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# Measurement report: High contribution of $N_2O_5$ uptake to particulate nitrate formation in $NO_2$-limited urban areas

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**Abstract:** Particulate nitrate ($pNO_3^-$) is a major component of fine particle in Chinese urban areas. However, the relative contributions of $pNO_3^-$ formation pathways in $NO_2$-limited urban areas remain poorly quantified, hindering further particulate pollution control. In this study, comprehensive winter field observations were conducted in urban Xiamen, Southeast China. We observed significantly elevated nighttime $pNO_3^-$ levels concurrent with increased $N_2O_5$ concentrations. Quantification using an observation-constrained model revealed that $N_2O_5$ uptake contributed 51.2% to total $pNO_3^-$ formation, which was comparable to that of the OH + $NO_2$ reaction. The $N_2O_5$ uptake was found to be mainly driven by nocturnal $NO_3$ oxidation capacity (modulated by $NO_2$ and $O_3$ levels) rather than by heterogeneous reaction conditions. Sensitivity simulations further demonstrated that $pNO_3^-$ formation rate was more sensitive to NO*x* variations than to VOCs variations. Implementing NO*x* control measures at nighttime was shown to effectively reduce $pNO_3^-$ by abating $N_2O_5$ uptake while simultaneously preventing daytime $O_3$ increase. Our findings enhance the understanding of $pNO_3^-$ formation in $NO_2$-limited urban areas and provide valuable insights for developing joint $PM_{2.5}$ and $O_3$ mitigation strategies.

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## 1 Introduction

Fine particulate matter ($PM_{2.5}$) contributes to various atmospheric environmental issues, including visibility deterioration, radiative forcing change, and adverse impacts on human health (Seinfeld, 1989; Lelieveld et al., 2015). Among its chemical components, particulate nitrate ($pNO_3^-$) has attracted increasing attention due to its rising mass fraction in $PM_{2.5}$ and its nonlinear responses to emission mitigation strategies (Xie et al., 2022; Zhai et al., 2021; Li et al., 2021; Zhang et al., 2021; Zhou et al., 2022; Zong et al., 2022; Wang et al., 2020). The primary formation pathways of $pNO_3^-$ include gas-phase oxidation through the reaction of hydroxyl radicals (OH) and nitrogen dioxides ($NO_2$) (R1–R2), and heterogeneous uptake of dinitrogen pentoxide ($N_2O_5$) which is produced via $NO_2$ oxidation by nitrate radicals ($NO_3$) (R3–R5) (Brown and Stutz, 2012). It is well recognized that the OH + $NO_2$ reaction dominates in daytime, while $N_2O_5$ uptake dominates in nighttime. During nocturnal $pNO_3^-$ formation, particulate chlorides can induce $N_2O_5$ heterogeneous uptake to produce $ClNO_2$, thereby competing with $pNO_3^-$ formation.

$$OH(g) + NO_2(g) + M \rightarrow HNO_3(g) + M \quad (R1)$$

$$HNO_3(g) + NH_3(g) \rightleftharpoons NH_4NO_3(p) \quad (R2)$$

$$NO_2(g) + O_3(g) \rightarrow NO_3(g) \quad (R3)$$

$$NO_2(g) + NO_3(g) \rightleftharpoons N_2O_5(g) \quad (R4)$$

$$N_2O_5(g) + H_2O/Cl^-(p) \rightarrow (2-\varphi)NO_3^-(p) + \varphi ClNO_2(g) \quad (R5)$$

Many studies have focused on quantifying the potential formation pathways of $pNO_3^-$ in urban areas of China. In major urban agglomerations such as the Beijing-Tianjin-Hebei (BTH) region (Chen et al., 2020; Ma et al., 2023; Zhao et al., 2023), Yangtze River Delta (YRD) (Sun et al., 2022; Zhai et al., 2023; Zhang et al., 2023b), and Pearl River Delta (PRD) (Yang et al., 2022; Niu et al., 2022; Cheng et al., 2024), $pNO_3^-$ formation was typically dominated by the gas-phase oxidation of OH + $NO_2$. In contrast, under special conditions such as the COVID-19 pandemic and $PM_{2.5}$ pollution events (Yan et al., 2023; Zhai et al., 2023), $N_2O_5$ uptake became the main pathway. Previous research has demonstrated that the formation rate of $pNO_3^-$ via $N_2O_5$ uptake is closely related to its precursor $NO_2$ and $O_3$, and the $N_2O_5$ formation can be classified into $NO_2$-limited and $O_3$-limited regimes based on the $NO_2/O_3$ ratio (Ma et al., 2023). The winter $NO_2/O_3$ ratios in the BTH, YRD, and PRD regions were generally above 1, placing $N_2O_5$ formation

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in the $O_3$-limited or transition regime (Ma et al., 2023; Wen et al., 2018; Li et al., 2021; Zhang et al., 2023b). However, $N_2O_5$ uptake served as the dominant pathway for $pNO_3^-$ formation, typically occurring under $NO_2$-limited conditions (e.g., reduced emissions during the pandemic) or highly favorable $N_2O_5$ uptake conditions (e.g., severe particulate pollution episodes). Collectively, these findings indicate that spatial variations in $NO_2$ and $O_3$ levels are likely a key driver of regional differences in the dominant formation pathways of $pNO_3^-$. The formation of $pNO_3^-$ primarily depends on precursors OH, $NO_2$, and $O_3$, with OH and $O_3$ concentrations being influenced by VOCs and NO*x* emissions. Thus, the different formation pathways of $pNO_3^-$ result in complex responses to NO*x*/VOCs emissions. As for the response of OH + $NO_2$ to precursors variation, it was relatively well-understood, as most Chinese urban areas are located in VOC-limited regimes for $O_3$ (Wang et al., 2023b; Wang et al., 2022c; Zhang et al., 2023a; Mao et al., 2022), and ammonia-rich regimes for $pNO_3^-$ (Xing et al., 2018; Sun et al., 2022; Fu et al., 2024; Liu et al., 2019). Under these conditions, VOCs reduction suppresses $pNO_3^-$ formation by decreasing OH concentrations, whereas NO*x* reduction enhances $pNO_3^-$ formation by weakening the NO*x* titration effect. Given the regional variations in the $NO_2/O_3$ ratio across urban areas of China (Ma et al., 2023), the response of $N_2O_5$ uptake to precursor changes (VOCs, $O_3$) likely exhibits spatial heterogeneity. A recent study has revealed that under $O_3$-limited conditions for $N_2O_5$ formation (Zhang et al., 2023b), NO*x* emissions had negligible effects, while VOCs reduction decreased the removal of $NO_3$ by VOCs, thereby enhancing $N_2O_5$ uptake. However, the response of $pNO_3^-$ formation to precursors under $NO_2$-limited conditions remains unclear. Aside from precursor availability, $N_2O_5$ uptake is also greatly influenced by heterogeneous reaction conditions like aerosol composition and aerosol surface area (Mcduffie et al., 2018b; Mcduffie et al., 2018a; Tham et al., 2018; Yu et al., 2020), which introduces additional uncertainty in determining the contribution of $pNO_3^-$ formation pathways and the effectiveness of precursor control strategies.

The $NO_2/O_3$ ratios in southeastern China predominantly fell within the $NO_2$-limited regime for $N_2O_5$ formation (Ma et al., 2023). Xiamen, as one of the most developed cities in southeastern China, exhibits relatively better air quality with low levels of VOCs and NO*x* compared to China's megacities (**Table S1)**. This pattern well represents the future urban atmospheric conditions following the implementation of air pollution control measures in China. From December 2022 to February 2023, we conducted comprehensive multi-parameter observations in urban Xiamen, including $N_2O_5$ and related chemical constituents. An observation-constrained box model incorporating the heterogeneous reaction parameters

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was utilized to quantify the rates of different $pNO_3^-$ formation pathways. Explainable machine learning (ML) method was applied to identify the driving factors of high $N_2O_5$ uptake rate. Additionally, multi-scenario simulations were performed to examine the joint responses of $pNO_3^-$ and $O_3$ formation to various NO*x* and VOCs emissions. These findings enhance our understanding of $pNO_3^-$ formation pathways and their environmental implications in $NO_2$-limited regions, providing valuable insights for developing joint $PM_{2.5}$ and $O_3$ mitigation strategies.

## 2 Methods

### 2.1 Field Observation.

Field observations were conducted during the winter period from 1 December 2022 to 3 February 2023, at an urban site (marked by the red star in **Figure S1**) in Xiamen, which is located in the southeastern coastal region of China. Detailed site information has been described in our previous studies (Yang et al., 2023; Liu et al., 2022). Trace gases (including PAN, HCHO, HONO, VOCs, $O_3$, NO*x*, CO, and $SO_2$), chemical components in $PM_{2.5}$ (including organic carbon and elemental carbon, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$, $Cl^-$), $PM_{2.5}$ mass concentration, and meteorological parameters (including ambient temperature (T), relative humidity (RH), atmospheric pressure (P), wind speed (WS), wind direction (WD), and photolysis rates) were continuously measured during the campaign. Detailed information about measurement methods and instruments is summarized in **Text S1**. A chemical ionization time-of-flight mass spectrometer equipped with an iodide source (iodide-TOF-CIMS, Aerodyne Research Inc., USA) was deployed to measure $N_2O_5$ and $ClNO_2$. The instrument configuration and calibration procedures for $N_2O_5$ and $ClNO_2$ are described in **Text S2**, following established methods (Wang et al., 2022b; Wang et al., 2022a; Thaler et al., 2011). Boundary layer height (BLH) data were obtained from the ERA5 dataset (Hersbach et al., 2020).

### 2.2 Determination of $pNO_3^-$ Formation Rate.

The interactive box model developed by Wagner et al. with a simplified mechanism was employed to obtain key parameters of the $N_2O_5$ uptake process (Wagner et al., 2013), including $kN_2O_5$ and $\varphi ClNO_2$ (**see in Text S3**). To validate the interactive box model results, these parameters were calculated concurrently based on the classical steady-state approximation method (**Text S4**) (Brown et al., 2003; Chen et al., 2022). As shown in **Figure S2**, the outcomes of the two methods exhibited strong consistency, with logarithmic correlation coefficients ($R^2$) as high as 0.76 and 0.73 for $kN_2O_5$, $\varphi ClNO_2$, respectively.

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Considering the larger number of valid data points, the model-derived parameters were adopted for subsequent analysis.

A Framework for 0-D Atmospheric Modeling (F0AM), incorporating the Master Chemical Mechanism (MCM v3.3.1) and heterogeneous mechanisms (**Table S2**), was employed to simulate nitrate formation rates for each day during the study period (Wolfe et al., 2016; Atkinson and Arey, 2003; Jenkin et al., 2015). The heterogeneous parameters derived from the interactive box model were implemented in F0AM. In addition, hourly interval data of trace gases, photochemically active species, meteorological variables, and reanalysis data were also applied to constrain the multiphase chemical box model. Detailed model configurations are provided in **Text S5**. As shown in **Figure S3**, the model performed well for $N_2O_5$ and $ClNO_2$ simulations with $R^2$ of 0.88 and 0.49, respectively. The simulated OH concentrations agreed well with parameterized method suggested by Ehhalt and Rohrer (**Figure S4**, $R^2 = 0.86$) (Ehhalt and Rohrer, 2000). Based on model simulation and precursor observations, we quantified $pNO_3^-$ formation rates through both OH + $NO_2$ and $N_2O_5$ uptake pathways by model integral. Note that the gas-particle partitioning coefficient was set to 100%, which might lead to in an overestimation of the OH + $NO_2$ pathway contribution.

**2.3 Identification of influencing factors for $N_2O_5$ uptake.**

Extreme gradient boosting (XGBoost), a machine learning technique, has been widely applied in atmospheric chemistry research (Gui et al., 2020; Wang et al., 2023c; Requia et al., 2020). Here, we built a XGBoost model to reproduce the $N_2O_5$ uptake rate with selected variables. The model was built using the "xgboost" library (https://github.com/dmlc/xgboost/tree/master) in a python environment. Explanatory variables included meteorological parameters (BLH, T, and RH), nocturnal atmospheric oxidation capacity P($NO_3$) calculated by $k_{NO_2+O_3}[NO_2][O_3]$, TVOCs, the logarithm of the ratio of $NO_2$ to $O_3$ (log($[NO_2]/[O_3]$)), NO, and heterogeneous uptake parameters ($\varphi ClNO_2$ and $kN_2O_5$). Only nighttime (18:00 – 06:00 the next day) data were considered to identify key drivers of $N_2O_5$ uptake. The hyperparameters of the XGBoost model were tuned by grid searching method and the established model was evaluated using $R^2$, Mean Absolute Error (MAE) and Root Mean Square Error (RMSE). By incorporating SHAP interpretation, the XGBoost-SHAP method could quantify factor contributions through SHAP values, where absolute SHAP values denote the relative importance. Detailed description and setup of the XGBoost-SHAP method can be found in **Text S6** and our previous study (Lin et al.,

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2024).

### 2.4 Emission Scenario Modelling.

Using the aforementioned multiphase chemical box model, we investigated changes in formation rates of $pNO_3^-$ ($PNO_3^-$) and $O_3$ ($PO_3$) under different VOCs and NO*x* emission scenarios. The base model simulation was performed using mean diurnal values from the winter 2022 observations. A series of emission scenarios were tested by scaling normalized VOCs and NO*x* concentrations from 0 to 2 times baseline levels to examine their impacts on $PNO_3^-$ and $PO_3$. Prior to each scenario simulation, 3-day spin-up was set to stabilize intermediate species concentrations. Isopleth diagrams of simulated $PNO_3^-$ and $PO_3$ were obtained from the base scenario and 120 emission change scenarios. In addition, response strength (RS) was calculated using **eq 2** as an indicator of emission sensitivity.

$$PO_3 = k_1[HO_2][NO] + \sum k_{2i}[RO_2][NO] \quad (1)$$

Where, $k_i$ is the corresponding chemical reaction rate constants.

$$RS = \frac{X_i - X_{base}}{V_i - V_{base}} \quad (2)$$

Where, $X_i$ and $X_{base}$ are the mean formation rates of dependent variables e.g. $PNO_3^-$, $PO_3$ in scenario i and base simulations, respectively. $V_i$ and $V_{base}$ are the emission rates for the scenario i and base simulations, respectively. Notably, the emission rates ranged from 0 to 2 times baseline levels, with the base simulation emission rate normalized to 1.

## 3 Results and Discussion

### 3.1 Overview of Observations.

The mean diurnal patterns of $pNO_3^-$, gaseous pollutants and relevant meteorological parameters are shown in **Figure 1**. During the entire observation period, mean concentrations of $NO_2$, $O_3$, total VOCs, and $PM_{2.5}$ were 10.9 ppb, 27.3 ppb, 18.2 ppb, and 14.3 μg $m^{-3}$, respectively, lower than those observed in most of China's key cities (refer to **Table S1**). Despite the low NO*x* levels, $pNO_3^-$ contributed 29.5% to $PM_{2.5}$ mass concentration, which was higher than proportions reported in Beijing urban area (24.7%) (Ma et al., 2023), Guangdong (24.0%) (Yun et al., 2018), and Nanjing (24%–27%) (Huang et al., 2020). This discrepancy suggests efficient conversion from $NO_2$ to $pNO_3^-$ in the study area. In addition, the proportion of $pNO_3^-$ increased with rising $PM_{2.5}$ concentration (**Figure S6**), indicating its importance to

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particulate pollution. This is consistent with the phenomenon widespread in urban areas of China where $pNO_3^-$ became dominant in inorganic aerosols despite NO*x* reduction, underscoring the need for efficient $pNO_3^-$ control strategies (Zhai et al., 2021; Zhao et al., 2020; Zhang et al., 2022).

The diurnal pattern of $pNO_3^-$ exhibited a bimodal characteristic, with peaks occurring at 4:00 and 16:00 LT, respectively. The daytime peak (07:00–17:00) was accompanied by low concentrations of NO*x* and high levels of $O_3$ and $JNO_2$, indicating that active photochemical conditions promoted daytime $pNO_3^-$ formation. During the nighttime (18:00–06:00 the next day), $pNO_3^-$ concentrations increased together with $NO_2$, $N_2O_5$ and $ClNO_2$ from 18:00 onward and remained elevated until early morning. This nighttime accumulation can be attributed to two factors. First, lower temperature, shallower boundary layer height, and reduced wind speed at night favored the accumulation of $pNO_3^-$ and related nitrogen-containing species. Second, higher RH and $PM_{2.5}$ concentrations at night enhanced aerosol water content and surface area, providing favorable conditions for heterogeneous hydrolysis of $N_2O_5$ to form $pNO_3^-$. The mean concentration of $N_2O_5$ was 0.19 ± 0.26 ppb (peaking at 2.52 ppb), which is relatively higher than values reported for China's megacities (Chen et al., 2020; Wang et al., 2017; Tham et al., 2018; Wang et al., 2022a; Liu et al., 2025; Li et al., 2023). Moreover, the observed elevation in nighttime $ClNO_2$, primarily produce via the reaction of $N_2O_5$ with Cl-containing particles, strongly supports the presence of active heterogeneous processes of $N_2O_5$. Collectively, these findings imply a likely significant contribution of $N_2O_5$ uptake to $pNO_3^-$ formation during the nighttime.

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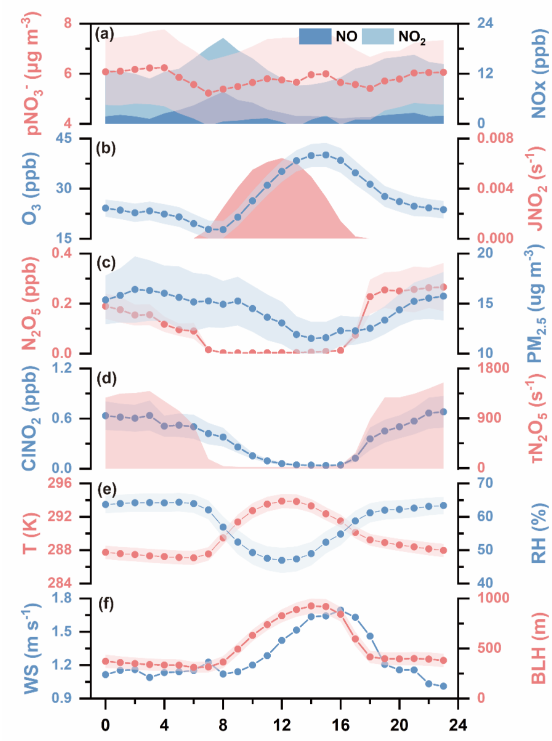


**Figure 1.** Diurnal variations of key parameters during the winter of 2022. The concentrations of $pNO_3^-$, NO$x$, $O_3$, $N_2O_5$, $PM_{2.5}$ and $ClNO_2$. The levels of the photolysis frequencies of $NO_2$ ($JNO_2$), ambient temperature (T), relative humidity (RH), the lifetime of $N_2O_5$ ($\tau N_2O_5$), wind speed (WS) and the boundary layer height (BLH). Shaded areas of $pNO_3^-$, $O_3$, $N_2O_5$, $PM_{2.5}$, $ClNO_2$, T, RH and BLH represent 95% confidence intervals.

### 3.2 High contribution of $N_2O_5$ uptake to $pNO_3^-$ formation in $NO_2$-limited conditions.

In view of the observed importance of daytime and nighttime $pNO_3^-$ formation, we further employed an observation-constrained model to quantify the potential formation pathways, including the gas-phase reaction of OH + $NO_2$ and heterogeneous $N_2O_5$ uptake. This model incorporated heterogeneous chemical mechanisms, with key heterogeneous parameters (e.g. the loss rate of $N_2O_5$ ($kN_2O_5$) and the production yield of $ClNO_2$ ($\varphi ClNO_2$)) obtained through simulation (See Methods for details). As shown in **Figure S7,** these simulated parameters exhibited good agreement with classical steady-state methods, demonstrating the model's capability to characterize heterogeneous uptake processes and thereby

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effectively evaluate $pNO_3^-$ formation processes.

As illustrated in **Figure 2a**, the diurnal pattern of $pNO_3^-$ formation rates exhibited a classical characteristic, with daytime dominated by gas-phase oxidation and nighttime dominated by $N_2O_5$ uptake. The daytime OH + $NO_2$ reaction had a mean $pNO_3^-$ formation rate of 1.62 μg $m^{-3}$ $h^{-1}$, while the nighttime $N_2O_5$ uptake pathway showed a formation rate of 1.18 μg $m^{-3}$ $h^{-1}$ (**Figure 2b-c**). For the whole day, $N_2O_5$ uptake contributed an average of 51.2% to $pNO_3^-$ formation, which was comparable to the contribution of the OH + $NO_2$ pathway (**Figure 2d**). Notably, the partitioning coefficient for gas-phase oxidation processes was assumed to be 1 in this study, meaning the contribution of OH + $NO_2$ represented an upper limit and the actual contribution of $N_2O_5$ uptake should be even greater. To exclude year-specific effects, we further analyzed the contributions of both pathways to $pNO_3^-$ formation during winters from 2019 to 2023. The results demonstrated that $N_2O_5$ uptake pathway consistently accounted for approximately half of $pNO_3^-$ formation in the study area (**Figure 3a**), which was also consistent with the observed high proportion of nighttime $pNO_3^-$ throughout the day (**Figure 3b**). Such a high contribution of $N_2O_5$ uptake to $pNO_3^-$ is generally uncommon in urban areas. A study in urban Beijing showed that during non-polluted periods, $N_2O_5$ uptake contributed only 18.9% to nitrate formation rates (Ma et al., 2023). Similarly, the contributions of $N_2O_5$ uptake were 10%–38% and 4% in urban areas of the YRD (Sun et al., 2022; Zhai et al., 2023; Zhang et al., 2023b) and PRD regions(Yang et al., 2022), respectively.

Previous studies have found that nocturnal $pNO_3^-$ formation via $N_2O_5$ uptake strongly depends on the ratio of $NO_2$ to $O_3$ (Ma et al., 2023). This process is suppressed in the $O_3$-limited regime ($NO_2/O_3 > 2$) but enhanced in the $NO_2$-limited regime ($NO_2/O_3 \leq 1$). The COVID-19 lockdown period was a typical example of this ratio dependence(Yan et al., 2023). In regions like Beijing, substantial reductions in NO*x* emissions caused a shift in nocturnal $pNO_3^-$ formation from the $O_3$-limited to the $NO_2$-limited regime. This shift resulted in elevated nighttime $O_3$ levels and a weakened NO titration effect, collectively promoting $N_2O_5$ formation and subsequent $pNO_3^-$ formation. The sensitivity of $N_2O_5$ uptake to $NO_2$ and $O_3$ during the campaign is presented in **Figure 3c-d**. The observed mean values of $NO_2/O_3$ (0.40) and the probability distributions of $NO_2/O_3$ ratios both indicate that $N_2O_5$ uptake was in the $NO_2$-limited regime. Based on $NO_2$ and $O_3$ observational data during 2015–2021 from the China National Environmental Monitoring Centre(Ma et al., 2023), most key urban regions in China (e.g., the NCP, YRD, and Beijing) were found to lie in the $O_3$-limited or transition regimes ($1 < NO_2/O_3 \leq 2$), whereas nocturnal $pNO_3^-$ formation in southeastern China was distinctly in $NO_2$-limited regime. These results confirm that the dominant

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$pNO_3^-$ formation mechanisms in our study area significantly differs from those in most urban areas of China, which might be attributed to the dependence of $N_2O_5$ uptake on precursor $NO_2$ and $O_3$. In addition, the dominance of $N_2O_5$ uptake in $pNO_3^-$ formation also occurred during haze pollution periods (Zhai et al., 2023; Wang et al., 2017), where increased aerosol surface area under high particulate loadings created favorable conditions for $N_2O_5$ heterogeneous reactions. Therefore, to evaluate the role of precursors, we conducted a comprehensive analysis of the factors driving $pNO_3^-$ formation via $N_2O_5$ uptake.

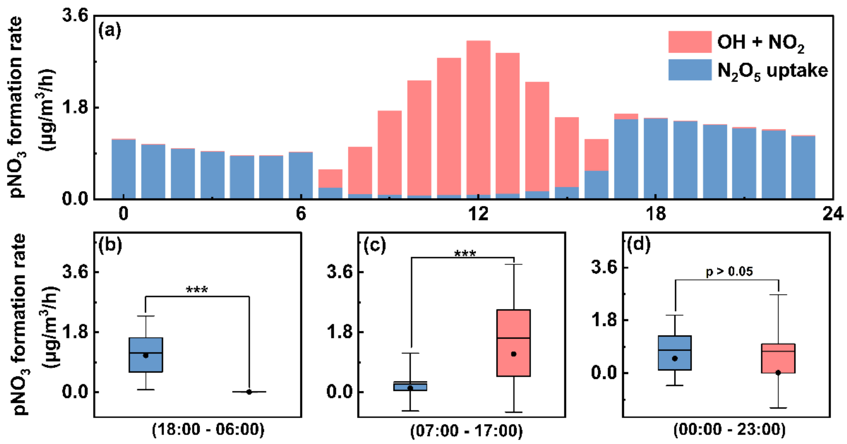


**Figure 2.** Simulated rates of key $pNO_3^-$ formation pathways obtained from the chemical box model incorporating heterogeneous parameters**.** Diurnal formation rates of $pNO_3^-$ via the OH + $NO_2$ and $N_2O_5$ uptake pathways **(a)** and comparison of the two pathways during the nighttime **(b)**, daytime **(c)**, and the whole day **(d)**. Note that the results in panel (a) represent the mean simulated formation rates over the entire observation period. The box shows the 25th–75th percentiles with whiskers representing the 5th–95th percentiles. The black line and dot inside the box represent the mean and median values, respectively. Statistical significance was determined using pair-sample *t*-tests with *** indicating $p < 0.001$.

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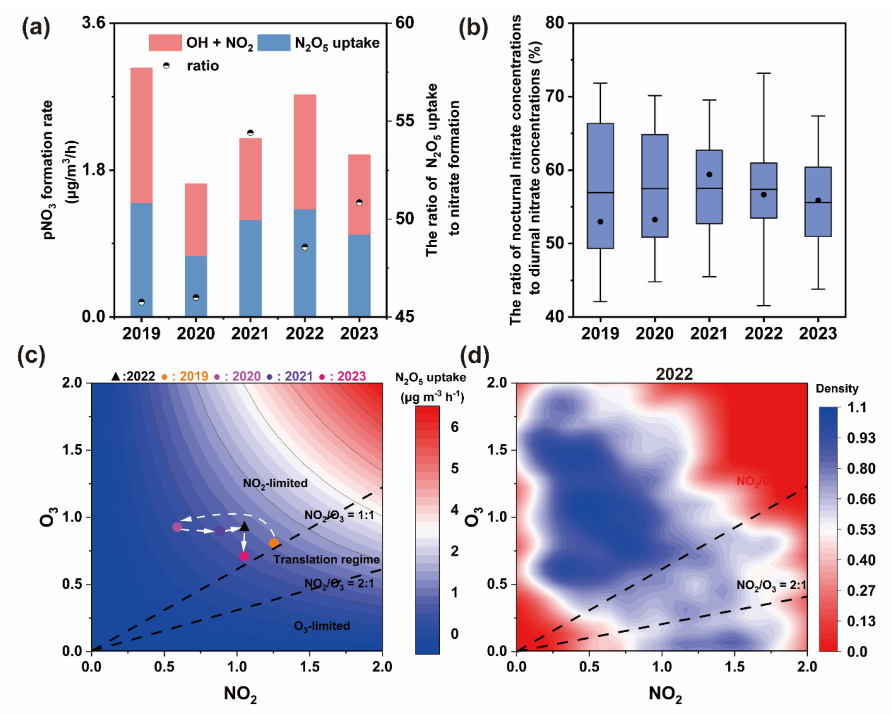


Figure 3. Inter-annual patterns of key $pNO_3^-$ formation pathways in urban Xiamen. The average $pNO_3^-$ formation rate from OH + $NO_2$ and $N_2O_5$ uptake **(a)**, and the average ratio of the sum of nocturnal $pNO_3^-$ concentrations to the sum of all-day $pNO_3^-$ concentration **(b)** in different winters from 2019 to 2023 based on the measured $pNO_3^-$ in $PM_{2.5}$. The sensitivity of nocturnal $N_2O_5$ uptake to $NO_2$ and $O_3$ from 2019 to 2023 **(c)**. And probability distribution of observed $NO_2/O_3$ at nighttime in winter 2022 **(d)**. The observed periods of different winters from 2019 to 2023 are summarized in **Table S3**. In panel (c), the black triangle indicates the base case of winter 2022, solid circles in different colors represent the average $NO_2$ to $O_3$ ratios in different years, and the predicted average formation rate of $N_2O_5$ uptake as the normalized emissions (average concentrations of $O_3$ and $NO_2$) varied between 0 to 2.

### 3.3 Driving Factors of Nocturnal $N_2O_5$ Uptake.

The $N_2O_5$ uptake rate is influenced by multiple factors including precursor levels, meteorological parameters, and heterogeneous reaction conditions (Ma et al., 2023; Chen et al., 2020; Chen et al., 2024). A machine learning method integrating these factors was employed to identify the key drivers of $N_2O_5$ uptake. The relative importance of each factor was evaluated by absolute SHAP values (**Figure 4a**), and

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their impacts were elucidated by examining the relationships between individual factors and their corresponding SHAP values (**Figure 4b-e** and **Figure S8**). Results showed that the nocturnal $NO_3$ formation rate ($P(NO_3)$), an integrated indicator of nocturnal atmospheric oxidation capacity (Wang et al., 2021), was the most important factor for $N_2O_5$ uptake with the highest absolute SHAP value. The steep slope of the positive correlation between $P(NO_3)$ and SHAP values indicated that $P(NO_3)$ strongly enhanced $N_2O_5$ uptake. $P(NO_3)$ is primarily formed through the reaction between $NO_2$ and $O_3$ ($P(NO_3) = k_{NO_2+O_3}[NO_2][O_3]$), suggesting that $NO_2$ and $O_3$ mainly influenced $N_2O_5$ uptake by modulating $NO_3$ radical formation. Notably, the factor $\log NO_2/O_3$ had relatively low importance, indicating concentrations of precursors were more important than $NO_2/O_3$ ratio in determining the $N_2O_5$ uptake under extremely $NO_2$-limited condition (mean $NO_2/O_3$ was 0.40). Furthermore, as shown in **Figure S8b**, $\log NO_2/O_3$ and its SHAP value shows a positive correlation when $\log NO_2/O_3$ is less than 0. Under $NO_2$-limited conditions ($\log NO_2/O_3 < 0$, $NO_2/O_3 < 1$), $N_2O_5$ uptake was driven by the elevated $NO_2$.

Compared with $P(NO_3)$, other factors exhibited weaker effects on $N_2O_5$ uptake. $\varphi ClNO_2$ emerged as the second most important factor and showed a negative correlation with SHAP values (**Figure 4c**), illustrating that $ClNO_2$ formation inhibited $pNO_3^-$ formation. This inhibitory effect could be attributed to high concentrations of Cl-containing particles ($0.94 \pm 1.11$ μg m$^{-3}$) in the study area. Chloride-containing aerosols promote $N_2O_5$ uptake to produce more $ClNO_2$ (as evidenced by the positive correlation between $\varphi ClNO_2$ and chloride ions, **Figure S9**), while simultaneously reducing $pNO_3^-$ formation (R5). Additionally, the nighttime produced $ClNO_2$ can undergo photolysis in following day to release Cl radicals, which further promote $O_3$ formation. This indirect effect must be considered when formulating control measures for particulate matter pollution. Interestingly, as shown in **Table S4** (Tham et al., 2016; Wang et al., 2018; Yun et al., 2018; Morgan et al., 2015), although the simulated $kN_2O_5$ ($7.64\times10^{-3} \pm 6.12\times10^{-3}$ s$^{-1}$) was higher than values reported in Beijing ($8.1\times10^{-4} – 1.42\times10^{-3}$ s$^{-1}$), Guangdong ($3.78\times10^{-3} – 9\times10^{-3}$ s$^{-1}$), and UK ($9.3\times10^{-5} – 10^{-3}$ s$^{-1}$), $kN_2O_5$ exerted only a weak positive effect on $N_2O_5$ uptake (**Figure 4d**). The large difference existing in importance of $P(NO_3)$ and $kN_2O_5$ indicated that the $N_2O_5$ uptake process was more limited by precursor levels rather than heterogeneous uptake conditions. Similar phenomenon was also found in winter in urban Beijing and Northern Utah mountain basins (Mcduffie et al., 2019; Chen et al., 2020). This situation is likely due to the favorable $N_2O_5$ uptake conditions during winter, e.g., low temperature, high aerosol surface area, and elevated aerosol liquid content (Wang et al., 2023a; Mcduffie et al., 2018b; Jia et al., 2020). The total concentrations of the observed VOCs (TVOCs)

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showed a weak negative correlation with $N_2O_5$ uptake (**Figure 4e**), reflecting their indirect inhibition on $N_2O_5$ formation by consuming $NO_3$ radicals. Moreover, we found that the effects of φ$ClNO_2$, k$N_2O_5$, and TVOCs on $N_2O_5$ uptake were subject to P($NO_3$) levels (**Figure 5a-5c**). Specifically, the negative effect of φ$ClNO_2$ and the positive effect of k$N_2O_5$ on $N_2O_5$ uptake became statistically significant when P($NO_3$) exceeded approximately 1.0 ppb $h^{-1}$ and 0.5 ppb $h^{-1}$, respectively. The negative correlation slope of TVOCs versus $N_2O_5$ uptake intensified with increasing P($NO_3$) levels, indicating that the $N_2O_5$ removal effect was enhanced through VOC-induced $NO_3$ depletion. These findings highlight the critical role of precursor $NO_2$ and $O_3$ in nocturnal p$NO_3^-$ formation, demonstrating that these precursors mainly affect this pathway by modulating $NO_3$ radical formation.

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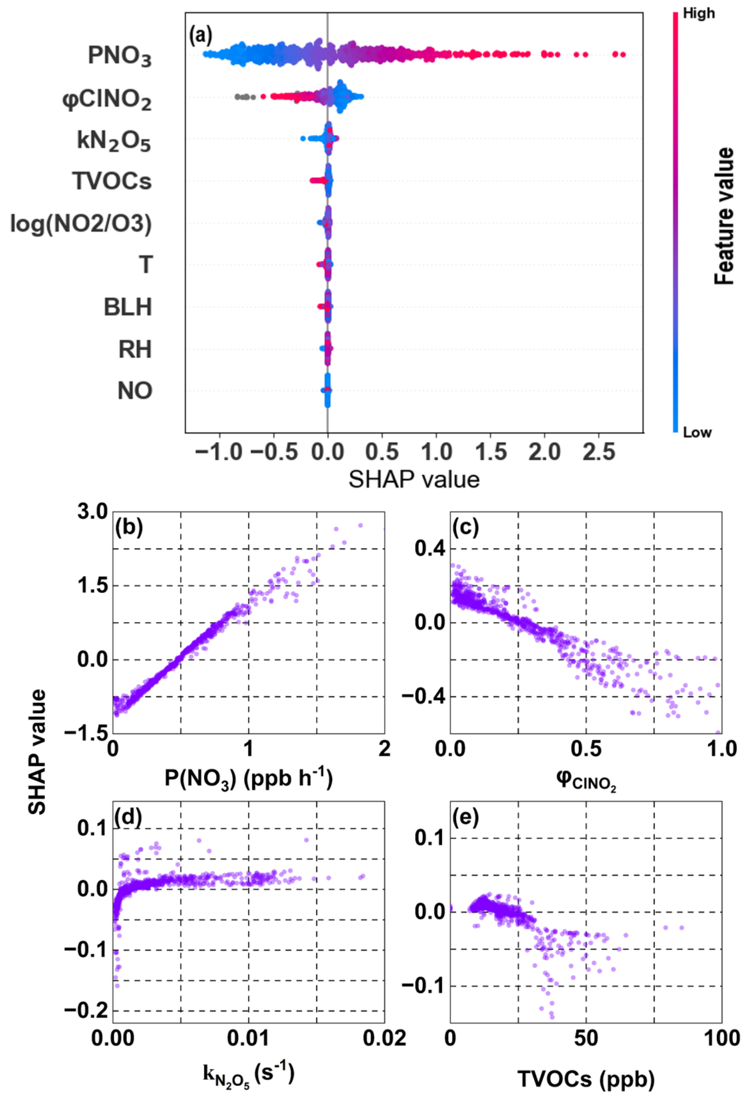


**Figure 4.** Feature importance **(a)** and the effects of key factors on $N_2O_5$ uptake **(b-e)** obtained by the XGBoost-SHAP method. The relationships between SHAP values and major features: P($NO_3$) **(b)**, φ$ClNO_2$**(c)**, k$N_2O_5$**(d)**, and TVOCs **(e)**. Feature importance ranking **(a)** is determined by mean absolute SHAP values (descending order, top to bottom). Relationships between SHAP values and other factors are shown in **Figure S8**.

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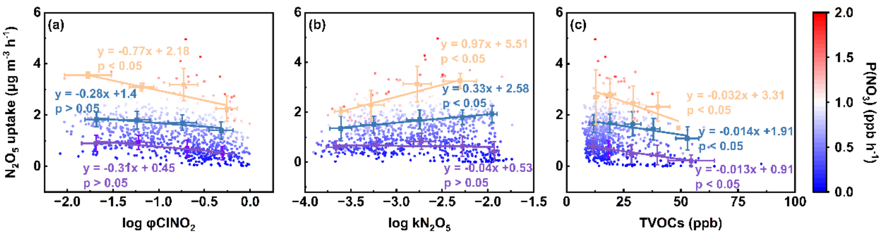


**Figure 5.** Relationships between $N_2O_5$ uptake and $\varphi ClNO_2$ **(a)**, $kN_2O_5$ **(b)**, and TVOCs **(c)** colored by $P(NO_3)$. Linear fit curves in purple, blue and orange represent the fitting results for $P(NO_3)$ in the ranges of 0–0.5 ppb $h^{-1}$, 0.5–1.0 ppb $h^{-1}$ and > 1.0 ppb $h^{-1}$, respectively.

### 3.4 Optimal Mitigation Strategies of $pNO_3^-$ under High $N_2O_5$ Uptake.

The above results revealed that $pNO_3^-$ formation through both the daytime OH + $NO_2$ reaction and nocturnal heterogeneous $N_2O_5$ uptake was closely linked to VOCs-NO*x*-$O_3$ chemistry (Yang et al., 2022). Using a multiphase box model, we systematically examined the responses of both $pNO_3^-$ and $O_3$ to varying NO*x* and VOC emission scenarios. **Figure 6a** shows $pNO_3^-$ formation located in the transition regime of VOCs and NO*x*. The formation rate of $pNO_3^-$ ($PNO_3^-$) decreased with the reductions of VOCs and NO*x*, and this trend became more pronounced under aggressive NO*x* reduction scenarios (**Figure 6c-d**). **Figure S10a-b** reveal that the mean response strength (RS, as defined in Methods) of $PNO_3^-$ to NO*x* was 0.75, higher than that for VOCs (RS = 0.29), suggesting that NO*x* reduction had a greater potential for $pNO_3^-$ mitigation compared to VOCs control. However, NO*x* and VOCs reductions exerted different impacts on $O_3$ formation rate ($PO_3$). In our study area, $PO_3$ located in the VOC-limited regime (**Figure 6b**). We found that $PO_3$ declined with VOCs reduction but increased with NO*x* reduction until NO*x* dropped below 20% of the base (**Figure 5c-d**). Moreover, detailed results distinguishing daytime and nighttime major formation pathways of $pNO_3^-$ are presented in **Figure 6e-f** and **Fig. S10c-d**. For VOC reduction scenarios, both the OH + $NO_2$ reaction and $N_2O_5$ uptake pathways showed declining nitrate formation rates, with comparable RS of 0.11 and 0.18, respectively. This occurs because reduced VOCs concentrations decrease OH radical and $O_3$ concentrations, thereby suppressing $pNO_3^-$ formation via both pathways. In contrast, NO*x* reduction yielded more complex behavior. The OH + $NO_2$ reaction rates remained nearly constant until NO*x* dropped to 60% of the base. This stability arises because NO*x* reduction diminishes the NO titration effect on $O_3$, thereby increasing OH radicals through $O_3$ photolysis.

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The competing effects of NO*x* reduction and OH enhancement led to an initial plateau in the OH + $NO_2$ reaction rate before its eventual decline. Differently, the $N_2O_5$ uptake rate decreased consistently and significantly with NO*x* abatement, exhibiting a high mean RS value of 0.61. This phenomenon was closely associated with the $NO_2$-limited regime of $N_2O_5$ uptake in the study area. As shown in **Figure S11,** the variation trends of $PNO_3^-$, $P(O_3)$, OH + $NO_2$, and $N_2O_5$ uptake were consistent across all VOCs/NO*x* combinations, indicating that the results robustly reflect the response mechanisms to precursor emission changes.

As mentioned above, VOC reduction proved effective yet limited in mitigating both $pNO_3^-$ and $O_3$, the effectiveness of NO*x* reduction exhibited significant regional and temporal variations. In China's megacities, including PRD, YRD, and BTH regions, $pNO_3^-$ initially increased and then decreased in response to the reduction of NO*x* emissions (Li et al., 2021; Zhang et al., 2023b; Yang et al., 2022). Under high-NO*x* conditions, mild NO*x* reduction would raise daytime OH and $O_3$ concentrations (Zhang et al., 2023b), rendering OH (rather than NO*x*) the limiting factor for the OH + $NO_2$ reaction, which consequently enhanced daytime $pNO_3^-$ formation. Additionally, as the season most susceptible to PM pollution, wintertime $N_2O_5$ formation in these regions was in an $O_3$-limited or transition regime (Ma et al., 2023), wherein the elevated daytime $O_3$ significantly enhanced $NO_3$ radical generation, thereby promoting nocturnal $N_2O_5$ uptake and subsequent $pNO_3^-$ formation. Conversely, in $NO_2$-limited regions (e.g., southeastern China), NO*x* reduction showed limited impact on daytime $pNO_3^-$ formation via the OH + $NO_2$ pathway but effectively suppressed nighttime $pNO_3^-$ formation via $N_2O_5$ uptake. This approach concurrently reduced $ClNO_2$ formation from $N_2O_5$ heterogeneous processes, consequently diminishing next-day Cl radical generation and its positive feedback on $O_3$ formation. Considering NO*x* reduction during the daytime would cause $O_3$ formation and only a slight reduction in $pNO_3^-$, it is preferable to regulate NO*x* at night (18:00–06:00 the next day). Our findings demonstrate that in $NO_2$-limited regions, targeted NO*x* reduction can synergistically decrease both $pNO_3^-$ and $O_3$ concentrations, highlighting the critical need to tailor mitigation strategies for different regions.

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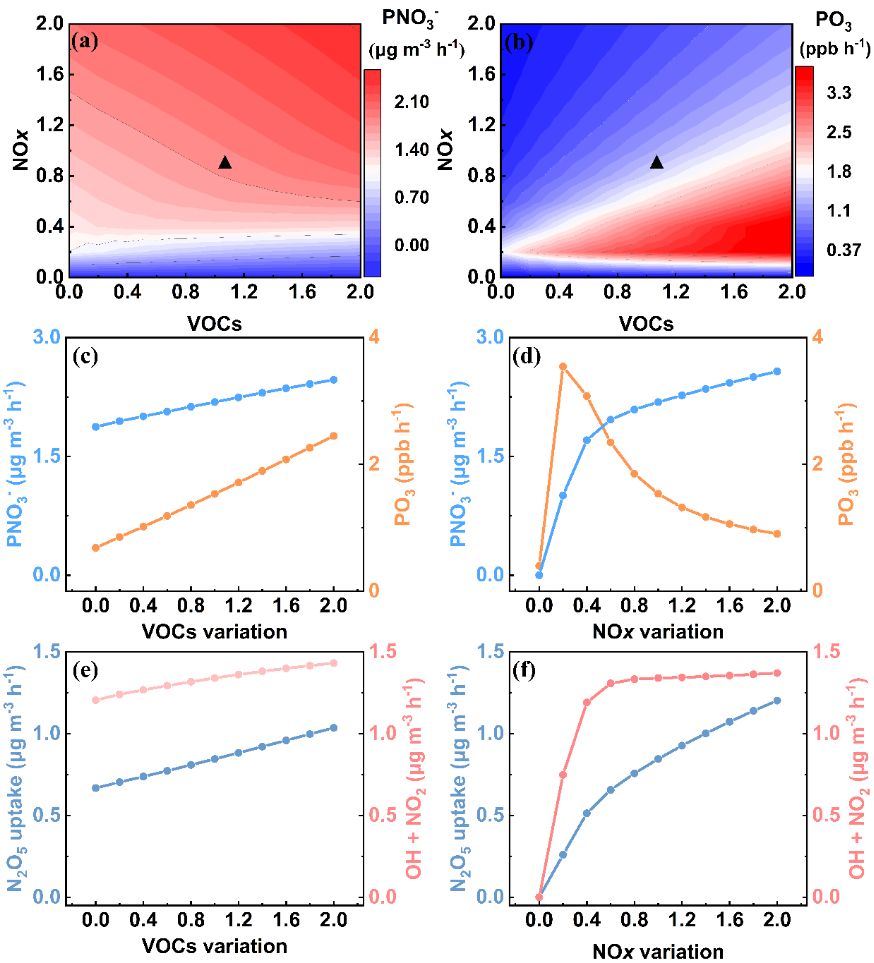


**Figure 6.** Results of multi-scenario simulations obtained from an observation-constrained box model. Isopleths of simulated PNO$_3^-$ **(a)** and PO$_3$ **(b)** with normalized VOCs and NO*x***.** Simulated mean formation rates of pNO$_3^-$ and O$_3$ **(c, d)**, as well as pNO$_3^-$ formation rates via $N_2O_5$ uptake and OH + $NO_2$ **(e, f)** with normalized VOCs and NO*x*. The PNO$_3^-$ and PO$_3$ denote the formation rates of pNO$_3^-$ and O$_3$, respectively. The simulated results are daily mean values, and the black triangle indicates the base case for winter 2022. In addition, the results in panel c-f were obtained by maintaining either NO*x* or VOCs at the base emission rate while varying the other.

## Conclusions and Implications

Our observations revealed a bimodal diurnal pattern of pNO$_3^-$ in winter in urban Xiamen. The cooccurrence of elevated nighttime $pNO_3^-$ levels with increased $N_2O_5$ implied a significant contribution of $N_2O_5$ uptake to $pNO_3^-$ formation. Quantitative model analysis showed that $N_2O_5$ uptake contributed 51.2% of the total daily $pNO_3^-$, which was comparable to the OH + $NO_2$ reaction. This high contribution of $N_2O_5$ uptake is not commonly observed across Chinese cities. Comparative analysis among different cities suggests that this phenomenon is likely associated with $NO_2$-limited conditions for $N_2O_5$ uptake in our study area. Machine learning results further demonstrated that $N_2O_5$ uptake was driven by nocturnal atmospheric oxidation capacity ($PNO_3$) rather than heterogeneous uptake conditions. The underlying mechanism is that the weakened NO*x* titration effects lead to nighttime $O_3$ accumulation, which promotes $NO_3$ radical generation and consequently enhances $N_2O_5$ and $pNO_3^-$ formation. The joint response of $pNO_3^-$ and $O_3$ to various NO*x* and VOCs emission scenarios indicated that $pNO_3^-$ was more sensitive to NO*x* reduction than to VOCs reduction. However, mild NO*x* reduction showed limited effectiveness in reducing daytime $pNO_3^-$ while simultaneously increasing $O_3$ concentrations. Our findings suggest that NO*x* reduction is more effective when implemented during nighttime, particularly in regions where $N_2O_5$ formation is $NO_2$-limited. This approach can effectively control $pNO_3^-$ formation by suppressing nocturnal $NO_3$ radical generation and consequently inhibiting $N_2O_5$ uptake, while simultaneously alleviate $O_3$ pollution by reducing $ClNO_2$ formation. With continuous NO*x* and VOCs emission reductions and renewable energy adoption in China, urban areas are transitioning from NO*x*-saturated to NO*x*-limited conditions, potentially increasing the importance of $N_2O_5$ uptake. In this context, comprehensive assessment of NO*x* reduction impacts on urban $pNO_3^-$ and $O_3$ pollution, along with the development of region-specific mitigation strategies, becomes critically important.

**Data Availability**

The dataset for this paper can be accessed at https://doi.org/10.6084/m9.figshare.29670629 (Lin et al., 2025).

**Code Availability**

Data analysis methods are available from the authors upon request.

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**Author Contribution**

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

**Competing interests**

The authors declare no competing interests.

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