB periods cannot be explained solely by the wider $HONO_{corr}$ range." (line 257-262)

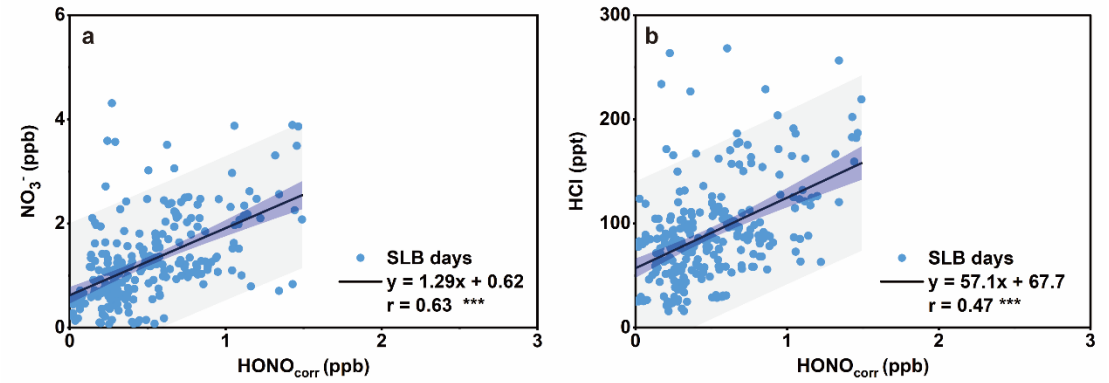

Figure R6. Relationship between $HONO_{corr}$ and the important products of heterogeneous chemical processes during nocturnal SLB when $HONO_{corr} < 1.5$ ppb. (a) Relationship between $HONO_{corr}$ and NO_3^-, (b) relationship between $HONO_{corr}$ and HCl.

3. Based on Fig. 3h, the authors suggest a synergistic interaction between Cl_{total} and RH (line 311), but this interaction is not obvious in the figure and needs to be more clearly demonstrated. In addition, the authors interpreted the role of RH as supplying water molecules for heterogeneous NO_2 uptake (lines 304-306). Given that the mean observed RH exceeds 60% on both SLB and non-SLB days (Fig. 1f), it is not clear if the amount of water is the limiting factor for NO_2 heterogeneous uptake, and more details should be provided.

Response: Thank you for this comment. We agree that the threshold-dependent nature of the interaction was not sufficiently described in the original manuscript. A closer examination of the bivariate partial dependence plot shows that kNO_2 increased most strongly only when RH exceeded approximately 80% and Cl_{total} exceeded approximately 0.5 μg/m^3, whereas the response was limited when either variable remained below these levels. Therefore, the mean RH values above 60% on both SLB and non-SLB days do not characterize the occurrence of the combined high-RH and high-chlorine conditions associated with the enhanced response. We have clarified this threshold-dependent interaction in the revised manuscript and moderated the interpretation by stating that the pattern "suggests" rather than demonstrates a synergistic effect. The corresponding revisions (**line 338-342**) in manuscript are as follows:

"Furthermore, Fig. 3h shows a threshold-dependent joint enhancement: kNO_2 increased when RH exceeded approximately 80% and Cl_{total} exceeded approximately 0.5 μg/m^3, whereas the response was limited when either variable remained below these levels. This pattern suggests a synergistic effect under combined high-RH and high-chlorine conditions and may partly explain their higher relative importance on SLB days" (line 338-342)

4. Some descriptions of the results in the manuscript are overstated and could be revised for accuracy. For example, several moderate correlation coefficients are described as "strong", e.g., line 213 "the Na^+-Cl^- correlation was strong on SLB days, r = 0.67"; lines 233-235, "a strong correlation between $HONO_{corr}$ and NO_3^-, with the correlation coefficient (r) increasing from 0.56 on non-SLB days to 0.76 on SLB days." Similarly, some statements overstate the strength of the evidence. For example, lines 297-299, "Subsequent interaction analysis provides evidence that the mechanisms described in reactions 4-5, originally identified under laboratory conditions, indeed occur within the coastal boundary layer". These should be toned down.

Response: Thank you for this important comment. We agree that several descriptions in the original manuscript overstated the strength of the correlations and the mechanistic evidence. We have therefore revised these statements throughout the manuscript.

First, the Na^+-Cl^- relationship on SLB days (r = 0.67) is now described as a "moderate positive correlation" rather than a "strong correlation," and its interpretation has been revised to state that it is "consistent with a greater sea-salt influence" rather than directly demonstrating a sea-salt source.

Second, we no longer describe the $HONO_{corr}$-NO_3^- correlations as strong. We now report the correlation coefficients directly and include an additional analysis within the overlapping $HONO_{corr}$ range below 1.5 ppb. Within this range, the correlation on SLB days decreased to (r = 0.63) and became close to that on non-SLB days (r = 0.56), indicating that the wider concentration range partly contributed to the full-range difference.

Finally, we revised the interpretation of the RF interaction analysis. The revised text states that the observed interaction patterns are "consistent with" the laboratory-proposed mechanism and "suggest that similar processes may operate" in the coastal boundary layer.

The corresponding modifications in main text are as follows:

*"Additionally, **Fig. S6** shows a moderate positive correlation between Na^+ and Cl^- on SLB days (r = 0.67), compared with a weaker relationship on non-SLB days (r = 0.28). Because sodium chloride (NaCl) is a major component of sea salt, this contrast is consistent with a greater sea-salt influence on Cl^- on SLB days." (line 227-230)*

*"Furthermore, **Figs. 2a-2b** indicate a moderate positive correlation between $HONO_{corr}$ and NO_3^-, with the correlation coefficient (r) increasing from 0.56 on non-SLB days to 0.76 on SLB days." (line 247-249)*

"Subsequent interaction analysis was consistent with the mechanisms proposed in laboratory studies (R4-R5) and suggest that similar processes may operate in the coastal boundary layer." (line 325-327)

Formatting issues

1. Line 134: the unit for k_{NO+OH} should be written as "cm^3 $molecule^{-1}$ s^{-1}"

Response: We have corrected it in the revised manuscript.

2. Line 162: "Cl_{total}" should be defined when it first occurs.

Response: We have corrected it in the revised manuscript.

3. Line 235: “reaction 1” should be written as “R1”, consistent with equation numbering below. Similar for other equation numbering.
Response: We have corrected it in the revised manuscript.

4. Line 269: in “$HONO_{corr}$”, the “corr” should be subscripted
Response: We have corrected it in the revised manuscript.

5. Line 340: the figure reference should be “Fig. S10”.
Response: We have corrected it in the revised manuscript.