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.

Editor comments:

1. Please clarify the ambiguity outlined in the review. Particulate Cl^- enhances NO_2 uptake. However, as pointed out with increased NO_2 uptake, one expects also more HCl formation. Accounting HCl as "particulate Cl^-", driving NO_2 uptake, may overestimate the effect of actual particulate Cl^- for NO_2 uptake?

Response: Thank you for this helpful suggestion. We have further revised the relevant text to clarify the definition, physical meaning, and intended use of Cl_{total}. We agree that gaseous HCl should not be treated as particulate Cl^- or as a species that directly promotes NO_2 uptake.

During SLB periods, pronounced chloride depletion was observed. H^+ generated during NO_2 uptake can protonate particulate Cl^- and release HCl into the gas phase. Consequently, the measured particulate Cl^- represents the residual particle-phase fraction after depletion, whereas gaseous HCl contains information on part of the chloride transferred from the particle phase. Cl_{total} is therefore used as a depletion-corrected proxy that approximately represents the particulate chloride burden before acid displacement.

To evaluate the suitability of this proxy, we constructed two additional RF models by replacing Cl_{total} with either particulate Cl^- or gaseous HCl. In both models, the respective chlorine variable ranked third after RH and SA (**Figs. S10-S11**), indicating that residual particulate Cl^- and gaseous HCl retain complementary information on the chloride burden before depletion. Combining these two fractions as Cl_{total} resulted in the highest factor importance and the highest R^2, although all three models showed similar predictive performance (R^2 = 0.89 – 0.91). Moreover, all VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics and the other predictors (**Table R1**).

Accordingly, we revised Section 2.3 (**line 166-175**) to clarify that Cl_{total} is a depletion-corrected proxy rather than actual surface-active particulate Cl^- and to explain the purpose of the additional RF models. We also revised Section 3.2 (**line 308-318**) to clarify the interpretation of the RF results and added the VIF analysis and corresponding results. The modifications in main text are shown as following:

"Cl_{total} was defined as the sum of particulate Cl^- and gaseous HCl. It was used as a depletion-corrected proxy for the particulate Cl^- burden before acid displacement. During NO_2 uptake, the generated H^+ can protonate particulate Cl^- and release HCl to the gas phase. Consequently, measured particulate Cl^- represents the residual fraction after depletion, whereas HCl retains information about part of the chloride transferred from the particle phase. Their sum therefore represents, to some extent, the chloride burden before depletion. To evaluate the suitability of Cl_{total} as a proxy for the depletion-

corrected Cl^- burden, two additional RF models were constructed by replacing Cl_{total} with either Cl^- or gaseous HCl. Variance inflation factors (VIFs) were calculated for the predictor set of each RF model. A VIF below 10 was used to indicate the absence of severe multicollinearity." (line 166-175)

"Replacing Cl_{total} with either Cl^- or HCl resulted in the respective chlorine variable ranking third after RH and SA (Fig. S10-S11). Particulate Cl^- represents the residual particle-phase fraction, whereas HCl contains information on the fraction transferred to the gas phase through chloride depletion. Their respective importance therefore suggests that the Cl_{total} signal was not determined by either component alone, but reflected their complementary information on the Cl^- burden before depletion. All VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics and the other predictors (Table S5). Because all three metrics retain part of the chlorine-related information, the RF models showed similar R^2 values (0.89 – 0.91); nevertheless, the Cl_{total}-based model had the highest R^2 and provided a more physically representative description of the association between depletion-corrected particulate chloride and kNO_2." (line 308-318)

Table R1. Variance inflation factors (VIFs) for predictor variables in RF models using different chlorine indicators during nocturnal SLB days.

Predictor	Model I: Cl^-	Model II: HCl	Model III: Cl_{total}
Cl^-	1.76	-	-
HCl	-	5.97	-
Cl_{total}	-	-	2.16
RH	2.59	2.27	2.33
SA	3.33	2.77	3.28
T	2.21	6.00	2.55
S_{ground}	1.48	1.89	1.53
pH	1.79	2.07	1.84
NH_3	2.03	2.00	1.96
NO_2	2.93	2.88	2.87

VIFs were calculated for the predictor set of each RF model as $VIFj = 1/(1 - Rj^2)$, where Rj^2 is obtained by regressing predictor j against all remaining predictors.

2. It looks like that RH and SA have a much stronger impact on kNO_2 (Fig. S10-S12). All shown scenarios are within an R^2 of 0.89 to 0.91 which does not indicate much difference. Does SA imply more particulate Cl^- during SLB? Does increased RH imply more accessibility of Cl^- at the particle surface?

Response: Thank you for this helpful suggestion. The similar R^2 values of the three RF models (0.89 – 0.91) indicate that replacing the chlorine metric had only a limited influence on the overall predictive performance. This is reasonable because particulate Cl^-, gaseous HCl, and Cl_{total} all retain part of the chlorine-related information. When particulate Cl^- or HCl was used separately, the corresponding chlorine variable ranked third after RH and SA. In comparison, combining the residual particulate Cl^- and the fraction transferred to the gas phase through chloride depletion resulted in Cl_{total} ranking

first and produced the highest R^2. These results indicate that Cl_{total} more comprehensively captures the chlorine information distributed between the particle and gas phases during chloride depletion.

A larger SA does not indicate a higher particulate Cl^- concentration during SLB periods. The direct correlation between SA and particulate Cl^- was weak (**Fig. R1**), suggesting that they represent different aspects of the heterogeneous process. SA mainly represents the available aerosol surface for heterogeneous reactions, whereas particulate Cl^- represents aerosol chemical composition.

Increased RH may increase aerosol liquid water and provide a more favorable aqueous interfacial environment for chloride-associated NO_2 uptake. This interpretation is consistent with laboratory studies showing that Cl^- is preferentially accessible at the air-aqueous interface of wetted NaCl particles and can enhance NO_2 adsorption and uptake (Zhang et al., 2025a; Wang et al., 2025a). This interpretation is consistent with the bivariate PDP result, which shows a clear enhancement in kNO_2 under combined high-RH and high-chlorine conditions.

In addition, all VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics, RH, SA, and the other predictors (**Table R1**). Accordingly, we revised Sections 3.2 (**line 308-318** and line **339-347**) to clarify the comparable performance of the three RF models, the reason for selecting Cl_{total}, and the different roles of SA, RH, and chlorine in heterogeneous NO_2 uptake. The corresponding modifications in revised manuscript are as follows:

"Replacing Cl_{total} with either Cl^- or HCl resulted in the respective chlorine variable ranking third after RH and SA (Fig. S10-S11). Particulate Cl^- represents the residual particle-phase fraction, whereas HCl contains information on the fraction transferred to the gas phase through chloride depletion. Their respective importance therefore suggests that the Cl_{total} signal was not determined by either component alone, but reflected their complementary information on the Cl^- burden before depletion. All VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics and the other predictors (Table S5). Because all three metrics retain part of the chlorine-related information, the RF models showed similar R^2 values (0.89 – 0.91); nevertheless, the Cl_{total}-based model had the highest R^2 and provided a more physically representative description of the association between depletion-corrected particulate chloride and kNO_2." (line 308-318)

"Furthermore, Fig. 3h shows a threshold-dependent joint enhancement: kNO_2 increased when RH exceeded approximately 80% and Cl_{total} exceeded approximately 0.5 $\mu g/m^3$, whereas the response was limited when either variable remained below these levels. Elevated RH can increase aerosol liquid water and maintain an aqueous particle phase, while Cl^- in wetted chloride-containing particles can be preferentially accessible at the air-aqueous interface and enhance NO_2 adsorption and uptake (Zhang et al., 2025a; Wang et al., 2025a). Therefore, the bivariate PDPs response is consistent with high RH providing a favorable aqueous interfacial environment for chloride-associated NO_2 uptake. This interaction may partly explain the higher importance of RH and Cl_{total} on SLB days." (line 339-347)

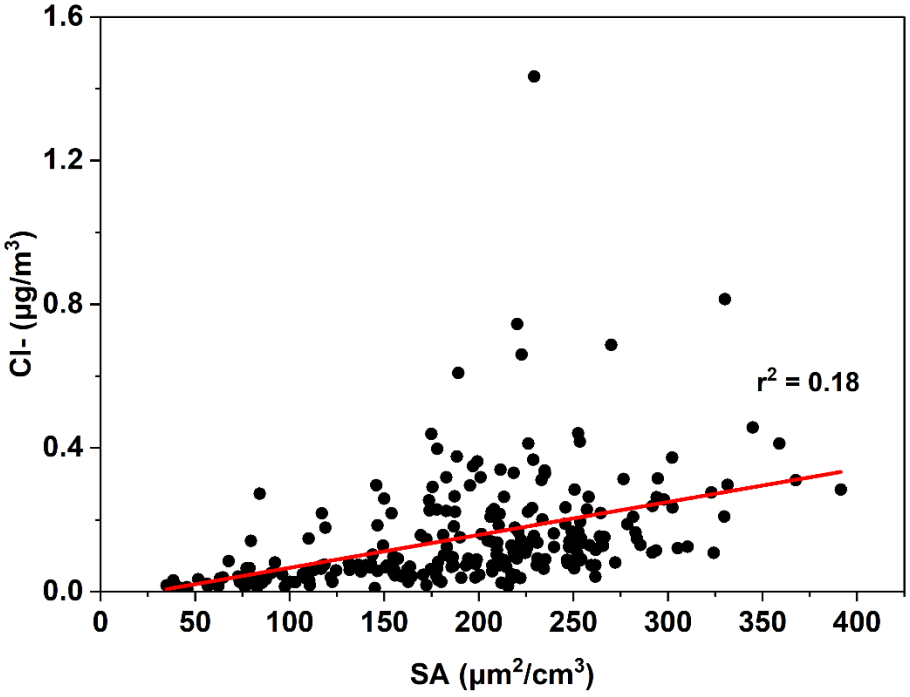

Figure R1. Relationship between observed SA and particulate Cl^-.

References:

Wang, G., Zhang, S., Wu, C., Zhu, T., Xu, X., Ge, S., Sun, H., Sun, Z., Wang, J., Ji, Y., Gao, J., Ren, Y., Li, H., Zhang, F., Wang, Y., and Seinfeld, J. H.: Atmospheric sulfate aerosol formation enhanced by interfacial anions, PNAS Nexus. 4, pgaf058, https://doi.org/10.1093/pnasnexus/pgaf058, 2025a.

Zhang, R., Minamikawa, R., Gen, M., Singh, N., Daniel, D., Li, Y. J., Wang, X., and Chan, C. K.: Evidence on Interfacial Reaction Governing NO2 Hydrolysis in Deliquesced Aerosol Particles, Environmental Science & Technology. 59, 11708-11719, https://doi.org/10.1021/acs.est.5c05223, 2025a.

3. The model underestimates HONO. When NO_2 uptake is considered, HONO is overestimated (in places almost by a factor of two). A correlation coefficient of 0.46 with $p < 0.05$, only indicates a very moderate relationship. If I understand this correctly, in a way, a low correlation should be expected, since this is a non-SLB scenario. However, assuming less particulate Cl^-, thus, slower NO_2 uptake is expected, why is HONO production significantly overestimated by the model?

Response: Thank you for your valuable suggestion. We have clarified to the reviewer about the purpose of comparing the model simulations with and without NO_2 uptake under SLB and non-SLB conditions, and we have also explained the reasons for the overestimation observed in the simulations under non-SLB conditions. Specifically, unlike the sustained nocturnal increase in $HONO_{corr}/NO_2$ observed on most SLB days (e.g., **Fig. S9**), no comparable persistent increase was evident on non-SLB days. This resulted in numerous negative estimates of kNO_2. Because these negative estimates were excluded, the resulting mean kNO_2 likely overestimated the effective NO_2 uptake

rate under non-SLB conditions. Applying this overestimated mean rate constant in the box model consequently produced excessive HONO.

The corresponding modifications in the main text (**line 381-389**) are shown below:

"In contrast, including NO_2 uptake under non-SLB conditions produced only limited in the simulated HONO and the temporal covariation between NO_3^- production rate and observed NO_3^- concentrations (Fig. S14). This suggests that NO_2 uptake had less explanatory importance under non-SLB conditions than during SLB periods, consistent with the stronger observed $HONO_{corr}$-NO_3^- relationship on SLB days. Moreover, unlike on SLB days (Fig. S9), $HONO_{corr}/NO_2$ did not exhibit a sustained nocturnal increase on non-SLB days, which resulted in numerous negative estimates of kNO_2 estimated using Eq. (5). Excluding these negative values likely led to an overestimated mean kNO_2 and, consequently, to the overprediction of HONO and NO_3^- under non-SLB conditions." (line 381-389)

Response to Reviewer #1:

General comment

The authors' detailed responses are appreciated, and substantial revisions have been made to address the concerns raised. An explanation for using Cl_{total} as a proxy for the chlorine involved in heterogeneous uptake of NO_2 has been provided, together with additional random forest (RF) analyses. kNO_2 calculation has been clarified, and a sensitivity analysis using different HONO emission factors has been conducted to evaluate their influence on kNO_2 results. For the box model, the scenario setup has been clarified, the HONO deposition velocity has been adjusted, and different γN_2O_5 parameterization schemes have been evaluated. The language throughout the manuscript has also been revised to be more accurate. These revisions have improved the quality of this manuscript. However, a few points regarding the major concerns raised in the first round, detailed below, still need further clarification or discussion.

Response: We are grateful for your thoughtful comments on the manuscript and we have made careful revisions accordingly. 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. The authors clarified the chemical relationship between gaseous HCl and kNO_2 (lines 166-173). However, regardless of whether gaseous HCl is a direct product of NO_2 hydrolysis or a secondary consequence of the uptake process via acid displacement, it remains a downstream product of the heterogeneous NO_2 uptake process and thus has an inherent correlation with the kNO_2 predicted by the RF model. To put it simply, enhanced heterogeneous NO_2 uptake would result in higher gaseous HCl, but the conclusion of this manuscript is that chlorine promotes the heterogeneous NO_2 uptake. The causal conclusion is not supported by the results. Additional RF analyses separating particulate Cl^- and gaseous HCl were conducted, and the performance of the RF model and factor importance were evaluated (lines 308-318, Figs. S10 11). The authors found that the factor importance for both particulate Cl^- and gaseous HCl declined when

analyzed separately, with RH and SA rising to the top two ranks (Fig. S11). This suggests chlorine might not be an independent causal driver of kNO_2, and that RH, SA, and chlorine may share a common upstream driver, such as the strength of the sea-land breeze circulation, which brings moist air and chlorine-enriched sea-salt aerosols. It is also noted that the overall model r^2 remains largely unchanged (0.89-0.91) across the original RF model and two additional RF analyses, which suggests that RH and SA already capture much of the predictive signal attributed to chlorine in the RF model. This implies that the attribution of high importance to chlorine cannot be taken as independent evidence for its mechanistic role. Calculations of the variance inflation factor or SHAP values for chlorine-related variables, RH and SA, are suggested.

Response: Thank you for your important comment. We agree that gaseous HCl is a downstream product of heterogeneous NO_2 uptake and therefore has an inherent relationship with kNO_2. We have clarified both the physical meaning of Cl_{total} and the interpretation of the RF results.

Cl_{total} is not intended to represent the instantaneous concentration of surface-active particulate Cl^-, nor do we assume that gaseous HCl directly promotes NO_2 uptake. During uptake, the generated H^+ can protonate particulate Cl^- and release HCl into the gas phase. Consequently, the measured particulate Cl^- represents the residual particle-phase fraction after chloride depletion, whereas HCl retains information about part of the chloride transferred from the particle phase. Cl_{total} is therefore used as a depletion-corrected proxy that approximately represents the particulate chloride burden before acid displacement.

The additional RF models were conducted to evaluate the suitability of this proxy rather than to establish causality. When Cl_{total} was replaced by particulate Cl^-, Cl^- remained the third-ranked predictor after RH and SA, indicating that the observed chlorine association was not attributable solely to the inclusion of downstream HCl. Gaseous HCl also ranked third when used separately, consistent with its representation of part of the chloride removed from the particle phase. These results suggest that residual particulate Cl^- and gaseous HCl contain complementary information on the chloride burden before depletion. Accordingly, combining them as Cl_{total} resulted in the highest factor importance and a slightly higher R^2.

The similar R^2 values of the three models (0.89 – 0.91) indicate that replacing the chlorine metric had only a limited effect on the overall predictive performance. This is reasonable because all three chlorine metrics retain part of the same chlorine-related information and because RH, SA, and chlorine are jointly influenced by SLB circulation. Following the reviewer's suggestion, we calculated VIFs for the predictor set of each model. All VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics and the other predictors (**Table R1**).

Accordingly, we revised Section 2.3 (**line 166-175**) to clarify the definition and intended use of Cl_{total} and the purpose of the additional RF models. We also revised the interpretation of the RF results in Section 3.2 (**line 308-318**) and added the VIF analysis and corresponding results to evaluate multicollinearity among the predictors. The corresponding modifications in the main text are shown below:

"Cl_{total} was defined as the sum of particulate Cl^- and gaseous HCl. It was used as

a depletion-corrected proxy for the particulate Cl^- burden before acid displacement. During NO_2 uptake, the generated H^+ can protonate particulate Cl^- and release HCl to the gas phase. Consequently, measured particulate Cl^- represents the residual fraction after depletion, whereas HCl retains information about part of the chloride transferred from the particle phase. Their sum therefore represents, to some extent, the chloride burden before depletion. To evaluate the suitability of Cl_{total} as a proxy for the depletion-corrected Cl^- burden, two additional RF models were constructed by replacing Cl_{total} with either Cl^- or gaseous HCl. Variance inflation factors (VIFs) were calculated for the predictor set of each RF model. A VIF below 10 was used to indicate the absence of severe multicollinearity." (line 166-175)

"Replacing Cl_{total} with either Cl^- or HCl resulted in the respective chlorine variable ranking third after RH and SA (Fig. S10-S11). Particulate Cl^- represents the residual particle-phase fraction, whereas HCl contains information on the fraction transferred to the gas phase through chloride depletion. Their respective importance therefore suggests that the Cl_{total} signal was not determined by either component alone, but reflected their complementary information on the Cl^- burden before depletion. All VIFs were below 10, indicating no severe multicollinearity between the chlorine metrics and the other predictors (Table S5). Because all three metrics retain part of the chlorine-related information, the RF models showed similar R^2 values (0.89 – 0.91); nevertheless, the Cl_{total}-based model had the highest R^2 and provided a more physically representative description of the association between depletion-corrected particulate chloride and kNO_2." (line 308-318)

Table R1. Variance inflation factors (VIFs) for predictor variables in RF models using different chlorine indicators during nocturnal SLB days.

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pH	1.79	2.07	1.84
NH_3	2.03	2.00	1.96
NO_2	2.93	2.88	2.87

VIFs were calculated for the predictor set of each RF model as $VIFj = 1/(1 - Rj^2)$, where Rj^2 is obtained by regressing predictor j against all remaining predictors.

2. The authors clarified the model setup for each scenario, which is appreciated (lines 190-195). However, it should be noted that even when the observation-derived kNO_2 is applied to the box model, the simulation still substantially overpredicted HONO and nitrate under non-SLB conditions (lines 374-381, Fig. S14). This indicates that the box model itself may have a systematic bias not related to kNO_2, which in turn raises

concern about the reliability of the good observation-model agreement for the SLB days (Fig. 4 a-b). The uncertainties and validation of the box model should be discussed in more detail, rather than being addressed only with the brief statement that "Given uncertainties in BLH, deposition, dilution and other loss processes, this bias cannot be attributed solely to kNO_2" (lines 378-379).

Response: Thank you for this important comment. We apologize that our previous description did not clearly distinguish the purpose of the SLB and non-SLB simulations. Our intention was to compare the incremental improvement obtained by including the NO_2 uptake mechanism under the two meteorological conditions. During SLB periods, including NO_2 uptake substantially improved the simulation of HONO concentrations and the temporal covariation between the simulated NO_3^- production rate and observed NO_3^- concentrations. In contrast, under non-SLB conditions, including this mechanism produced only a limited improvement in the corresponding correlations. This contrast suggests that heterogeneous NO_2 uptake provides substantially greater explanatory power under SLB conditions, whereas its role is weaker or other unresolved processes become relatively more important under non-SLB conditions. The stronger observed relationship between $HONO_{corr}$ and NO_3^- during SLB periods also supports this interpretation.

We agree that the overprediction under non-SLB conditions requires a more direct explanation, rather than the general attribution to uncertainties in BLH, deposition, dilution, and other loss processes provided in our previous response (lines 378–379). Unlike the sustained nocturnal increase in $HONO_{corr}/NO_2$ observed on most SLB days (e.g., **Fig. S9**), no comparable persistent increase was evident on non-SLB days. Consequently, the interval-based calculation using Eq. (5) produced numerous negative kNO_2 estimates under non-SLB conditions. Because these negative estimates were excluded when calculating the condition-specific mean kNO_2 used in the box model, the retained mean was likely biased high, thereby contributing to the overestimation of simulated HONO and NO_3^-. Therefore, the non-SLB overprediction cannot be used to infer that the actual SLB/non-SLB difference exceeds the observation-derived factor of 1.44. We have removed this interpretation.

The corresponding modifications in the main text (**line 381-389**) are shown below:

"In contrast, including NO_2 uptake under non-SLB conditions produced only limited in the simulated HONO and the temporal covariation between NO_3^- production rate and observed NO_3^- concentrations (Fig. S14). This suggests that NO_2 uptake had less explanatory importance under non-SLB conditions than during SLB periods, consistent with the stronger observed $HONO_{corr}$-NO_3^- relationship on SLB days. Moreover, unlike on SLB days (Fig. S9), $HONO_{corr}/NO_2$ did not exhibit a sustained nocturnal increase on non-SLB days, which resulted in numerous negative estimates of kNO_2 estimated using Eq. (5). Excluding these negative values likely led to an overestimated mean kNO_2 and, consequently, to the overprediction of HONO and NO_3^- under non-SLB conditions." (line 381-389)