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Key Points:

- Nocturnal pNO_3^- formation via N_2O_5 hydrolysis is dependent on the regime defined by the ratio of NO_2 to O_3
- Nocturnal pNO_3^- formation via N_2O_5 hydrolysis in the residual layer over megacity Beijing is more efficient than at ground level
- Nocturnal pNO_3^- formation via N_2O_5 hydrolysis is suppressed in an O_3-limited regime but enhanced in a NO_2-limited regime

Supporting Information:

Supporting Information may be found in the online version of this article.

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Regime-Dependence of Nocturnal Nitrate Formation via N_2O_5 Hydrolysis and Its Implication for Mitigating Nitrate Pollution

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Abstract The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) is an important pathway in nitrate formation; however, its formation rate and relative contribution to total particulate nitrate (pNO_3^-) are highly variable. Here we report that nocturnal pNO_3^- formation via N_2O_5 hydrolysis is dependent on the regime defined by the ratio of NO_2 to O_3. Nocturnal pNO_3^- formation via N_2O_5 hydrolysis is suppressed in an O_3-limited regime but enhanced in a NO_2-limited regime. The results have crucial implications for effective control of nitrate pollution in the future. An exclusive decrease in NO_2 will decrease nocturnal pNO_3^- formation in a NO_2-limited regime but may be less effective or even increase nocturnal pNO_3^- formation in an O_3-limited regime.

Plain Language Summary Our observations show that nocturnal pNO_3^- formation via dinitrogen pentoxide (N_2O_5) hydrolysis in the residual layer over megacity Beijing is more efficient than at ground level. Further investigations suggest nocturnal pNO_3^- formation via N_2O_5 hydrolysis is dependent on the regime defined by the ratio of NO_2 to O_3. Nocturnal pNO_3^- formation via N_2O_5 hydrolysis is suppressed in an O_3-limited regime but enhanced in a NO_2-limited regime. As a result, an exclusive decrease in NO_2 will decrease nocturnal pNO_3^- formation in a NO_2-limited regime but may be less effective or even increase nocturnal pNO_3^- formation in an O_3-limited regime. The above result is also substantiated by observations during the COVID-19.

1. Introduction

Particulate nitrate (pNO_3^-) is a major component of fine particles in urban regions (Baasandorj et al., 2017; Hoesly et al., 2018; McDuffie et al., 2019; Peng et al., 2021; Zheng et al., 2016). Nocturnal N_2O_5 hydrolysis represents an important pathway of nitrate formation (Brown & Stutz, 2012; McDuffie et al., 2019; Seinfeld & Pandis, 2006; Zhang et al., 2015). Since the short lifetime of its precursor, NO_3, against photolysis and reaction with NO prevents buildup of appreciable N_2O_5 mixing ratios during daytime (Brown et al., 2006), high N_2O_5 mixing ratios and N_2O_5 hydrolysis occur mainly at night. Compared to the relatively well-understood formation of nitrate via the gas-phase oxidation (OH + NO_2), our understanding of N_2O_5 hydrolysis remains elusive and the relative contribution from the N_2O_5 hydrolysis on pNO_3^- is widely divergent in the literature, still lacking a comprehensive explanation. For example, some studies suggest that nocturnal heterogeneous chemistry outweighs the gas-phase oxidation pathway (Fan et al., 2021; Pathak et al., 2011; Prabhakar et al., 2017; Wang, Lu, et al., 2017; Yun et al., 2018), whereas others suggest that the gas-phase oxidation is dominant over the nocturnal N_2O_5 hydrolysis reactions (Chen et al., 2020; Kuprov et al., 2014; Womack et al., 2019). These differences reflect in regional, seasonal, and even vertical aspects. For example, the relative contribution of N_2O_5 hydrolysis reactions in summer and winter exhibit opposite trends in literature (Chen et al., 2020; Kenagy et al., 2018; Pathak et al., 2011). Furthermore, high concentrations of NO_3 and N_2O_5 in the residual layer (RL) are observed in some experiments (Wang et al., 2018; Yan et al., 2021), suggesting nocturnal nitrate formation in the RL may be

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enhanced despite low NO_x in this layer. The RL locates above the nocturnal stable boundary layer (SBL), which forms with radiative cooling of the ground after sunset.

N_2O_5 formation depends on both NO_x and O_3, while the latter is nonlinearly sensitive to NO_x and volatile organic compound (VOC) (Sillman & He, 2002). The O_3 formation rate or yield may either increase or decrease with increasing NO_x, depending on the VOC concentration and composition. In a NO_x-limited regime of O_3 formation, NO is oxidized dominantly by HO_2 and RO_2 to form NO_2, which then enhances O_3 formation through photolysis (Atkinson, 2000; Sillman & West, 2009). Hence, an increase in NO emission will enhance both NO_2 and O_3, which further enhances nocturnal pNO_3^- formation via N_2O_5 hydrolysis. While in a VOC-limited regime, the consumption of radicals by excess NO_x limits O_3 formation. Furthermore, photolytic production of radicals and O_3 halts at night, and excess NO titrates the O_3 to NO_2. As a result, an increase in NO emission enhances NO_2 but decreases O_3, which may suppress nocturnal pNO_3^- formation. Therefore, the nocturnal pNO_3^- formation via N_2O_5 hydrolysis may also be regime-dependent, affected by O_3 formation sensitivity. In order to address this issue, the dependence of nocturnal pNO_3^- formation on its precursors is investigated in this work. We show, based on continuous observations and model simulations, that nocturnal pNO_3^- formation via N_2O_5 hydrolysis can be divided into NO_2-limited, O_3-limited and transition regimes based on the ratio of NO_2 to O_3, which is pertinent to understanding nocturnal pNO_3^- formation, and has crucial implications for mitigating pNO_3^- pollution.

2. Methods and Measurements

The comprehensive field campaign was conducted at the CITIC station and the BUCT station from October 17 to 12 November 2020. The BUCT station is located on the top floor of a five-story building (18 m above ground) with inlet lines going through the ceiling, which is used to represent observations near ground level, and the CITIC station is located on the roof of CITIC Tower with a height of 528 m above the ground. The measurements included aerosol composition (SO_4^{2-}, NO_3^-, NH_4^+, Chl^-, and organic aerosols (OA)) by a Time-of-Flight aerosol chemical speciation monitor (ToF-ACSM), trace gases (SO_2, NO_x, CO, O_3), and meteorological variables. Radiosondes was used in boundary layer analysis, which was operated at the Guanxiangtai (GXT) meteorological station. To understand the dependence of N_2O_5 on its precursors, observations of N_2O_5 by a high-resolution Time-of-Flight chemical ionization mass spectrometer using iodide as the reagent ion (I-CIMS), $PM_{2.5}$, trace gases (NO_x, O_3), and meteorological variables were conducted at the BUCT station from 1 to 31 October 2021. The locations of the stations are illustrated in Figure S1 in Supporting Information S1and the details of the measurements are described in Supporting Information S1. Observations from 17 October to 12 November 2020 at the CITIC station and the BUCT station are shown in Figure S2 in Supporting Information S1. Nitrogen chemistry and calculation of the formation rate of pNO_3^- through the N_2O_5 heterogeneous reactions are described in Supporting Information S1.

3. Results and Discussion

3.1. Efficient Nocturnal pNO_3^- Formation in the RL

The time series of $PM_{2.5}$ chemical compositions, NO_x, and O_3, at the CITIC (China International Trust and Investment Corporation, 528 m above ground) and the BUCT (Beijing University of Chemical Technology, 18 m above ground) stations from 17 October to 12 November 2020, are shown in Figure S2 in Supporting Information S1. The observations indicated that nitrate was a dominant component in non-refractory $PM_{2.5}$ (NR-$PM_{2.5}$) (Figures S2a and S2b in Supporting Information S1) at both the BUCT and CITIC stations. In polluted episodes, nitrate increased rapidly, with an increasing rate of 0.3–2.4 μg m^{-3} h^{-1} at the BUCT station, and 0.8–2.1 μg m^{-3} h^{-1} at the CITIC station. The mass fraction of nitrate in NR-$PM_{2.5}$ increased from 17.8 ± 10.2% in clean episodes to 40.8 ± 11.7% in polluted episodes at the CITIC station, and from 24.7 ± 11.8% to 45.1 ± 10.2% at the BUCT station, respectively. The clean and polluted groups are defined based on the $PM_{2.5}$ mass concentration of <35 μg m^{-3} and ≥35 μg m^{-3}, respectively. Although nitrate mass concentration at the CITIC station was consistent with that at the BUCT station, its precursor gases, NO_x (NO + NO_2), at the CITIC station was much lower than that at the BUCT station (Figures S2c and S2d in Supporting Information S1), suggesting that the nitrate formation might be enhanced at the CITIC station. Moreover, striking differences existed in the diurnal variation of pNO_3^- and NO_x between the two stations (Figure 1). The mass concentration of pNO_3^- increased at night at the CITIC station with maximum pNO_3^- appeared in the early morning (11.0 μg m^{-3}, 04:00 LST), while at the

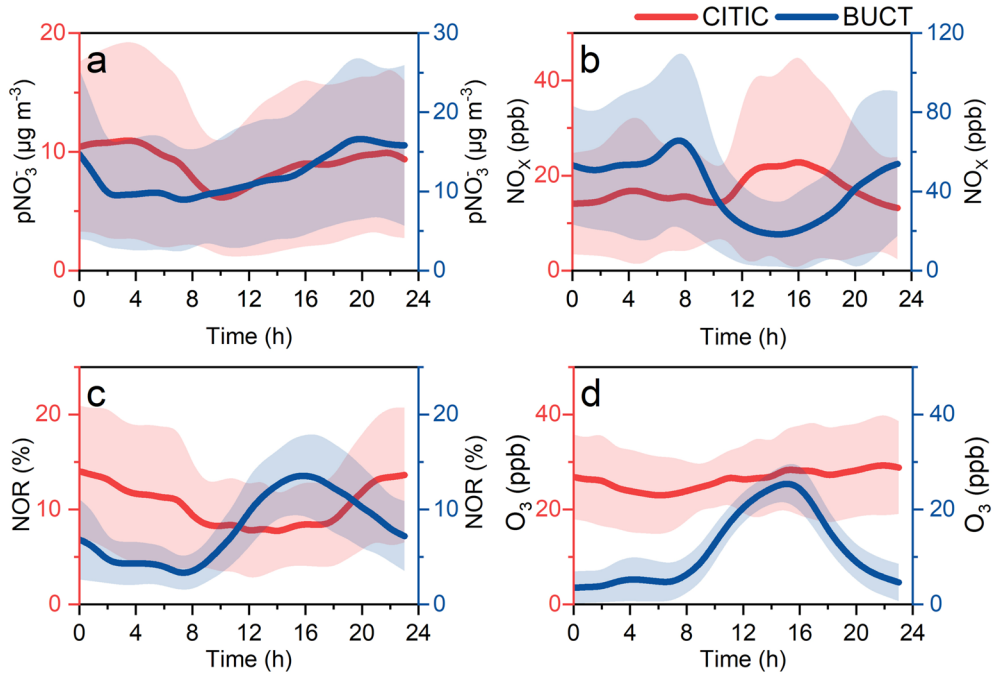

Figure 1. Diurnal variations of pNO_3^- mass concentrations, NO_x, O_3, and NOR from October 17 to 12 November 2020, at the CITIC (red) and BUCT (blue) stations, respectively. The shaded areas denote standard deviation. The NOR is defined as the mole ratio of particle phase of nitrogen (pNO_3^-) to total nitrogen (both pNO_3^- and NO_x).

BUCT station pNO_3^- decreased at night with maximum pNO_3^- appeared at early night (16.7 μg m^{-3}, 20:00 LST). Conversely, the maximum NO_x appeared in the daytime at the CITIC station, but at night at the BUCT station. As a result, the maximum of the nitrogen oxidation ratio (NOR), that is, the mole ratio of particle phase of nitrogen (pNO_3^-) to total nitrogen (both pNO_3^- and NO_x), appeared at night at the CITIC station but in the daytime at the BUCT station. The averaged NOR during nighttime (18:00–06:00) was 12.2 ± 13.5% at the CITIC, which was higher than that at the BUCT station (7.1 ± 7.4%) by 70.9%. While in the daytime (07:00–17:00), the NOR at the CITIC (8.5 ± 9.8%) was consistent with that at the BUCT station (9.0 ± 7.7%). These observations substantiated that the nocturnal pNO_3^- production at the CITIC station was more efficient than at the BUCT station.

Combined analyses of boundary layer height and pollutants, indicate that vertical transport of pollutants from ground to the RL at night is significantly weakened. After sunset, the stable boundary layer (SBL) forms with radiative cooling of the ground and the daytime convective boundary layer (CBL) separates into SBL and RL (Stull, 1988). The decoupling between RL and SBL substantially weakens the vertical turbulent mixing of pollutants between the two layers. The RL largely maintains the atmospheric chemical state of the daytime CBL while the pollutants emitted near ground at night are trapped in the shallow SBL. An analysis of the boundary layer structure indicates that the CITIC station was located inside the RL at night while the BUCT station was located inside the SBL. The SBL height was usually lower than 300 m during the campaign based on radiosonde data at 08:00 and 20:00 LST (40 in 52 cases, Table S1 in Supporting Information S1). The contrary trends of NO_x in the CITIC and BUCT stations from 18:00 to 24:00 substantiated these analyses (Figure 1b). For example, NO_x increased at the BUCT station from 27.1 ± 27.1 ppb to 53.9 ± 30.0 ppb, but decreased from 20.9 ± 18.2 ppb to 13.2 ± 10.7 ppb at the CITIC station. The above analyses collectively indicate that high concentration of pNO_3^- in the RL at night is due mainly to efficient nocturnal pNO_3^- formation in the RL, rather than vertical transport from ground level, and it is important to investigate the mechanisms underlying this difference between the two layers.

3.2. Regimes in Nocturnal pNO_3^- Formation

N_2O_5 hydrolysis is the dominant pathway of nocturnal pNO_3^- formation (Brown et al., 2006; Zhang et al., 2015). Primary emission of NO reacts with HO_2/RO_2/O_3 to form NO_2. The reaction of NO_2 with O_3 produces the NO_3 radical, which further reacts with NO_2 to yield N_2O_5 (Seinfeld & Pandis, 2006). The heterogeneous uptake of

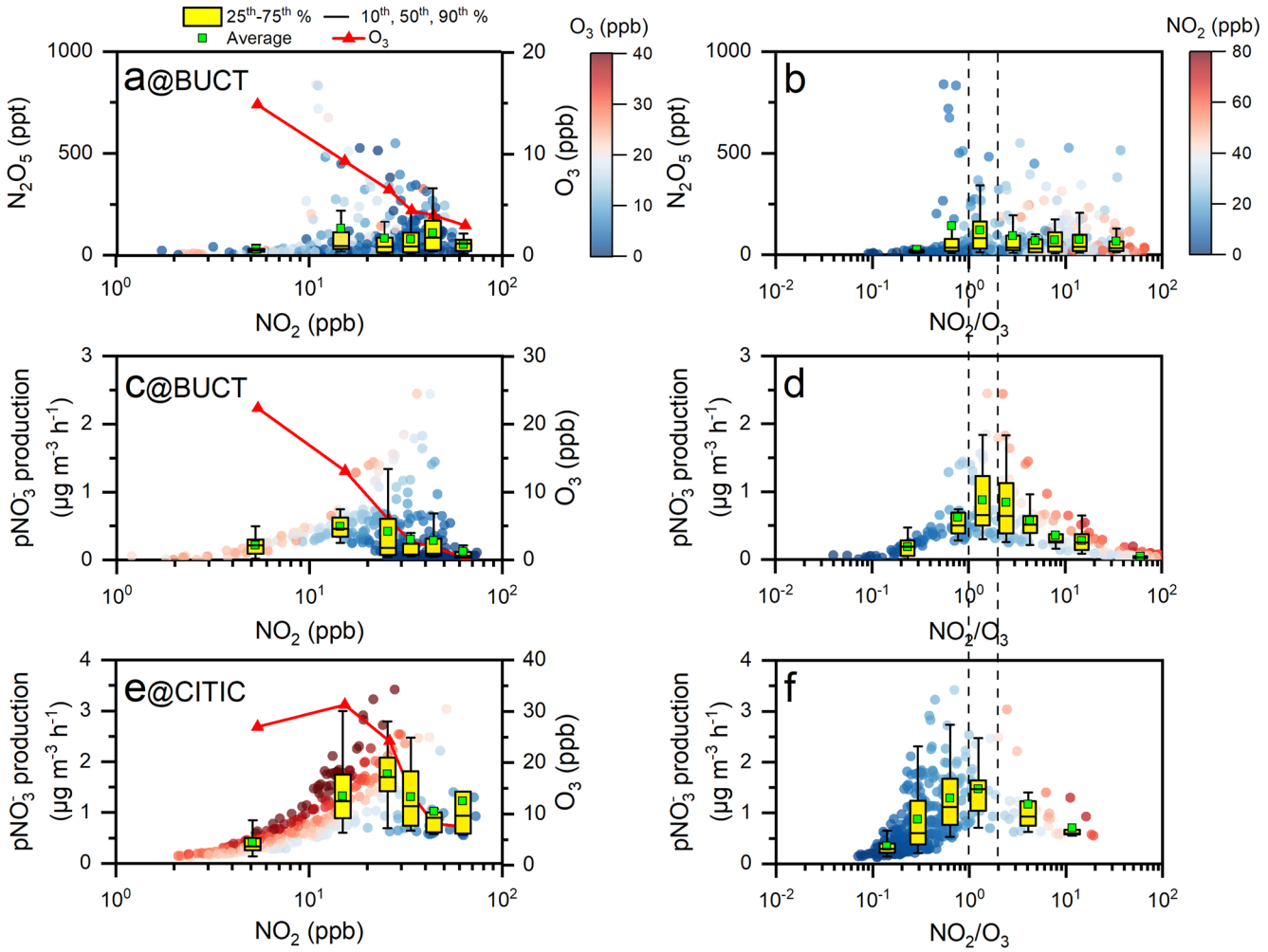

Figure 2. Relationships of the observed nocturnal N_2O_5 to NO_2 (a) and NO_2/O_3 (b) at the BUCT station during 1–31 October 2021, and the simulated pNO_3^- via N_2O_5 hydrolysis to NO_2 (c, e) and NO_2/O_3 (d, f) at the BUCT and CITIC stations, respectively, from 17 October to 12 November 2020. The dashed lines represent fixed value of NO_2/O_3 of 1 and 2, respectively. Box and whisker plots show the 10th–90th percentile distributions of each bins, which are [0–10), [10–20), [20–30), [30–40), [40–50), [50–70) ppb for NO_2 (a, c, e), and [0–0.5), [0.5–1), [1–2), [2–4), [4–6), [6–10), [10–20), [20–100) for NO_2/O_3 (b, d, f). The red triangles show averaged O_3 in each bin.

N_2O_5 on and within aerosol particles or fog/cloud droplets produces soluble nitrate. In spite of the well-known net reaction (i.e., $N_2O_5 + H_2O \rightarrow 2HNO_3$), the actual efficiency of N_2O_5 hydrolysis is variable and difficult to quantify (McDuffie et al., 2018). This section investigates the complex relationships of nocturnal pNO_3^- formation to its precursors by both observations and model simulations.

The observational results show that the key nocturnal nitrogen species, N_2O_5, measured with an iodide-based chemical ionization mass spectrometer at the BUCT station on 1–31 October 2021 (see Methods and extended data shown in Figure S5 in Supporting Information S1), exhibited a nonlinear relationship with NO_2. The N_2O_5-NO_x relationship exhibited a sign change from positive under low NO_2 to negative under high NO_2 concentration though with small fluctuations (Figure 2a). N_2O_5 first increases with increasing NO_2, reaches its maximum when NO_2 ranges from 10 to 20 ppb, and then decreases slightly with a further increase in NO_2, likely caused by decreased O_3. The relationship between N_2O_5 and the ratio of NO_2 to O_3 (NO_2/O_3) supports the above analyses, that is, high N_2O_5 appears under a moderate NO_2/O_3 (Figure 2b).

Simulations with a box model developed by Wagner et al. (2013) further support the observational result that the nocturnal formation rate of pNO_3^- is closely related to NO_2/O_3 (Figures 2c–2f). Detailed description of the model and simulation setup is provided in Supporting Information S1. The simulations indicate that an increase in

NO_2 enhances nocturnal pNO_3^- formation under a fixed O_3 level (Figures 2c and 2e). Whereas, nocturnal pNO_3^- formation is suppressed with a further increase in NO_2 after the latter exceeds a certain threshold value, likely caused by a fast decrease in O_3. The relationship of nocturnal pNO_3^- formation rate to NO_2/O_3 indicates that a maximum nocturnal pNO_3^- formation occurs in a moderate NO_2/O_3, ranging from 1 to 2, at both the CITIC and BUCT stations (Figures 2d and 2f).

Photochemical O_3 production in Beijing near ground is often in a VOC-limited regime (Lu et al., 2010; Wang, Xue, et al., 2017). This means that high NO_x concentration strongly inhibits O_3 formation. Recent observations indicate that the ratio of VOCs to NO_x increased with altitude (Tang et al., 2021), suggesting a change from a VOC-limited regime in O_3 formation near ground to a NO_x-limited regime at higher elevation (Chen et al., 2020; Lu et al., 2010; Tang et al., 2021; Wagner et al., 2013; Wang et al., 2018). In our observations, the O_x ($NO_2 + O_3$) are similar between CITIC and BUCT stations, but a high ratio of NO to NO_x (0.4–0.7) at night at the BUCT station, suggested that NO titration was mainly responsible for the sharp O_3 drop near ground at night (Figure S7a in Supporting Information S1), resulting in a negative relationship between O_3 and NO_x near ground (Figure S7b in Supporting Information S1). In a VOC-limited environment of O_3 formation, the O_3 near ground is very low at night due to NO_x suppression of O_3 production during the previous day and NO titration at night. The averaged nocturnal (18:00–06:00) O_3 was 7.0 ± 8.5 ppb from 17 October to 12 November 2020. High NO_2 (30.0 ± 15.7 ppb) and low O_3 result in high NO_2/O_3 (4.3). On the contrary, in the RL with a NO_x-limited environment, the nocturnal NO_2/O_3 is much lower than that near ground. The averaged nocturnal O_3 and NO_2 were 26.5 ± 9.5 and 13.1 ± 12.1 ppb, respectively, with the NO_2/O_3 of 0.49 during the same period. As a result, the modeled nocturnal pNO_3^- formation in the RL (0.82 μg m^{-3} h^{-1}) was much higher than that near ground (0.28 μg m^{-3} h^{-1}) though the nocturnal NO_2 in the RL was much lower than that near ground. These analyses suggest that nocturnal pNO_3^- formation depends not only on its precursor (NO_x) but also strongly on NO_2/O_3.

Based on R4 and R7 (in Supporting Information S1), one O_3 molecule reacts with two NO_2 molecules to form N_2O_5. Hence, NO_2 will be in excess if the NO_2/O_3 is higher than 2. The rate limiting step for this reaction (R4) is very slow. There is a separate, faster rate constant for titration of O_3 by NO (R1), which occurs in a 1:1 ratio of NO_x and O_3. Thus the initial O_x partitioning between NO_2 and O_3 has a 1:1 stoichiometry, and O_3 will be in excess if the ratio of NO_x (either emitted at the surface or remaining in the residual layer) to initial (late day) O_3 is lower than 1. Hence, the NO_2/O_3 of 1 and 2 can be used to identify whether O_3 or NO_2 is in excess, respectively, in N_2O_5 and hence pNO_3^- formation, where values below 1 or above 2 result in NO_x or O_3 limitations, respectively. The dependence of both observed N_2O_5 and simulated pNO_3^- formation rate on NO_2/O_3 supports the theoretical analyses. Efficient pNO_3^- formation will occur with a moderate NO_2/O_3 ranging 1–2 (Figure 2). Based on the above analyses, the nocturnal pNO_3^- formation via N_2O_5 hydrolysis is divided into three regimes based on NO_2/O_3: an O_3-limited regime ($NO_2/O_3 > 2$), a NO_2-limited regime ($NO_2/O_3 \leq 1$), and a transition regime ($2 \geq NO_2/O_3 > 1$). We plot the relationship of modeled nocturnal pNO_3^- formation to NO_2 and O_3 based on data at the CITIC and BUCT stations from 17 October to 12 November 2020 (Figure 3), which clearly shows the regimes in nocturnal pNO_3^- formation. As analyzed above, nocturnal pNO_3^- formation at the BUCT station was in an O_3-limited regime from 17 October to 12 November 2020, with averaged nocturnal NO_2/O_3 of 4.3. An increase in NO_2 from 22.4 ± 11.4 ppb in clean episodes to 43.5 ± 13.0 ppb in polluted episodes, accompanied by a sharp decrease in O_3 from 8.8 ± 8.8 ppb to 3.8 ± 7.0 ppb, results only in a slight increase in nocturnal pNO_3^- formation from 0.27 to 0.31 μg m^{-3} h^{-1}, with the $\Delta pNO_3^-/\Delta NO_2$ of 0.0017 μg m^{-3} h^{-1} ppb^{-1}. On the other hand, nocturnal pNO_3^- formation at the CITIC station was in a NO_2-limited regime with averaged nocturnal NO_2/O_3 of 0.49 during the same period. An increase in NO_2 from 7.4 ± 4.4 ppb in clean episodes to 23.3 ± 14.7 ppb in polluted episodes, accompanied by a slight increase in O_3 from 26.1 ± 5.7 to 27.0 ± 13.8 ppb, results in a significant increase in nocturnal pNO_3^- formation from 0.51 to 1.36 μg m^{-3} h^{-1} (Figure 3), with the $\Delta pNO_3^-/\Delta NO_2$ of 0.053 μg m^{-3} h^{-1} ppb^{-1}. These analyses indicate that the nocturnal pNO_3^- formation strongly depends on the regimes as defined by NO_2/O_3; nocturnal pNO_3^- formation is suppressed in the O_3-limited regime while enhanced in the NO_2-limited regime. Sensitivity analysis further reveals that nocturnal pNO_3^- formation near ground will increase from 0.28 to 1.9 μg m^{-3} h^{-1} if the corresponding O_3 increases from 7.0 to 26.2 ppb, same as in the RL, while other pollutants (e.g., NO_x and $PM_{2.5}$) and meteorological variables (e.g., T and RH) remain unchanged, further confirming that the nocturnal pNO_3^- formation at ground level is strongly suppressed in an O_3-limited environment.

To understand the relative contribution of N_2O_5 hydrolysis to pNO_3^- formation, we also simulate the pNO_3^- formation via gas-phase oxidation (OH + NO_2) (see Supporting Information S1). The result indicates that the

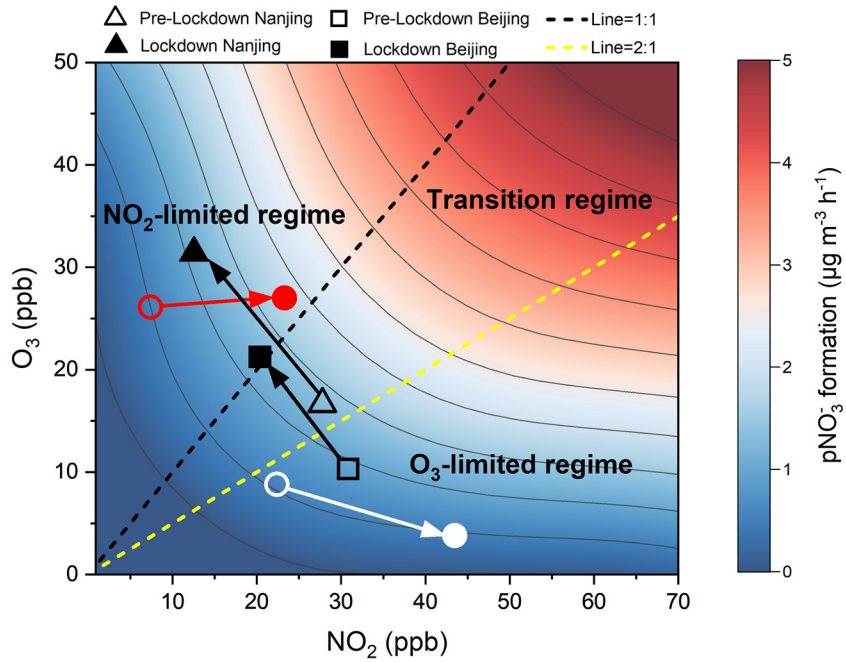

Figure 3. Sensitivity of the pNO_3^- formation via N_2O_5 hydrolysis to O_3 and NO_2, with the data at CITIC and BUCT from 17 October to 12 November 2020 (same as Figures 2c–2f). The red and white circles represent averaged O_3 and NO_2 at the CITIC and BUCT stations in clean (hollow) and polluted episodes (solid), respectively. The hollow and solid squares represent Beijing during Pre-lockdown and Lockdown, and the hollow and solid triangles represent Nanjing during Pre-lockdown and Lockdown.

rate of pNO_3^- formation via gas-phase oxidation between the two stations was very similar (with averaged 1.43 and 1.45 μg m^{-3} h^{-1} at the CITIC and BUCT station for the entire study period, respectively), suggesting that the N_2O_5 hydrolysis contributes 40.5% in total nitrate formation at the CITIC station from 17 October to 12 November 2020, which was much higher than the 18.9% at the BUCT station. Such differences were more evident in polluted episodes than in clean episodes. In clean episodes, the N_2O_5 hydrolysis contributed 18.1% and 29.5% in total nitrate formation at the BUCT and CITIC stations, respectively; while in polluted episodes its contribution was 20.3% and 54.2% at the BUCT and CITIC stations, respectively. The NO_2-limited regime in the RL favors efficient nocturnal pNO_3^- formation, which well explained the higher nocturnal NOR in the RL in observations, rather than near ground (Figure 1c). In the calculation, the steady-state assumption of NO_3 and N_2O_5 may not hold if there is strong NO emission nearby, especially at ground level with large on-road traffic volume. While in the residual layer, NO_3 and N_2O_5 were likely in a steady state since there has not fresh NO emission the residual layer. As a result, the calculation of nocturnal nitrate formation in the residual layer is less affected while the calculation at ground level may be overestimated.

The different regimes between the ground level and RL influence the overall vertical distribution of pNO_3^- and other pollutants. Also influence the vertical transport of nitrate and its precursors. The weakened nocturnal pNO_3^- formation at ground due to O_3-limited regime may enhance NO_x accumulation at night. As a result, more NO_x is upwards transported to high layer next morning and stores in the RL, where NO_x is converted to pNO_3^- efficiently via N_2O_5 hydrolysis at night. The pNO_3^- formed in the RL at night may be entrained downward to ground level in the following morning through convective mixing and deteriorates air pollution near the ground (Pathak et al., 2011). Hence, the nocturnal pNO_3^- formation in the RL is an important source of pNO_3^- and should be considered in evaluating the source of pNO_3^- in the troposphere, including at surface level.

3.3. Implication for Future pNO_3^- Control

An analysis of the ratio of nocturnal NO_2 to O_3 in China, based on observations at 2024 stations during 2015–2021 (CNEMC, 2023), shows that the regime of nocturnal pNO_3^- formation exhibits obvious regional and seasonal variations (Figure S8 in Supporting Information S1). In summer and spring, most regions in China lies in the

NO_2-limited regime; while the situation is more complicated in autumn and winter, with some regions (e.g., North China Plain (NCP), Guanzhong Basin, and Chengdu-Chongqing Zone) transitioning to the O_3-limited regime. Such regime variations well explain the variations in nocturnal nitrate formation rate via N_2O_5 hydrolysis estimated in previous studies for different regions and seasons, for example, higher formation rate in south China (Yang et al., 2022; Yun et al., 2018) than north China (Chen et al., 2020), in summer (Pathak et al., 2011; Tan et al., 2021) than in winter (Chen et al., 2020). This general explainability further reinforces our proposal that nocturnal pNO_3^- formation via N_2O_5 hydrolysis is highly regime-dependent.

Reducing NO_x emission from traffic sectors has long been considered as a normal protocol in implementing regulatory policies (Guo et al., 2016). Based on this study, the nocturnal pNO_3^- formation via N_2O_5 hydrolysis depends strongly on the regimes as defined by the ratio of NO_2 to O_3. Hence, the regime behavior should be considered in pNO_3^- control. The outbreak of COVID-19 provides an exceptionally unique opportunity to assess the responses of nitrate chemistry to NO_x reduction under different regimes. To control the COVID-19 pandemic, a lockdown was imposed, during which a dramatic reduction in NO_x concentration was observed worldwide (Cooper et al., 2022; Miyazaki et al., 2021; Shi et al., 2021; Venter et al., 2020). In China, NO_x concentration decreased by up to 93% during the Lockdown period (Huang & Sun, 2020; Le et al., 2020; Shi & Brasseur, 2020). However, such a sharp decrease in NO_x did not result in a clear decrease in $PM_{2.5}$. A possible explanation is that a decrease in NO_x resulted in O_3 enhancement, which strengthened the atmospheric oxidizing capacity and facilitated secondary aerosol formation (Huang et al., 2021; Le et al., 2020; Li et al., 2022). Even more surprising is that both the mass concentration of nitrate and its mass fraction in $PM_{2.5}$ during the Lockdown period exhibited opposite changes between south and north China despite similar sharp decrease in NO_x emission, an increase in north China (e.g. Beijing) but a decrease in south China (e.g. Nanjing) (Ren et al., 2021).

To understand the regime effect on nitrate control, nocturnal pNO_3^- formation during Pre-Lockdown (1 to 22 January 2020) and Lockdown period (23 January to 15 February 2020) is also simulated with the box model developed by Wagner et al. (2013) (Figure 4). As shown in Figure S8 in Supporting Information S1, nocturnal pNO_3^- formation in north China is under an O_3-limited regime in winter, but under NO_2-limited or transition regime in south China. Beijing and Nanjing are selected to represent north and south China, respectively. The nocturnal NO_2/O_3 were 3.0 and 1.7 at Beijing and Nanjing, respectively, during the Pre-lockdown, indicating a typical O_3-limited regime at Beijing, but a transition regime at Nanjing. Nocturnal NO_x in Beijing decreased from 51.1 ± 42.2 ppb during the Pre-Lockdown to 21.5 ± 14.7 ppb during the Lockdown, among which NO decreased sharply from 20.3 ± 32.4 to 1.2 ± 3.0 ppb with a decreasing rate of 94.3%, indicating that O_3 depletion due to NO titration was sharply weakened during the Lockdown. As a result, O_3 increased from 10.3 ± 11.1 to 21.3 ± 13.1 ppb and the NO_2/O_3 decreased to 0.96 during the Lockdown, suggesting a conversion from O_3-limited regime during the Pre-Lockdown to NO_2-limited regime during the Lockdown. As a result, the nocturnal pNO_3^- formation via N_2O_5 hydrolysis increased from 0.37 μg m^{-3} h^{-1} during the Pre-Lockdown to 0.74 μg m^{-3} h^{-1} during the Lockdown though NO_x decreased by 56.1%. By contrast, nocturnal NO_x in Nanjing decreased from 34.5 ± 23.7 ppb during the Pre-Lockdown to 12.9 ± 6.9 ppb during the Lockdown, among which NO also decreased sharply from 6.7 ± 17.1 ppb to 0.36 ± 1.8 ppb. As a result, O_3 increased from 16.6 ± 13.3 ppb to 31.4 ± 13.0 ppb and the NO_2/O_3 further decreased to 0.4 during the Lockdown, suggesting a conversion from transition regime during the Pre-Lockdown to NO_2-limited regime. Contrary to Beijing, the nocturnal pNO_3^- formation in Nanjing decreased from 0.90 μg m^{-3} h^{-1} during the Pre-Lockdown to 0.78 μg m^{-3} h^{-1} during the Lockdown, with a decreasing rate of 13.2%. The above results are consistent with the opposite trends of pNO_3^- mass concentration from the Pre-Lockdown to the Lockdown in the two cities in observations (Ren et al., 2021). The contrary trends in nocturnal pNO_3^- formation between Beijing and Nanjing under similar NO_x decrease confirm the analysis in this paper that the nocturnal pNO_3^- formation is strongly regime-dependent; a decrease in NO_2 will decrease nocturnal pNO_3^- in a NO_2-limited or transition regime, but will be less effective or even increase nocturnal pNO_3^- in an O_3-limited regime (Figure 3). It is noteworthy that only nocturnal pNO_3^- formation via N_2O_5 hydrolysis in response to changing NO_x emissions were investigated in this work, while daytime nitrate formation, gas-particle partitioning, and particulate nitrate lifetime also need to be considered when determining how particulate nitrate concentrations would change in response to changing emissions (Zhai et al., 2021).

4. Summary

Nitrate is a major component of fine particles in cities and mitigation strategies have been normally focused on NO_x control. This study suggests that nocturnal pNO_3^- formation via N_2O_5 hydrolysis depends on the regime

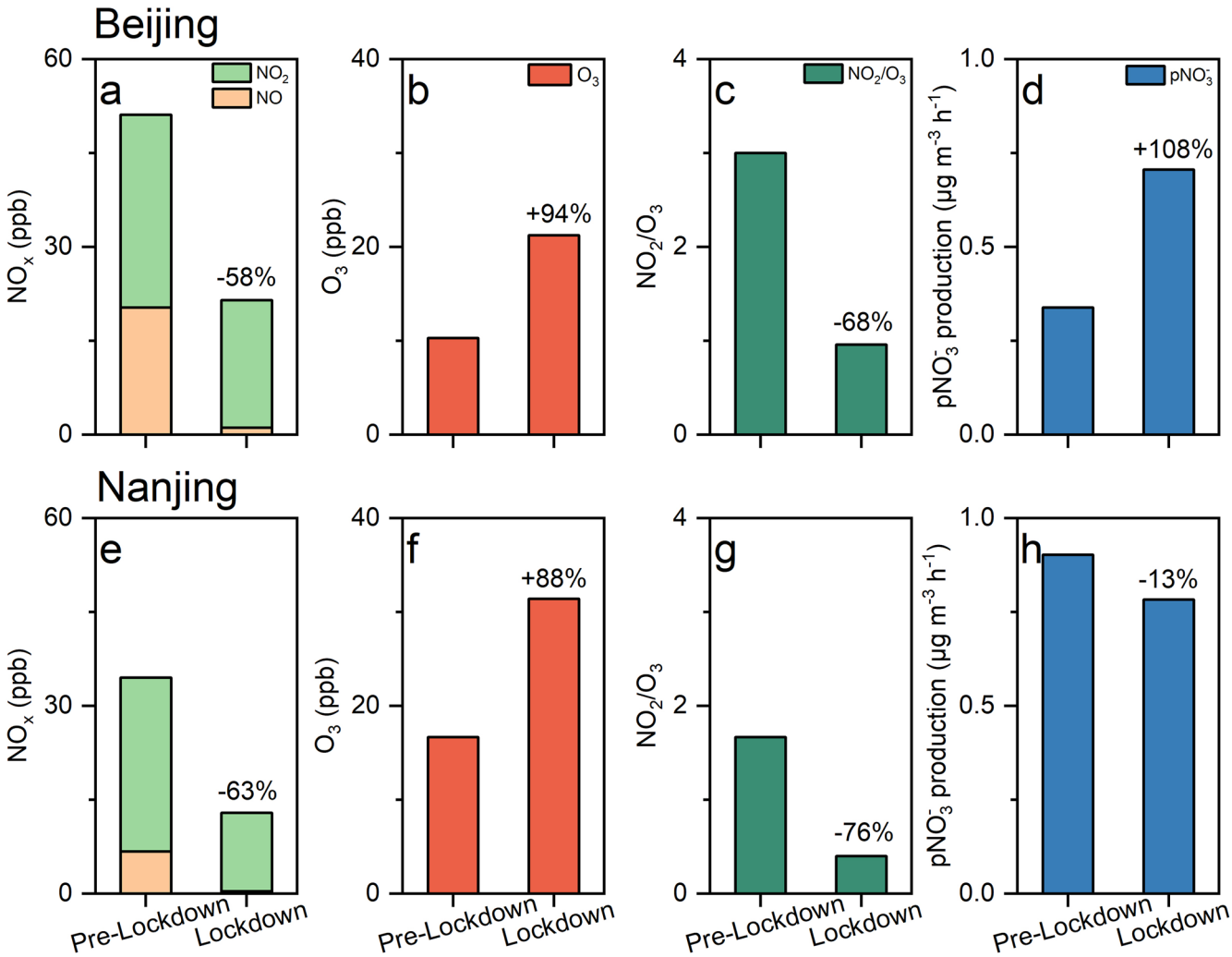

Figure 4. Variations in NO_x, O_3, NO_2/O_3, and pNO_3^- formation via N_2O_5 hydrolysis in Beijing (upper panel) and Nanjing (bottom panel) during the Lockdown and Pre-Lockdown, respectively.

as defined by the ratio of NO_2 to O_3. A NO_2-limited regime in the RL favors nocturnal pNO_3^- formation while an O_3-limited regime at ground level suppresses nocturnal pNO_3^- formation. As a result, more NO_x is upwards transported in the daytime and converted to pNO_3^- efficiently via N_2O_5 hydrolysis at night in the RL. Hence, the nocturnal pNO_3^- formation in the RL is an important source of pNO_3^- and should be considered in evaluating the source of pNO_3^- in the troposphere, including at surface level. Regime-dependence of nocturnal nitrate formation has crucial implications for effective control of nitrate pollution. A reduction in NO_x alone can only reduce nocturnal pNO_3^- formation when the atmosphere is in the NO_2-limited regime; it becomes less effective or may even enhance nocturnal pNO_3^- when the atmosphere is in the O_3-limited regime. Therefore, a more comprehensive regulation of precursor gases (e.g., VOCs and NO_x) is needed when developing an emission control strategy to mitigate nitrate pollution.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data are available through Quan (2023).

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