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.