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Chlorine enhances nocturnal heterogeneous uptake of NO_2 in coastal atmosphere under sea-land breeze circulation

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Abstract: Heterogeneous uptake of NO_2 serves as a significant source for reactive nitrogen species, playing an important role in atmospheric chemistry. Laboratory studies have demonstrated that chlorine can promote the heterogeneous NO_2 uptake, yet this effect under real ambient conditions remains poorly elucidated. Based on comprehensive field observations, a machine learning technique, and a multiphase chemical box model in the coastal city of Xiamen, China, this study reveals the enhancement effect of chlorine (Cl) on NO_2 uptake and quantifies the impact of this enhanced uptake on reactive nitrogen species during nocturnal sea-land breeze (SLB) periods. Compared with non-SLB days, nocturnal concentrations of nitrous acid (HONO) and particulate nitrate (NO_3^-) increased significantly during SLB days, with high mean value of NO_2 uptake rate constant (kNO_2) reaching 9.70×10^{-6} s^{-1}. Machine learning revealed that chlorine was the most important influencing factor for the enhanced kNO_2. Incorporating this kNO_2 into the chemical box model substantially resolved the underestimation of HONO concentration and NO_3^- production under SLB conditions. Notably, nocturnal NO_2 uptake dominated HONO formation (83.9%), while making a substantial contribution (47.9%) to nitrate formation. This study highlights the critical role of chlorine-enhanced NO_2 uptake in atmospheric reactive nitrogen cycling and provides valuable insights for nocturnal chemistry in complex coastal environments.

1. Introduction

Nitrous acid (HONO) and nitrate (NO_3^-) are key reactive nitrogen species in the atmosphere. HONO, a major source of OH radicals, significantly contributes to the formation of O_3 and secondary aerosols by influencing radical budget (Acker et al., 2006; Alicke et al., 2003). NO_3^- is an important chemical component of particulate matter (PM), contributing to PM pollution and acid rain (Cao et al., 2022; Qu and Han, 2021). As a crucial source of both HONO and NO_3^-, the heterogeneous uptake of NO_2 has attracted considerable attention (Xuan et al., 2025; Carter et al., 1982).

Traditionally, the uptake of NO_2 in bulk solution was considered extremely slow, and thus this process was often negligible (Lee and Schwartz, 1981). However, numerous field observations have indicated that NO_2 uptake plays a significant role in the formation of HONO and NO_3^-. Previous studies have revealed a strong correlation between NO_2 and HONO after excluding homogeneous formation and primary emissions, suggesting efficient heterogeneous conversion of NO_2 to HONO

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(Su et al., 2008; Zhang et al., 2024). Studies have also found that incorporating NO_2 uptake mechanisms into models can substantially improve the HONO simulation, especially at night (Zhang et al., 2023; Xuan et al., 2024; Zhang et al., 2024; Shi et al., 2020). Using an aerosol-fog sampling system and a box model, Xu et al (Xu et al., 2024), found that NO_2 uptake was the primary driver of the rapid increase in NO_3^- during fog events. Currently, the reported reaction rate constant for NO_2 uptake vary widely across different types of surfaces, spanning several orders of magnitude from 10^{-7} s^{-1} to 10^{-5} s^{-1} (Zhang et al., 2025b). Multiple factors have been demonstrated to affect the NO_2 uptake rate constant (kNO_2) in laboratories, including NO_2 concentrations, aerosol particle size, ionic strength, pH, NH_3, and liquid water content (Liu and Abbatt, 2021; Gen et al., 2024; Zhang et al., 2025a). In the real atmosphere, research during haze events showed that parameterization schemes of kNO_2 considering relative humidity (RH) and NH_3 influences significantly improved the simulation results of heterogeneous HONO formation (Zhang et al., 2023). Long-term observations revealed that changes in aerosol chemical composition could alter aerosol pH, consequently affecting the uptake kinetics of NO_2 to HONO (Zhang et al., 2025b).

Investigations in coastal areas reported higher NO_2 uptake rates in marine air masses compared to continental ones (Zha et al., 2014; Yang et al., 2021), overall surpassing those measured at continental urban, suburban, and rural sites (Wentzell et al., 2010; Kleffmann et al., 2003; Zhang et al., 2020; Hao et al., 2020; Cui et al., 2018). These findings suggests that heterogeneous NO_2 uptake plays a particularly critical role in the coastal troposphere. Within the marine boundary layer, chloride ions are abundant due to sea spray. Chloride ions exhibit special surface propensity, making them tend to distribute at the air-water interface (Knipping et al., 2000; Piatkowski et al., 2014; Jungwirth and Tobias, 2006). Laboratory studies demonstrated that chloride ions can establish a surface-directed electric field, which attracts atmospheric NO_2 molecules and promotes their further uptake at air-water interface (Wang et al., 2025a; Zhang et al., 2025a). Nevertheless, the influence of chlorine on NO_2 uptake in realistic coastal atmosphere and the consequent impacts on reactive nitrogen cycling remain to be fully elucidated.

Sea-land breeze (SLB) events occur frequently in coastal urban areas (Chen et al., 2023; Liu et al., 2025; Xie et al., 2023). During SLB periods, the coastal boundary layer experiences intensive interactions between marine and continental air masses, providing a natural laboratory to investigate the effect of sea-salt chloride on NO_2 uptake. In this study, a multi-parameter field observation was conducted in Xiamen, a typical coastal city in China, during the autumn and winter seasons characterized by frequent SLB events (Chen et al., 2023). Based on observations, the characteristics of SLB days were revealed and kNO_2 under both SLB and non-SLB conditions were quantified. Using machine learning method, the significant promoting effect of chlorine on NO_2 uptake during nocturnal SLB periods was demonstrated. Furthermore, the obtained kNO_2 was incorporated into an advanced multiphase box model to evaluate the impact of chlorine-enhanced NO_2 uptake on atmospheric reactive nitrogen cycling. This study highlights the role of previously overlooked chlorine on NO_2 uptake for nocturnal chemistry in coastal atmosphere.

2. Methods

2.1 Field measurements and sea-land breeze identification

Our observations were conducted at the Atmospheric Observation Supersite (24.61°N, 118.06°E) of the Institute of Urban Environment (IUE), Chinese Academy of Sciences in Xiamen, from November 18, 2023 to January 6, 2024. Xiamen is a coastal city in southeastern China. The

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observation site is located approximately 5 km from the shore and is surrounded by residential, commercial areas and major traffic arteries. Instruments were deployed on the roof of the IUE building at approximately 70 m above ground level. Virtually no high buildings obstructed the path between the site and the coast, making it a typical coastal urban site.

A suite of atmospheric parameters was observed simultaneously. Ambient HONO was measured online by a water-based long-path absorption photometer (Zhichen Beijing, China) (Xuan et al., 2024). Sulfuric acid (H_2SO_4) and HCl were measured using a long time-of-flight chemical ionization mass spectrometer, equipped with a nitrate reagent ion source (Aerodyne Research Inc., USA) (Yang et al., 2023). The chemical composition of $PM_{2.5}$ was analyzed using both a MARGA ADI 2080 (Metrohm Applikon, Switzerland) and an ACSM (Aerodyne Research Inc., USA) (Liu et al., 2022; Chen et al., 2022). Particle number size distribution (PNSD) in the range of 2–300 nm was measured by two scanning mobility particle sizers (TSI inc., USA) equipped with a long-DMA (2.5–62 nm) and a nano-DMA (7–300 nm), respectively (Li et al., 2025). Additionally, a range of commercial instruments were employed to monitor trace gases (NO, NO_2, SO_2, O_3, and VOCs), meteorological parameters (ambient temperature, RH, wind-speed, wind-direction and ultraviolet radiation), and photolysis rates (JO^1D, JNO_2, $JHONO$, JNO_3, $JHCHO$ and JH_2O_2) (Liu et al., 2022). Detailed descriptions of instrument operation, species identification, and calibration are provided in **Text S1**. Hourly BLH data were obtained from the ERA5 reanalysis dataset (Hersbach et al., 2020).

Sea-land breeze days were identified based on observed wind-speed and wind-direction according to the criteria established in our previous work (Chen et al., 2023). Briefly, the coastline in Xiamen is characterized by a northeast-southwest trend, the sea breeze is blowing from the east-south, and the land breeze is blowing from the west-north-northeast. According to observed wind direction, a natural day could be divided into four periods. Specifically, 01:00-08:00 LT (land breeze period), 13:00-20:00 LT (sea breeze period), and 09:00-12:00 LT and 21:00-24:00 LT (mixed sea-land breeze period). A day was classified as an SLB day if the following three conditions were met: (1) the 24-hour mean wind speed was < 10 m/s; (2) during the land breeze period, the land breeze persisted for ≥ 4 hours and the sea breeze lasted ≤ 2 hours; and (3) during the sea breeze period, sea breeze persisted for ≥ 4 hours and the land breeze lasted ≤ 2 hours. As shown in **Fig. S1** (light blue areas), a total of 23 SLB days were identified during the observation period. The remaining days were classified as non-SLB days. **Fig. S2** illustrates that the wind patterns on SLB days differed from those on non-SLB days, characterized by a higher prevalence of southeasterly sea breezes.

2.2 Calculation of HONO from heterogeneous formation processes and NO_2 uptake rate

Due to the absence of agricultural fields near the sampling site and its proximity to major traffic arteries, the primary emission of HONO was attributed to vehicles. Only nighttime data were used in our study, the uncertainties associated with photochemical process, such as NO_3^- photolysis were excluded. Therefore, the nighttime corrected HONO ($HONO_{corr}$) is calculated as follows:

$$HONO_{corr,t} = HONO_t - E_{vehicle,t} - P_{NO+OH,t} \quad (1)$$

where $HONO_t$ is the observed HONO concentration, $E_{vehicle,t}$ is the HONO emission from vehicles, and $P_{NO+OH,t}$ is the HONO production from homogeneous reactions. $E_{vehicle,t}$ is calculated as the NO*x* concentration multiplied by the emission factor 0.005, which was set as a lower limit to prevent underestimating the secondary formation of HONO (Zhang et al., 2025b). $P_{NO+OH,t}$ is calculated as follows:

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

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where k_{NO+OH} (cm^3/molecules/s) is calculated in the Master Chemical Mechanism 3.3.1 (MCM v3.3.1 https://mcm.york.ac.uk/MCM/), and the concentration of OH radicals is estimated based on the steady-state balance of H_2SO_4 (Nie et al., 2022). Because H_2SO_4 is primarily produced by the reaction of SO_2 and OH and is mainly lost via condensation sink (CS) onto particle surfaces, the OH concentration can be estimated as below:

$$[OH] = \frac{[H_2SO_4]\times CS}{k_{OH+SO2}\times[SO_2]} \quad (3)$$

where k_{OH+SO2} is 5×10^{-13} cm^3/s (Seinfeld et al., 1998), and CS (/s) is calculated as follows (Kulmala et al., 2012):

$$CS = 2\pi D_v \int_0^{d_{p,max}} d_p\, \beta n(d_p) dd_p \quad (4)$$

where D_v is the diffusion coefficient of H_2SO_4, d_p is the particle diameter derived from the measured PNSD, β is the transitional correction factor, and $n(d_p)$ is the particle number concentration of diameter d_p.

In line with previous studies (Zhang et al., 2025b; Zhang et al., 2020; Zhang et al., 2024), the variation in the $HONO_{corr}/NO_2$ ratio (equation 5) was applied to calculate the reaction rate constant of NO_2 uptake (k_{NO2}) in our study 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.

2.3 Machine learning technique

Random Forest (RF) algorithm, a machine learning technique extensively applied in atmospheric (Yang et al., 2024; Lin et al., 2026a; Zhang et al., 2025b), was employed to elucidate the primary drivers of kNO_2. The model was built using the "scikit-learn" library (https://github.com/scikit-learn/scikit-learn/blob/fe2edb3cd/sklearn/ensemble/, last access: June 10, 2026) in a python environment. Drawing upon previously identified factors influencing kNO_2 (e.g., pH, RH, NH_3) (Liu and Abbatt, 2021; Gen et al., 2024; Zhang et al., 2025a; Zhang et al., 2023) alongside the specific characteristics of the coastal urban environment, we incorporated meteorological parameters (RH and T), atmospheric reactive species (Cl_{total}, NH_3, and NO_2), and heterogeneous-related parameters (pH, SA, and ground surfaces areas) as input variables for the RF model. To account for the chloride depletion phenomenon, Cl_{total} was utilized as a proxy to represent overall chlorine levels. Only nighttime data was trained in model to eliminate the effects of photochemical processes on kNO_2 quantification, thereby enabling a more precise identification of key drivers. Detailed RF hyperparameter configurations and model evaluation are provided in **Text S2**. In this study, the dominant factors were identified based on RF factor importance, which quantifies the percentage contribution of each variable to kNO_2 (Breiman, 2001; Gregorutti et al., 2017). Furthermore, one-dimensional partial dependence plots (PDPs) were employed to delineate the main effects of individual variables, while bivariate PDPs were utilized to visualize and accesses the interaction effects between pairs of factors on kNO_2 (Goldstein et al., 2015).

Multiphase chemical box model. The multiphase chemical box model was established based on the Framework for 0-D Atmospheric Modeling (F0AM) (Wolfe et al., 2016). As shown in **Table. S1** and **Table. S2**, comprehensive HONO and NO_3^- budgets were incorporated into the F0AM model

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to simulate the variations of HONO and NO_3^-. The ISORROPIA II model (Seinfeld et al., 1998) was integrated into the model to determine aerosol pH, aerosol liquid water content and the partitioning ratio of HNO_3 and NO_3^-. This study designed six simulation scenarios: excluding the NO_2 uptake mechanism in simulation on (1) SLB and (2) non-SLB days; including NO_2 uptake with the calculated mean kNO_2 on (3) SLB and (4) non-SLB days; and including NO_2 uptake on SLB days using the (5) 25th and (6) 75th percentiles of the calculated kNO_2. The ability of the model to reproduce real atmospheric processes was evaluated by comparing the simulated HONO and NO_3^- with observations. Due to the underestimation of total particulate nitrate concentrations measured by instruments, the performance of NO_3^- simulations was evaluated by comparing the trends of the simulated NO_3^- production rate with the observed NO_3^- concentration. In contrast, as HONO predominantly exists in the gas phase, the simulated HONO was evaluated directly against the observed HONO concentrations.

As for the model simulation, each simulation was preceded by a 3-day spin-up to allow intermediate species concentrations to stabilize. The mean diurnal pattern of trace gas concentrations, meteorological parameters, and the results from the ISORROPIA II model during SLB days and non-SLB days were used as input data to constrain the box model. Notably, the concentrations of HONO and NO_3^- were not constrained by observed values. More details about the model incorporating mechanisms, modules, and simulation settings are provided in **Text S3** and our previous study (Lin et al., 2026b).

3 Results and discussion

3.1 Characteristics of atmospheric species during SLB days

Fig. S1 shows the time series of the observed parameters. Based on the identification criteria detailed in the Methods section, 23 days were classified as SLB days, accounting for 48% of entire observation period. The diurnal patterns of major observed parameters are summarized in **Fig. S3**, revealing that the primary differences between the two types of days predominantly emerged at night. Compared to non-SLB days, SLB days exhibited rapid nighttime accumulation of HONO and NO_3^-, accompanied by elevated chlorine levels, NOx concentrations, and aerosol surface area (SA) concentrations. Additionally, consistent with our previous study, SLB days were characterized by higher temperature and RH at night (Chen et al., 2022). **Fig. 1** and **Table S3** further summarizes the nighttime observational results on SLB and non-SLB days. By definition, SLB days are influenced by persistent sea breezes, which likely enhances the impact of sea-salt aerosols. As shown in **Fig. 1a**, the particulate chloride (Cl^-) concentrations were comparatively higher on SLB days (0.154 $\mu g/m^3$) than on non-SLB days (0.139 $\mu g/m^3$). Specifically, this overall increase (**Fig. S4**) was primarily driven by elevated levels during the sea breeze (18:00-20:00 LT) and mixed sea-land breeze (21:00-00:00 LT) periods, while concentrations declined during the land breeze (01:00-06:00 LT) period. The elevation pattern of Cl^- indicates that the more abundant Cl^- transported by stronger sea breezes on SLB days can persist into the subsequent mixed sea-land breeze periods. Additionally, **Fig. S5** shows that the Na^+-Cl^- correlation was strong on SLB days ($r = 0.67$), while it was weak on non-SLB days ($r = 0.28$). Since sodium chloride (NaCl) is a major component of sea-salt, the stronger Na^+-Cl^- correlation on SLB days than on non-SLB days indicates that sea salt is indeed an important source of Cl^- on SLB days. As for gaseous chlorine, **Fig. 1b** shows that the concentration of gaseous hydrogen chloride (HCl) was significantly higher on SLB days (96.2 ppt) than on non-SLB days (67.5 ppt). This further confirms that, under the influence of sea-salt aerosols on SLB

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days, chlorine levels are distinctly elevated in the nighttime coastal troposphere.

Fig. 1c indicates that the concentration of NO_2 on SLB days (mean: 28.3 ppb) was significantly higher than that on non-SLB days (23.2 ppb). Within our study area, ship emissions, cross-sea bridge traffic, and road traffic contribute substantial NO*x*, and the enhanced local circulation on SLB days can promote NO_2 accumulation (Chen et al., 2023). The mean concentrations of HONO and NO_3^- on SLB day were 0.836 ppb and 3.61 μg/m^3, respectively, which were significantly higher than the corresponding values of 0.497 ppb and 3.13 μg/m^3 on non-SLB days (**Figs. 1d-1e**). To better understand the elevated HONO levels, $HONO_{corr}$ concentrations, defining as the observed HONO concentration subtracts contributions from primary emissions and gas-phase production, were calculated to represent the nocturnal HONO produced from heterogeneous conversion. The ratio of HONOcorr/NO_2 was notably higher on SLB days (0.030) than on non-SLB days (0.021), indicating more active heterogeneous conversion of NO_2 to HONO on SLB days. Multiple studies have confirmed that NO_2 uptake is a primary source of nocturnal heterogeneous HONO formation (Zhang et al., 2023; Zhang et al., 2022). Here, the higher SA concentrations on SLB days were also conducive to heterogeneous reactions (**Fig. 1g**). Furthermore, **Figs. 2a-2b** indicate 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. As shown in reaction 1, NO_2 uptake via disproportionation simultaneously produces HONO and HNO_3, the latter of which is further converted to NO_3^- via gas-particle partitioning. Thus, nocturnal NO_2 uptake is also likely an important contributor to the formations of NO_3^- on SLB days. **Fig 2c-2d** show that the correlation of $HONO_{corr}$ with gaseous HCl was significantly elevated on SLB days (r = 0.58) than on non-SLB days (r = 0.16), reflecting a strong coupling between NO_2 uptake and chlorine activation under high halogen conditions. The H^+ generated by NO_2 uptake can combine with Cl^- (reactions 2-3). Simultaneously, the aerosol pH in the coastal region of southeastern China was relatively low (approximately 1.92 ± 0.34 during nocturnal SLB periods), chloride depletion could easily occur, leading to the observed positive correlation between $HONO_{corr}$ and HCl. The enhanced chloride depletion can also explain our observations of a significant increase in gaseous HCl but not in Cl^- concentrations on SLB days. Similarly, the rapid decline in Cl^- concentration during land breeze periods (**Fig. S4**) could also be explained by chloride depletion.

$$2NO_2 + H_2O(ad) + \text{aerosol/ground surface} \rightarrow HNO_3 + HONO \quad (R1)$$

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq) \quad (R2)$$

$$H^+(aq) + Cl^-(aq) \rightarrow HCl(aq) \leftrightarrows HCl(g) \quad (R3)$$

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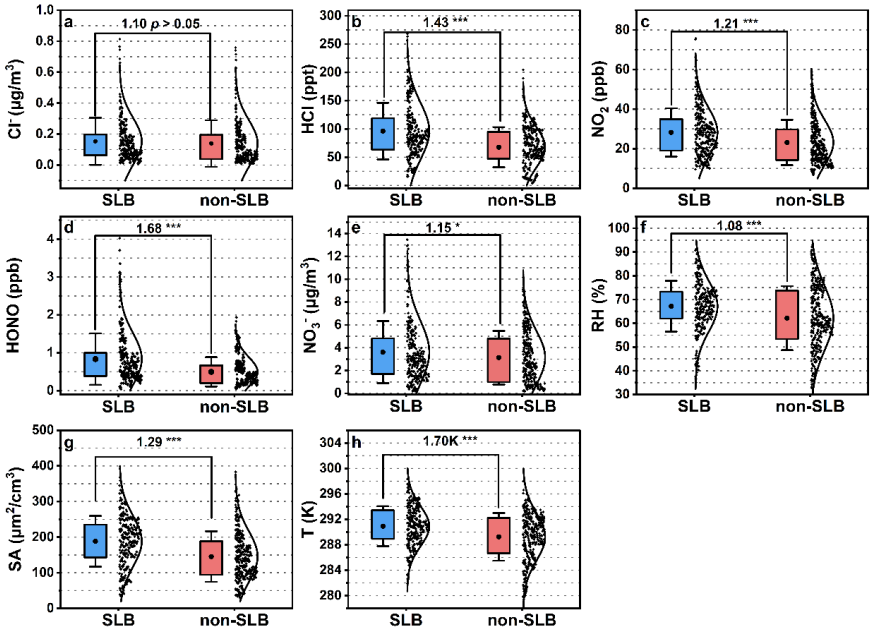

Figure 1. Box plots of key observed parameters during nocturnal SLB and non-SLB periods. (a) Cl^-, (b) HCl, (c) NO_2, (d) HONO, (e) NO_3^-, (f) RH, (g) SA, and (h) ambient temperature (T). The box shows the 25th–75th percentiles with whiskers representing ±1 standard deviation. The black dot within the box represents the mean. Differences between SLB and non-SLB days were tested using a two-sample t-test. Statistical significances are denoted as *($p < 0.05$), **($p < 0.01$) and ***($p < 0.001$). For all panels except (h), the number adjacent to the significance symbol denotes the ratio of the mean value on SLB days to that on non-SLB days; in panel (h), it denotes the absolute difference between the means.

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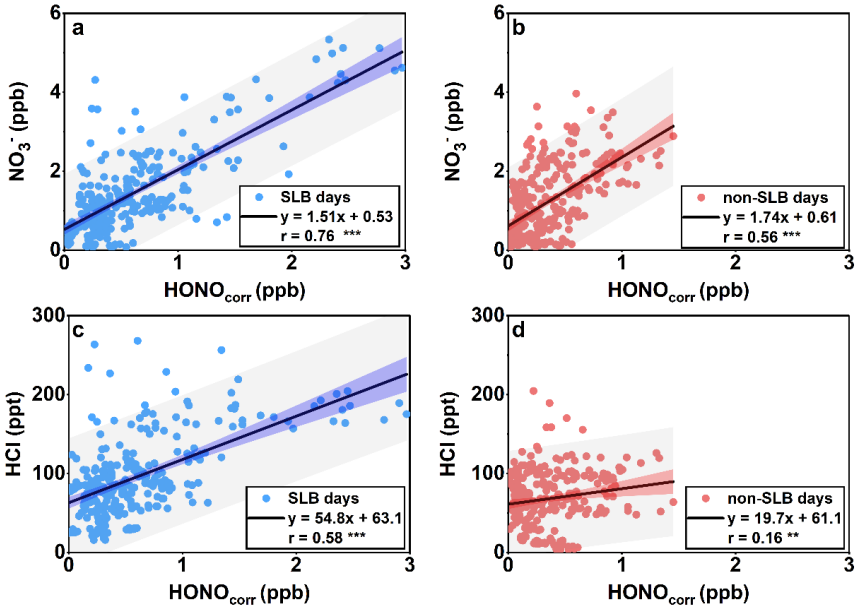

Figure 2. Relationship between $HONO_{corr}$ and the important products of heterogeneous chemical processes during nocturnal SLB and non-SLB periods. $HONO_{corr}$ denotes the corrected HONO concentration from secondary conversion. The products include (a, b) NO_3^- and (c, d) HCl. Blue and red dots represent observations during SLB days and non-SLB days, respectively. Each panel displays the linear regression fits and Pearson correlation coefficients (r) for the corresponding periods.

3.2 Enhanced rate of NO_2 uptake and its influencing factors

Using the variation of HONOcorr/NO_2 ratio, the values of kNO_2 on SLB days and non-SLB days were derived as **Fig. S6**. Overall, the average kNO_2 values on SLB days (9.70×10^{-6} s^{-1}) were significantly higher than those on non-SLB days (6.72×10^{-6} s^{-1}), by a factor of approximately 1.44. As presented in **Table S4**, a prolonged increase in the $HONO_{corr}/NO_2$ ratio was observed during 17 of the 23 SLB days (see an example in **Fig. S7**). In contrast, this phenomenon was virtually absent on non-SLB days, indicating a sustained nocturnal enhancement of kNO_2 during SLB periods. Compared with existing field observations, the kNO_2 on SLB days was broadly consistent with the levels reported under the sea-case scenario in coastal cities of China such as Qingdao(1.25×10^{-5} s^{-1}) and Hong Kong(8.81×10^{-6} s^{-1}) (Yang et al., 2021; Zha et al., 2014), while it was markedly higher than those values observed in major non-coastal cities including Beijing (7.78×10^{-7} – 5.75×10^{-6} s^{-1}) (Wang et al., 2017b; Zhang et al., 2020; Xuan et al., 2023; Jia et al., 2020; Zhang et al., 2022), Nanjing (1.19×10^{-6} – 2.22×10^{-6} s^{-1}) (Zheng et al., 2020; Liu et al., 2019), and Guangzhou (4.44×10^{-6} – 6.67×10^{-6} s^{-1}) (Su et al., 2008; Li et al., 2012; Qin et al., 2009). The consistently higher kNO_2 in coastal areas implies that coastal atmospheric environments are likely more conducive to NO_2 uptake.

A machine learning technique was used to further identify key drivers of the enhanced kNO_2 on SLB days. **Fig. S8** demonstrates that the constructed random forest model exhibits good

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performance, successfully reproducing the calculated kNO_2 during both SLB and non-SLB periods, making it suitable for subsequent factor analysis. The factor importance analyses (**Figs. 3a-3b**) reveal that Cl_{total} (the sum of gaseous HCl and particulate Cl^-), RH, and SA were major drivers of kNO_2 on SLB days, with Cl_{total} exhibiting the highest relative importance. Notably, the role of Cl_{total} and RH diminished substantially on non-SLB days, 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 (reaction 4) to form interfacial intermediates $[Cl\text{-}NO_2]^-$, thereby facilitating the overall NO_2 uptake process. 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. **Fig. 3f** demonstrates that at a fixed NO_2 concentration, elevated chloride levels amplify the positive effect of NO_2 molecules on kNO_2. This indicates that chloride ions actively promote the heterogeneous uptake of NO_2, consequently accelerating the kNO_2. Similar halogen-promoted effect has also been revealed in NO_2-initiated aqueous-phase oxidation of dissolved SO_2 at the air-aqueous interface and of nitrate photolysis at the aqueous-phase surface (Wang et al., 2025a; Shen et al., 2025). **Fig. 3d** shows a significant positive relationship exists between RH and kNO_2, suggesting that moist sea breezes effectively supply the water molecules essential for the heterogeneous NO_2 uptake. This finding aligns with previously reported field observations highlighting RH-driven NO_2 uptake (Xuan et al., 2024). Analogous to Cl_{total}, the interaction between RH and NO_2 reveals that at a constant NO_2 level, the positive impact of NO_2 on kNO_2 is enhanced under elevated RH. It implies that RH also facilitates NO_2 uptake by promoting the interaction between NO_2 molecules and heterogeneous interface. Furthermore, the interaction between Cl_{total} and RH (**Fig. 3h**) reveals a positive synergistic effect, which partially explains the pronounced increase in their relative importance for kNO_2 on SLB days. As a primary factor on both SLB and non-SLB days, SA positively correlates with kNO_2 (**Fig. 3e**). This indicates that an increase in aerosol surface area concentrations provides effective reaction interfaces for NO_2 uptake process, consistent with most atmospheric heterogeneous processes (Wang et al., 2017a; Ma et al., 2026). Moreover, **Fig. S9** show that on SLB days, concentrations of the major NO_2 uptake products (HONO and NO_3^-) increased with those key factors including Cl_{total}, RH, and SA, providing additional support for the above driving factor analysis. In general, the reasons underlying the enhanced kNO_2 on SLB days help to explain the muti-fold higher kNO_2 observed in coastal areas compared to non-coastal urban areas, highlighting ambient chlorine levels and RH as non-negligible contributors.

$$Cl^-(aq) + NO_2 \rightarrow [Cl\text{-}NO_2^-]_{surface} \quad (R4)$$

$$[Cl\text{-}NO_2^-]_{surface} + NO_2 + H_2O(ad) \rightarrow Cl^-(aq) + HONO + NO_3^- + H^+ \quad (R5)$$

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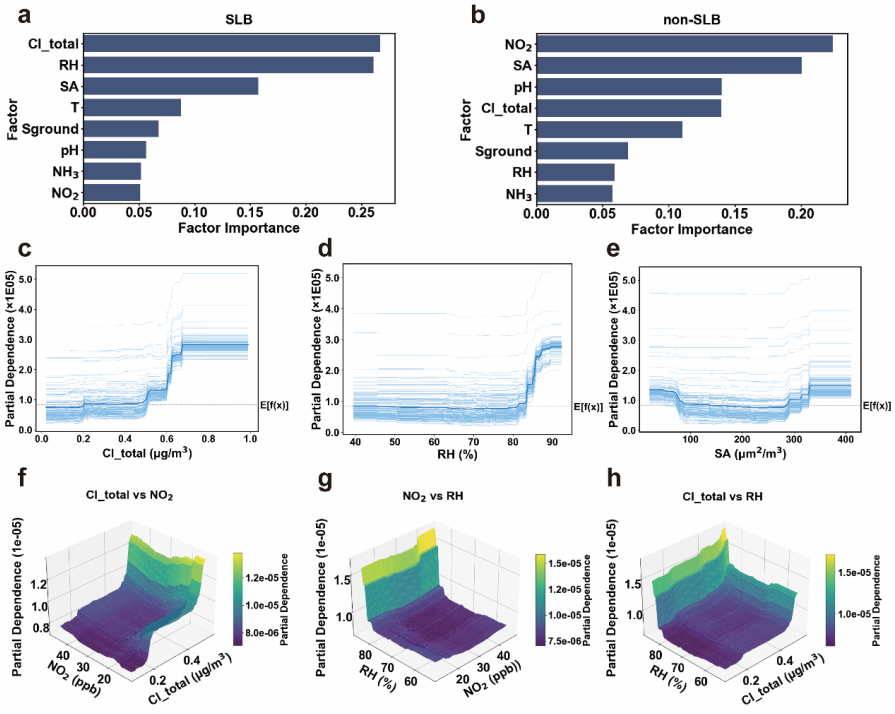

Figure 3. Main and interaction effects of influencing factors for k_{NO2}. Factor importance determined by the random forest (a) SLB days and (b) non-SLB days. Partial dependence plots for the primary drivers on SLB days: (c) Cl_{total}, (d) RH, and (e) SA. Interactions between key factors on SLB days: (f) Cl_{total} and NO_2, (g) RH and Cl_{total}, and (h) RH and NO_2. In panels (a-b), S_{ground} denotes ground surface areas calculated by 1/BLH (boundary layer height). In panels (c-h), partial dependence reflects the extent to which the influencing factors affect kNO_2.

3.3 Enhanced NO_2 uptake promote the atmospheric reactive nitrogen cycle

The above correlations analysis suggests that NO_2 uptake could play an important role in the production of HONO and NO_3^- on SLB days. Since the HONO and NO_3^- formation were influenced by multiple meteorological factors and many atmospheric reaction pathways, a multiphase chemical box model was employed to evaluate the role of enhanced NO_2 uptake. As described in Methods, six simulation scenarios were set up. Incorporating NO_2 uptake mechanism, the model accurately reproduced HONO and NO_3^- observations on SLB days compared to without incorporating it (**Figs. 4a-4b**), substantially improving r values from 0.55 to 0.93 and from statistically insignificant to 0.74, respectively. Additionally, the NO_2 uptake could robustly explain the enhancements in both reactive atmospheric nitrogen species on SLB days across various kNO_2 quantiles (**Fig. 10**). Conversely, applying the current calculated kNO_2 to non-SLB days overpredicted HONO and NO_3^- levels (**Fig. S11**). 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.

Figs.4c-4d illustrate the simulated HONO and NO_3^- budgets for the scenarios incorporating

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NO_2 uptake on SLB days. Despite potential overestimations of non-SLB kNO_2, the mean NO_2 uptake rate remained significantly higher on SLB days than on non-SLB days, with an average rate of 1.03 ppb/h (**Fig. S12**). During nighttime, NO_2 uptake accounted for 83.8% of HONO formation (**Fig. 4e**). The predominance of NO_2 uptake in nocturnal HONO formation has also been observed during PM pollution episodes in urban areas (Xuan et al., 2024; Jia et al., 2020). However, unlike the chlorine-driven reason identified here, those prior cases were primarily attributed to favorable heterogeneous reaction conditions, such as larger SA concentrations, lower BLH, and higher RH. In addition to NO_2 uptake, primary emissions from vehicle exhaust, coal combustion, and biomass burning are also recognized as major contributors to nighttime HONO in urban areas (Wang et al., 2025b; Zhang et al., 2022). In this study, primary emissions contributed only 15.5% to nocturnal HONO formation, substantially less than the contribution from NO_2 uptake. As for nighttime NO_3^- formation, many studies had indicated that N_2O_5 uptake was the dominant pathway in urban areas (Chen et al., 2020; Wang et al., 2018). However, the situation changed under the impact of the enhanced NO_2 uptake. **Fig. 4f** shows that NO_2 uptake contributed 47.9% to nocturnal NO_3^- formation, which was almost comparable to that of N_2O_5 uptake (50.0%). While chlorine can also promote the uptake of N_2O_5 (Bertram and Thornton, 2009), the relative enhancement in the contribution of NO_2 uptake to nocturnal NO_3^- formation was more pronounced. This might be related to the suppression of N_2O_5 uptake caused by increased NO_3^- generating directly from NO_2 uptake. The increase in NO_3^- component of aerosol can shift the equilibrium between N_2O_5 and NO_3^- toward N_2O_5, thereby reducing the contribution of N_2O_5 to NO_3^- formation (Bertram and Thornton, 2009; Wagner et al., 2013). Additionally, the enhanced NO_2 uptake process also competed for NO_2, an important precursor of N_2O_5 formation, especially in the NO_2-limited regime for N_2O_5 formation (Lin et al., 2025), ultimately reducing the overall enhancement effect on N_2O_5 generation. Moreover, this comparable contribution of NO_2 and N_2O_5 uptake NO_3^- formation was also found during fog events (Xu et al., 2024). Although the observed phenomenon was similar, the dominant drivers differed between fog conditions and coastal SLB periods. The former was primarily attributed to favorable uptake conditions such as abundant aerosol water content and high surface area concentration, whereas the latter was more due to the enhancement effect of chlorine levels and RH on the NO_2 uptake process. Overall, these results reveal the high contribution of NO_2 uptake to HONO and NO_3^- formation during SLB circulation periods, demonstrating that enhanced NO_2 uptake can significantly influence the atmospheric reactive nitrogen cycle in coastal urban areas.

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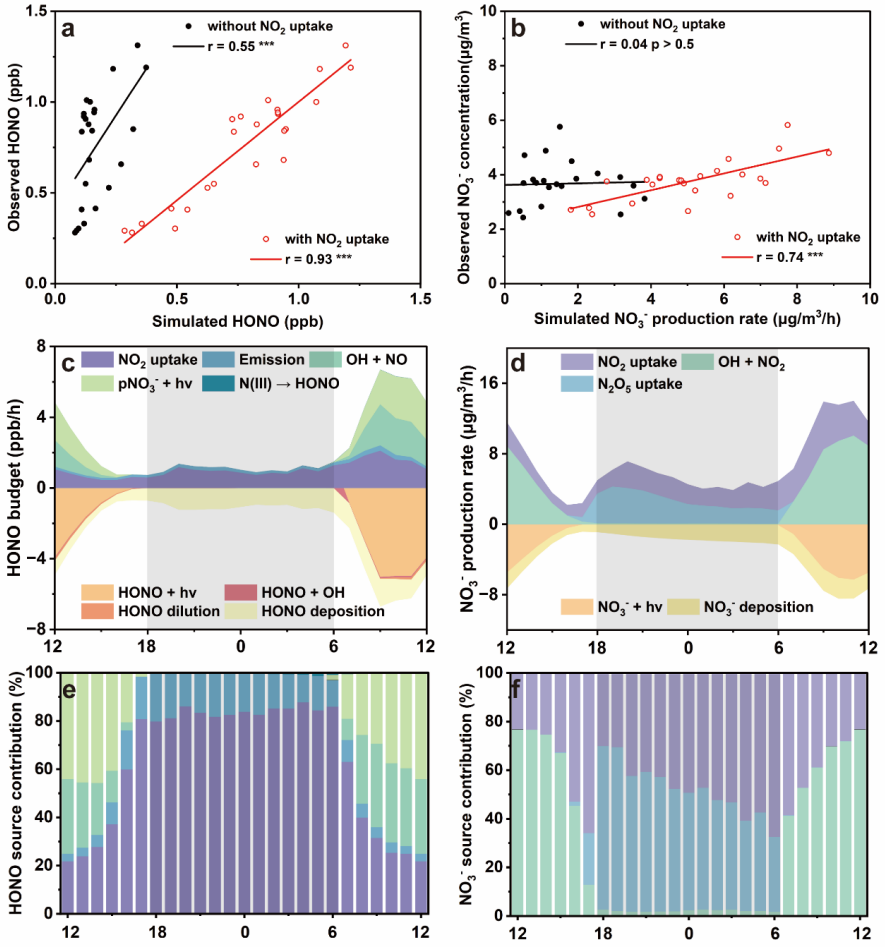

Figure 4. Quantified results from the multiphase chemical box model. Relationship between (a) simulated HONO and observed HONO concentrations, (b) simulated NO_3^- production rate and observed NO_3^- concentration during SLB days, comparing the scenarios with and without considering heterogeneous NO_2 uptake mechanism. Diurnal variations of HONO (c) and NO_3^- budgets (d) during SLB days. Diurnal variations of source contributions to (e) HONO and (f) NO_3^-. The grey shaded areas represent the nighttime period.

4. Conclusions

Overall, our observations show that nighttime sea-land breeze period in coastal urban areas were characterized by stronger sea-salt aerosol influence, higher relative humidity, and elevated HONO and nitrate concentrations. Nighttime conditions led to a significant enhancement in the NO_2 uptake rate constant, mainly driven by increased chlorine levels and relative humidity. Multiphase chemical box model simulations further confirmed that this enhanced NO_2 uptake promoted HONO and nitrate formation. **Fig.5** illustrates a schematic diagram of chlorine-enhanced heterogeneous uptake of NO_2 during sea-land breeze days. Under the influence of strong sea-land breeze circulation, the

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continuous influx of sea-salt aerosols transported by moist sea breezes leads to high chlorine levels during the night. Meanwhile, emission from vehicles and ships contribute substantial NO_2, which accumulates in the coastal atmospheric boundary layer (Wen et al., 2023; Sun et al., 2025). Under these conditions, abundant chloride can effectively facilitate kNO_2 and promote the NO_2 uptake process, thereby influencing the formation of key atmospheric reactive nitrogen species, HONO and NO_3^-, as well as broader reactive nitrogen cycling. Notably, other sea-salt halides (Br^-, I^-) exhibit similar chemical properties to chlorine and may also contribute to the elevated kNO_2 (Zhang et al., 2025a). Additionally, our study focuses specifically on nocturnal NO_2 uptake to form HONO, given that daytime HONO formation involves more complex factors such as photo-enhanced heterogeneous reactions of NO_2 and nitrate photolysis (Stemmler et al., 2006; Han et al., 2016; Ye et al., 2017; Zhou et al., 2011), Future investigations are warranted to explicitly evaluate the impact of chlorine on daytime NO_2 uptake. Moreover, current air quality models often exhibit considerable biases in simulating secondary pollutants such as O_3 and $PM_{2.5}$ over coastal areas (Huang et al., 2025; Ma et al., 2025; Mao et al., 2022). One possible reason is that the influence of chlorine on chemical processes like NO_2 uptake has not yet been adequately considered. Given the dense traffic and substantial NO_2 emission in coastal cities of China, greater attention should be paid to the chlorine-enhanced NO_2 uptake process and its subsequent impact on nocturnal chemistry in coastal urban atmosphere.

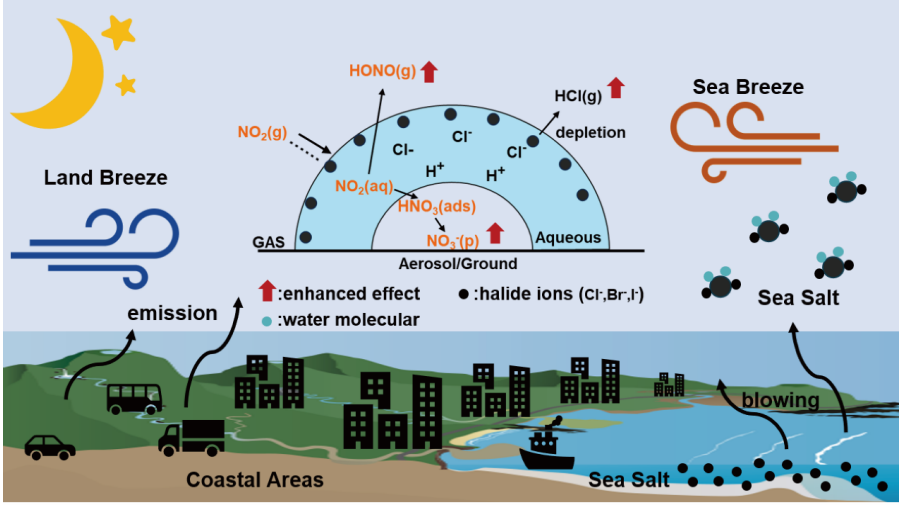

Figure 5. Schematic of the chlorine-enhanced heterogeneous uptake of NO_2 during sea-land breeze days in coastal areas. Red arrows, black solid circles, and blue solid circles represent the enhancement of the uptake process, halide ions and water molecular, respectively.

Code availability. Data analysis methods are available on request from Jinsheng Chen (jschen@iue.ac.cn).

Data availability. The dataset can be accessed at Zenodo website (Lin et al., 2026).

Author contributions:

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Z.L. contributed to the conceptualization, investigation, methodology, data curation, software, analysis and writing of the original draft. L.X., and J.C. contributed to the data curation, reviewing and editing the text, supervision, and funding acquisition X.Y., L.L., C.Y., X.J., Y.C., K.Z., F.Z., Z.C., G.C., X.F., and M.L. provided useful advice and revised the manuscript.

Competing interests:

The authors declare no competing interests.

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