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Fast particulate nitrate formation via N₂O₅ uptake aloft in winter in Beijing

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Abstract. Particulate nitrate (pNO_3^-) is an important component of secondary aerosols in urban areas. Therefore, it is critical to explore its formation mechanism to assist with the planning of haze abatement strategies. Here we report vertical measurements of NO_x and O_3 by in situ instruments on a movable carriage on a tower during a winter heavy-haze episode (18 to 20 December 2016) in urban Beijing, China. Based on the box model simulation at different heights, we found that pNO_3^- formation via N₂O₅ heterogeneous uptake was negligible at ground level due to N2O5 concentrations of near zero controlled by high NO emissions and NO concentration. In contrast, the contribution from N₂O₅ uptake was large at high altitudes (e.g., >150 m), which was supported by the lower total oxidant $(NO_2 + O_3)$ level at high altitudes than at ground level. Modeling results show the specific case that the nighttime integrated production of pNO_3^- for the high-altitude air mass above urban Beijing was estimated to be $50 \,\mu g \, m^{-3}$ and enhanced the surface-layer pNO_3^- the next morning by 28 µg m⁻³ through vertical mixing. Sensitivity tests suggested that the nocturnal NO_x loss by NO₃-N₂O₅ chemistry was maximized once the N₂O₅ uptake coefficient was over 2×10^{-3} on polluted days with S_a at $3000 \,\mu\text{m}^2 \,\text{cm}^{-3}$ in wintertime. The case study provided a chance to highlight the fact that pNO_3^- formation via N₂O₅ heterogeneous hydrolysis may be an important source of particulate nitrate in the urban airshed during wintertime.

1 Introduction

Winter particulate matter (PM) pollution events occur frequently in China and have drawn widespread and sustained attention in recent years (Guo et al., 2014; Zhang et al., 2015; Huang et al., 2014; Wang et al., 2016). PM pollution reduces visibility (Lei and Wuebbles, 2013) and has harmful effects on public health (Cao et al., 2012). Particulate nitrate (pNO_3^-) is an important component of secondary inorganic aerosols and contributes 15-40 % of the PM2.5 mass concentration in China (Sun et al., 2013, 2015a, b; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015). The main atmospheric pathways of nitrate formation are (1) the reaction of OH with NO₂ and (2) N₂O₅ heterogeneous hydrolysis (Seinfeld and Pandis, 2006). The reaction of OH with NO₂ is a daytime pathway, as OH is very low in concentration at night, and N₂O₅ uptake is a nighttime pathway, as NO₃ and N₂O₅ are easily photolabile.

Particulate nitrate formation via N₂O₅ heterogeneous hydrolysis in summer was proved efficient by ground-based observation in North China (Wang et al., 2017b; Z. Wang et al., 2017) and found comparable to or even higher than the daytime formation. Several studies showed that N₂O₅ hydrolysis is responsible for nocturnal pNO_3^- enhancement in summer in Beijing (Pathak et al., 2009, 2011; Wang et al., 2017a). Although pNO_3^- formation via N₂O₅ uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in N₂O₅ chemistry exist between winter and summer. First, as the key precursor of NO₃ and N₂O₅, O₃ has a much lower concentration in winter than in summer owing to the short daytime length and



weak solar radiation. Second, colder temperatures and high NO₂ levels favor partitioning towards N₂O₅. Third, longer nighttime length in winter makes N₂O₅ heterogeneous hydrolysis potentially more important in pNO_3^- formation. Finally, the N₂O₅ uptake coefficient, as an important parameter in N₂O₅ heterogeneous hydrolysis, is likely very different from that in summer. This is because the properties of aerosol particles (e.g., organic compounds, particulate nitrate, liquid water contents, solubility, and viscosity) and meteorological conditions (e.g., temperature and relative humidity) differ between summer and winter (Chen et al., 2015; Zhang et al., 2007). These effects would result in large variations in the N₂O₅ uptake coefficient (Wahner et al., 1998; Mentel et al., 1999; Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003; Bertram and Thornton, 2009; Tang et al., 2012; Wagner et al., 2013; Grzinic et al., 2015). Several parameterization methods did not have good performance in predicting N₂O₅ uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences in pNO_3^- formation via N₂O₅ uptake, modeling and field studies showed high levels of NO₃ and N₂O₅ at high altitudes within the nocturnal boundary layer (NBL) owing to the stratification of surface NO and volatile organic compound (VOC) emissions, which lead to gradients in the loss rates for these compounds as a function of altitude (e.g., Brown et al., 2007; Geyer and Stutz, 2004; Stutz et al., 2004). The pNO_3^- formation via N₂O₅ uptake contributes to the gradients in the compound percentage and size distribution of the particle (Ferrero et al., 2010, 2012). On nights when NO₃ cannot accumulate in the surface layer owing to high NO emissions, N₂O₅ uptake can still be active aloft without NO titration. The N₂O₅ uptake aloft leads to elevated pNO_3^- formation in the upper layer as well as effective NO_x removal (Watson and Chow, 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Pusede et al., 2016; Baasandorj et al., 2017). Field observations at high-altitude sites in Kleiner Feldberg, Germany (Crowley et al., 2010a), the London British Telecommunications tower, UK (Benton et al., 2010), and Boulder, CO, USA (Wagner et al., 2013) showed elevated N_2O_5 concentrations aloft. Model studies showed that pNO_3^- varied at different heights and stressed the importance of the heterogeneous formation mechanism (Kim et al., 2014; Ying, 2011; Su et al., 2017). The mass fraction and concentration of pNO_3^- in Beijing was reported higher aloft (260 m) than at the ground level (Chan et al., 2005; Sun et al., 2015b), which was explained by favorable gas-particle partitioning aloft under lower temperature conditions. Overall, the active nighttime chemistry in the upper level plays an important role in surface PM pollution through mixing and dispersing within the planet boundary layer (PBL; Prabhakar et al., 2017), and the pollution was even worse in valley terrain regions coupled with adverse meteorological processes (Baasandorj et al., 2017; Green et al., 2015).

To explore the possible sources of pNO_3^- and the dependence of its formation on altitude in wintertime in Beijing, we conducted vertical profile measurements of NO, NO₂, and O₃ with a moving cabin at a tower platform in combination with simultaneous ground measurements of more comprehensive parameters in urban Beijing. A box model was used to investigate the reaction rate of N₂O₅ heterogeneous hydrolysis and its impact on pNO_3^- formation at different altitudes during a heavy-haze episode over urban Beijing. Additionally, the dependence of NO_x removal and pNO_3^- formation on the N₂O₅ uptake coefficient was investigated.

2 Methods

2.1 Field measurement

Ground measurements (15 m above the ground) were carried out on the campus of Peking University (PKU; 39°59'21" N, 116°18'25" E) in Beijing, China. The vertical measurements were conducted at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58'28" N, 116°22′16″ E). The IAP site is within 4 km of the PKU site. The locations of the PKU and IAP sites are shown in Fig. 1. At the PKU site, the dry-state mass concentration of PM_{2.5} was measured using a TEOM 1400A analyzer. NO_x was measured via a chemiluminescence analyzer (Thermo Scientific, TE-42i-TR), and O₃ was measured with a UV photometric O₃ analyzer (Thermo Scientific, TE-49i). Dry-state particle number and size distribution (PNSD) were measured from 0.01 to 0.7 µm with a scanning mobility particle sizer (SMPS; TSI Inc. 3010). The instrumental parameters are summarized in Table S1 in the Supplement. The data were collected from 16 to 22 December 2016. Additionally, relative humidity (RH), temperature (T), and wind direction and speed data were available during the measurement period.

Vertical profile measurements were conducted from 18 to 20 December 2016 from the tower-based platform (maximum height 325 m) on the IAP campus. The NO_x and O_3 instruments were installed aboard a movable cabin on the tower. NO_x and O_3 were measured with two low-power, lightweight instruments (model 405 nm and model 106-L, 2B Technologies, USA). The model 405 nm instrument measures NO₂ directly based on the absorbance at 405 nm, and NO is measured by adding excess O_3 (conversion efficiency ~ 100 %). The limit of detection of both NO and NO₂ is 1 part per billion volume (ppbv), with an accuracy of 2 ppbv or 2 % of the reading, and the time resolution is 10 s (Birks et al., 2018). The model 106-L instrument measures O₃ based on the absorbance at 254 nm, with a precision of 1 ppbv, or 2% of the reading, and a limit of detection of 3 ppbv. NO_x calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with an NO standard (9.8 ppmv). The O₃ calibration was done with an O₃ calibrator (TE 49i-PS), which was traceable to NIST



Figure 1. Location of the monitoring sites used in this study, including PKU (red diamond), IAP (blue diamond), and other national monitoring sites (green circles). Vertical profiles of NO_x and O_3 were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate N_2O_5 and particle nitrate formation) were collected from a ground site at PKU. Additional measurements of PM_{2.5} concentrations were continuously taken at national monitoring sites throughout Beijing.

(National Institute of Standards and Technology) standards annually. Before the campaign, the NO_x monitor was compared with a cavity attenuated phase shift (CAPS) particle light extinction monitor, and the O₃ monitor was compared to a commercial O₃ analyzer (TE-49i, Thermo Electron, USA). Good agreement was found between the portable instruments and the conventional monitors. Height information was retrieved via the observed atmospheric pressure measured by the model 405 nm instrument. The cabin ascended and descended at a rate of 10 m min^{-1} , with a height limit of 260 mduring the daytime and 240 m at night. The cabin stopped after reaching the peak, and parameters were measured continually during the last 10 min of each cycle. One vertical cycle lasted for approximately 1 h. We measured two cycles per day, one in the morning and the other in the evening. Six cycles were measured in total during the campaign.

2.2 Box model simulation

A simple chemical mechanism (see Reactions R1–R5) was used in a box model to simulate the nighttime NO₃ and N₂O₅ chemistry under NO free-air-mass conditions. Physical mixing, dilution, deposition, or interruption during the transport of the air mass was not considered in the base case, and the physical influence on the model result will be discussed in Sect. 3.4. Here, *f* represents the ClNO₂ yield from N₂O₅ uptake. Homogeneous hydrolysis of N₂O₅ and NO₃ heterogeneous uptake reaction were neglected in this analysis because of the low level of absolute humidity and the extremely low NO₃ concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of Reactions (R1)– (R3) are those reported by Sander et al. (2011).

$110_2 + 0_3 + 110_3 + 0_2$ (11)	$NO_2 + O_3 \rightarrow NO_3 + O_2$	(R1)
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 $NO_2 + NO_3 + M \to N_2O_5 + M \tag{R2}$

 $N_2O_5 + M \to NO_2 + NO_3 + M \tag{R3}$

$$NO_3 + VOCs \rightarrow Products$$
 (R4)

$$N_2O_5 + (H_2O \text{ or } Cl^-) \rightarrow (2 - f)NO_3^- + fCINO_2$$
 (R5)

Following the work of Wagner et al. (2013), the box model can be solved using six equations (Eqs. 1-6). In the framework, O_3 is only lost via the reaction of $NO_2 + O_3$ and the change in the O_3 concentration can be expressed as Eq. (1). Equation (2) can express the losses of NO₂. The s(t) is between 0 and 1 and is expressed as Eq. (5), and the physical meaning of s(t) is the ratio of NO₃ production, which goes through N_2O_5 (either as N_2O_5 or lost through uptake) to the total NO₃ production (Wagner et al., 2013). The s(t)favors 0 when direct loss of NO₃ dominates and favors 1 when N2O5 uptake dominates NO3 loss. The model calculation has two steps. The first step is to calculate the mixing ratio of NO₂ and O₃ at time zero (herein designated as sunset). According to Eqs. (1) and (2), the initial NO₂ (t = 0) and O₃ (t = 0) concentrations can then be integrated backward in time starting with the measured concentrations of NO₂ and O₃ at each height. During the pollution period in winter in Beijing (NO₂ = 45 ppbv, temperature = 273 K, $S_a = 3000 \,\mu\text{m}^2 \,\text{cm}^{-3}$), the ratio of N₂O₅ to NO₃ is large enough, i.e., 450. The pseudo-first-order loss rate of N2O5 heterogeneous uptake will be $1 \times 10^{-3} \text{ s}^{-1}$, with an N₂O₅ uptake coefficient of 5×10^{-3} . N₂O₅ uptake contributes to the NO₃ loss rate of 0.4 s^{-1} , which is much higher than the direct NO₃ loss through the reaction of NO₃ with VOCs. Therefore, N₂O₅ uptake was proposed to be dominantly responsible for the NO₃ loss and the initial s(t) was set to 1. Equation (3) can describe the sum concentration of NO₃ and N₂O₅. Assuming that equilibrium between NO₃ and N₂O₅ is maintained after a certain period, based on the temperaturedependent equilibrium rate constant (k_{eq}) and the modeled NO_2 at a certain time, Eq. (4) can be used to determine the ratio of N₂O₅ to NO₃. Combined, Eqs. (1)-(4) allow for the calculation of NO3 and N2O5 concentrations considering stable NO₃ and N₂O₅ loss rate constants (k_{NO_3} and $k_{N_2O_5}$, respectively). In the second step, a new s(t) was calculated using the data from the first step (Eq. 5); new initial NO₂ and O₃ concentrations were then approximated, and NO₃ and N_2O_5 values were derived using the same method as in the first step. This process was repeated until the difference between the two s(t) values was less than 0.005. The number of adjustments to a new s(t) could not be calculated more than 10 times. Otherwise, the calculating process would become non-convergent.

The modeled N₂O₅ concentrations and given $k_{N_2O_5}$ were then used to estimate pNO_3^- formation. The HNO₃ produced in Reaction (R4) was not considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here, k_{NO_3} and $k_{N_2O_5}$ denote the pseudo-first-order reaction rate constants of the total NO₃ reactivity caused by ambient VOCs and N₂O₅ heterogeneous uptake, respectively. $k_{N_2O_5}$ is given in Eq. (6). S_a is the aerosol surface area, *C* is the mean molecular speed of N₂O₅, and $\gamma_{N_2O_5}$ is the N₂O₅ uptake coefficient. Sunset and sunrise times during the measurements were 16:55 and 07:30 (Chinese National Standard Time, CNST), and the running time of the model was set to 14.5 h from sunset to sunrise.

$$\frac{d[O_3]}{dt} = -k_{NO_2+O_3}[O_3][NO_2]$$
(1)

$$\frac{d[NO_2]}{dt} = -(1+s(t)) \times k_{NO_2+O_3}[O_3][NO_2]$$
(2)

$$\frac{d[NO_3 + N_2O_5]}{dt} = k_{NO_2 + O_3} [O_3] [NO_2] - k_{N2O5} [N_2O_5]$$

$$-k_{\rm NO3}[\rm NO_3] \tag{3}$$

$$\frac{[N_2O_5]}{[NO_3]} = k_{eq}[NO_2]$$
(4)

$$s(t) = \frac{\int_0^t k_{N2O5} \cdot [N_2O_5] dt + [N_2O_5]_t}{[O_3](0) - [O_3](t)}$$
(5)

$$k_{\rm N2O5} = \frac{C \times S_a \times \gamma_{\rm N2O5}}{4} \tag{6}$$

Dry-state S_a at the PKU site was calculated based on the PNSD measurement, which was corrected to ambient (wet) S_a for particle hygroscopicity via a growth factor (Liu et al., 2013). The uncertainty of the wet S_a was estimated to be $\sim 30\%$, which was associated with the error from dry PNSD measurement ($\sim 20\%$) and the growth factor $(\sim 20\%)$. Nighttime averaged S_a on the night of 19 December was about $3000 \,\mu\text{m}^2 \,\text{cm}^{-3}$. PM measurements at the national monitoring sites proved that this heavy-haze pollution episode was a typical regional event (Fig. S1 in the Supplement). Furthermore, a synchronous study on the night of 19 December 2016 showed small variation in the vertical particle number concentration, with a boundary layer height of 340 m (Zhong et al., 2017). Overall, the S_a measured at the PKU site can represent the urban Beijing conditions on a horizontal and vertical scale (< 340 m). Although the PNSD information for particles larger than 0.7 µm was not valid during the study period, the particles smaller than 0.7 µm dominated more than 95 % of the aerosol surface area in a subsequent pollution episode (1 January to 1 July 2017), and similar results also were reported in other studies (e.g., Crowley et al., 2010a; Wang et al., 2018). The possible lower bias of S_a (5%) only led to a small overestimation of N₂O₅, i.e., 3.6– 4.2 %, and an underestimation of pNO_2^- of 0.2–2.5 % when $\gamma_{N_2O_5}$ varied from 1×10^{-3} to 0.05.

The N₂O₅ uptake coefficient and ClNO₂ yield are key parameters in the estimation of pNO_3^- formation (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016). Wagner et al. (2013) show the significant pNO_3^- suppression of N₂O₅ uptake aloft in the wintertime in Denver, CO, USA; the uptake coefficient is 0.005 when the percentage of pNO_3^- in the PM_{2.5} mass concentration is 40 %. As the proportion of nitrate in the particle mass concentration is similarly high in North China during wintertime (Sun et al., 2013, 2015a; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015), herein we fixed the uptake coefficient to 0.005 for the base model initial input. Because the model input of CINO₂

 Table 1. List of the parameter sets in the base case and sensitivity tests.

Cases	$k_{\rm NO_3}~({\rm s}^{-1})$	$\gamma_{N_2O_5}$
Base case	0.02	0.005
k _{NO3} test 1	0.001	0.005
$k_{\rm NO_3}$ test 2	0.01	0.005
$k_{\rm NO_3}$ test 3	0.05	0.005
$\gamma_{N_2O_5}$ test 1	0.02	0.001
$\gamma_{N_2O_5}$ test 2	0.02	0.01
$\gamma_{N_2O_5}$ test 3	0.02	0.05

yield only affects the value of produced pNO_3^- concentration and would not change the modeled N_2O_5 concentration, we set the initial f_{CINO_2} to zero. Previous work showed the averaged $k_{\rm NO_3}$ was 0.01–0.02 s⁻¹ in summer in Beijing, with BVOCs contributing significantly (Wang et al., 2017a; Wang et al., 2018). The intensity of BVOC emissions decreased in wintertime owing to the lower temperature and weak solar radiation, and thus the k_{NO_3} should be smaller than it is in summer. In this work, the model input k_{NO_3} was set to an arbitrary and relatively high value of $0.02 \,\mathrm{s}^{-1}$ (equivalent to 0.2 ppbv isoprene +40 parts per trillion volume (pptv) monoterpene +1.0 ppbv *cis*-2-butene) to constrain the impact of N₂O₅ uptake in the model. A series of sensitivity tests was conducted to study the uncertainties of the model simulation, and the detailed test sets are listed in Table 1, including the test of N2O5 uptake coefficient and k_{NO_3} . The $\gamma_{N_2O_5}$ sensitivity tests were set from 0.001 to 0.05, and the k_{NO3} tests were set to 0.001, 0.01, and $0.1 \, \mathrm{s}^{-1}$.

In the calculation of particulate nitration formation by N₂O₅ uptake, an assumption is that all soluble nitrate formed from N_2O_5 uptake goes to the particle phase rather than the gas phase. The assumption would lead to an upper bias due to the degassing of gas-phase HNO₃ from particulate nitrate. While in winter in Beijing, the mixing ratio of NH₃ was rich to tens of ppbv and always much higher than the nocturnal gas-phase HNO₃ (e.g., Liu et al., 2017). The high NH₃ suppressed the degassing of particulate nitrate effectively. The measurement of gas-phase HNO₃ and pNO_3^- in the surface layer of Beijing showed that soluble nitrate favors the particle phase in winter, especially on polluted days. For example, the nocturnal ratio of pNO_3^- to total soluble nitrate was larger than 0.95 on average (Liu et al., 2017). Due to the low temperature and high RH at high altitude, the ratio would increase and the degassing of particulate nitrate is negligible.

3 Results and discussion

3.1 Ground-based observations

A severe winter PM pollution event lasted from 16 to 22 December 2016 in Beijing. Figure 2a shows the time series of



Figure 2. Time series of (a) $PM_{2.5}$ and O_3 , (b) NO and NO_2 , (c) temperature (*T*) and relative humidity (RH), and (d) wind direction (WD) and wind speed (WS) from 16 to 22 December 2016 at the PKU site in Beijing, China. The shaded region represents the nighttime periods. The red line in (a) shows an example of fast $PM_{2.5}$ enhancement on the night of 19 December and the green lines are the time periods when the vertical measurements were conducted at the IAP site.

PM_{2.5} and other relevant parameters based on ground measurements at the PKU site. The mass concentration of PM2.5 began to increase from 16 December, reaching $480 \,\mu g \, m^{-3}$ on 20 December. A fast PM growth event was captured, with an overall increment of $100 \,\mu g \, m^{-3}$ on the night of 19 December (Fig. 2a). Throughout the pollution episode, the meteorological conditions included high RH (50 $\% \pm 16\%$) and low temperature $(2 \pm 3 \,^{\circ}\text{C})$. The slow surface wind speed $(<3 \,\mathrm{m \, s^{-1}})$ implied the atmosphere was stable (Fig. 2c, d). The daytime O₃ concentration was low owing to high NO emission and weak solar radiation. After sunset, O₃ at the surface layer was rapidly titrated to zero by the elevated NO. The presence of high NO concentrations would have strongly suppressed the concentration of NO₃, further suppressing N₂O₅ near the ground. Figure 2b depicts the high amounts of NO and NO₂ that were observed at ground level during the PM pollution episode, suggesting that pNO_3^- production via N₂O₅ uptake was not important near the ground during the winter haze episode.

3.2 Tower observations

Six vertical measurements of the total oxidants ($O_x = O_3 + NO_2$) below 50 m were consistent with those measured at ground level and are shown in Fig. S2, confirming that the two sites are comparable. On the night of 20 December (Fig. 3a), the NO₂ and NO from 0–240 m were abundant



Figure 3. Vertical profiles of NO and NO₂ (**a**) and of O₃ and O_x (**b**) at 20:38–21:06 on the night of 20 December 2016.

and conservative around 21:00, with concentrations of 80 and 100 ppbv, respectively. The O₃ concentrations remained zero during the nighttime (Fig. 3b). The vertical profile on 20 December suggests that at least below 240 m, the N₂O₅ chemistry was not important, which is consistent with the results at ground level as mentioned above. The vertical profile on 19 December was different from that on 20 December. Figure 4a shows the vertical profiles around 21:00 on 19 December; NO was abundant from the ground to 100 m, then gradually decreased to zero from 100 to 150 m and remained at zero above 150 m. The observed NO₂ concentration was 85 ± 2 ppbv below 100 m, which gradually decreased from 100 to 150 m and was 50 ± 2 ppbv from 150 to 240 m. The observed O3 concentrations below 150 m were below the instrumental limit of detection (Fig. 4b). Above 150 m, the O₃ concentration was 20 ± 2 ppbv, corresponding to zero NO concentration. With respect to O_x , the mixing ratio of was 85 ± 2 ppbv at lower altitudes, whereas the concentration at higher altitudes was 15 ppbv lower than at lower altitudes (Fig. 4b). The O_x missing from the higher-altitude air mass indicated an additional nocturnal removal of O_x aloft.

Figure 5 depicts the vertical profiles of NO_x, O₃, and O_x at 09:30 on the morning of 20 December, which have similar features to those observed at 21:00 on 19 December. The vertical profiles suggest that stratification still existed at that time. The amount of O_x missing aloft in the morning increased to 25 ppbv at 240–260 m, demonstrating that an additional 25 ppbv of O_x was removed or converted to other compounds at higher altitudes than at the surface layer during the night from 19 to 20 December. Figure S3 shows the vertical profiles of NO, NO₂, O₃, and O_x at ~ 12:00 on 18 December, when solar radiation was strong enough to mix the trace gases well in the vertical direction. NO_x and O₃ were found to be well mixed indeed, with small variation from the ground level to 260 m.



Figure 4. O_x missing case presented by the vertical profiles of (a) NO and NO₂ and of (b) O₃ and O_x at 20:38–21:13 on the night of 19 December 2016.

3.3 Particulate nitrate formation aloft

N₂O₅ uptake is one of the two most important pathways of ambient NO_x loss and pNO₃⁻ formation (Wagner et al., 2013; Stutz et al., 2010; Tsai et al., 2014). At high altitudes (e.g., > 150 m), NO₃ and N₂O₅ chemistry can be initiated in the copresence of high NO₂ and significant O₃ levels. Therefore, N₂O₅ uptake could represent a plausible explanation for the O_x observed to be missing at high altitude on the night of 19 December. To explore this phenomenon, a time-step box model was used to simulate the NO₃ and N₂O₅ chemistry based on the observed vertical profiles of NO₂ and O₃ on the night of 19 December.

In the base case, the average initial NO_2 and O_3 levels above 150 m at sunset were 61 ± 3 and 27 ± 6 ppbv, respectively. The measured NO₂ concentration at the PKU site at sunset (local time 16:55) was 61 ppbv and showed good consistency with the model result. The modeled N_2O_5 concentration was zero below 150 m, as the high level of NO made for rapid consumption of the formed NO₃. In contrast, the modeled N₂O₅ concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The pNO_3^- formation by N₂O₅ heterogeneous uptake from sunset to the measurement time can be calculated using Eq. (7), which was significant at 24 μ g m⁻³ after sunset above 150 m. The *p*NO₃⁻ formed in 4.5 h was equivalent to 13 ppbv O_x loss and consistent with the observation (15 ppby; Fig. 6b). The 1.5:1 relationship between O_x and pNO_3^- was used to calculate the O_x equivalence (S. S. Brown et al., 2006a).

$$\sum p \mathrm{NO}_{3}^{-} = \int_{0}^{t} (2 - f) \cdot k_{\mathrm{N2O5}} \cdot [\mathrm{N_{2}O_{5}}] \mathrm{d}t$$
(7)

The box model enabled the analysis of the integrated $pNO_3^$ and ClNO₂ via N₂O₅ uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO_3^- went as high as 50 µg m⁻³. The integrated pNO_3^- at surrise was equal to the loss of 27 ppbv O_x, showing a good agreement with the ob-



Figure 5. Vertical profiles of (a) NO and NO₂ and of (b) O₃ and O_x at 09:06–09:34 on the morning of 20 December 2016.

served O_x missing (25 ppbv) aloft in the morning hours. During the nighttime, the pNO_3^- formed aloft via N₂O₅ uptake led to a much higher particle nitrate concentration than in the surface layer, which has been reported in many field observations (Watson and Chow, 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Ferrero et al., 2012; Sun et al., 2015b). The elevated pNO_3^- aloft was well dispersed through vertical mixing and enhanced the surface-layer PM concentration; this phenomenon was also observed in previous studies (Watson and Chow, 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Prabhakar et al., 2017). Zhong et al. (2017) showed that the NBL and PBL both were at 340 m from 19 to 20 December 2016 in Beijing. Daytime vertical downward transportation was helpful in mixing the air mass within the PBL. Assuming the newly formed pNO_3^- aloft from 150 to 340 m is $50 \,\mu g \,m^{-3}$ during the nighttime and is well mixed within the PBL the next morning, the pNO_3^- enhancement at the surface layer $(\Delta p NO_3^-)$ can be simplified to the calculation in Eq. (8) as follows.

$$\Delta p \mathrm{NO}_3 = \frac{\int_0^{150} P(p \mathrm{NO}_3) \mathrm{d}H + \int_{150}^{340} P(p \mathrm{NO}_3) \mathrm{d}H}{340} \tag{8}$$

Here, $P(pNO_3^-)$ is the integral production of pNO_3^- and H represents height. Owing to high NO below 150 m, the pNO_3^- formation via N₂O₅ uptake was zero. The enhancement of pNO_3^- from 150 to 340 m was calculated as 28 µg m⁻³, which is in good agreement with the observed PM peak in the morning on 20 December, with PM enhancement of ~ 60 µg m⁻³. The result demonstrated that the nocturnal N₂O₅ uptake aloft and downward transportation were critical for understanding the PM growth process.

3.4 Sensitivity studies

Previous studies have emphasized that the N_2O_5 uptake coefficient varies greatly (0.001–0.1) in different ambient conditions (Chang et al., 2011; Brown and Stutz, 2012; Wang and Lu, 2016), which is the main source of uncertainties in



Figure 6. Base case ($\gamma = 0.005$) and sensitivity tests of the vertical profile on the night of 19 December at different N₂O₅ uptake coefficients, including (**a**) the mixing ratio of N₂O₅ at 21:00, (**b**) the integral pNO_3^- production from sunset to 21:00, and (**c**) the time series of the integral pNO_3^- formed at 240 m via N₂O₅ uptake from sunset (17:00) to sunrise (07:30; nighttime length 14.5 h). The squares represent the pNO_3^- equivalent weight from the observed O_x missing in the two vertical measurements at ~ 21:00 and ~ 09:30 on the following morning.

this model. In the present research, sensitivity studies showed the modeled N₂O₅ concentration dropping from 3 ppbv to 60 pptv when the N_2O_5 uptake coefficients increased from 0.001 to 0.05 (Fig. 6a), as the N₂O₅ concentration is very sensitive to loss from heterogeneous reactions. Compared to the base case, the accumulated pNO_3^- was evidently lower at $\gamma = 0.001 \ (44 \ \mu g \ m^{-3})$. Low N₂O₅ uptake coefficients correspond to several types of aerosols, such as secondary organic aerosols (Gross et al., 2009), humic acids (Badger et al., 2006), and certain solid aerosols (Gross and Bertram, 2008). When the N_2O_5 uptake coefficient increased from 0.005 to 0.05 (Fig. 6b, c), the increase in integral pNO_3^- was negligible. The conversion capacity of N_2O_5 uptake to pNO_3^- is maximized for a given fixed value of the ClNO₂ yield. The conversion of NO_x to pNO_3^- was not limited by the N₂O₅ heterogeneous reaction rate, but limited by the formation of NO₃ via the reaction of NO₂ with O₃ during the polluted night.

For describing the nocturnal NO_x removal capacity and pNO_3^- formation via NO₃ and N₂O₅ chemistry, the overnight NO_x loss efficiency (ε) was calculated using 10490



Figure 7. The dependence of overnight NO_x loss via N₂O₅ uptake on $\gamma_{N_2O_5}$ in typical winter pollution conditions. The initial NO₂ and O₃ were set to 60 and 30 ppby, respectively; S_a was set to 3000 µm² cm⁻³, the ClNO₂ yield was zero, and k_{NO_3} was 0.02 s⁻¹. The reaction time was set to 14.5 h. The blue and orange zones represent the contribution by NO₃ + VOCs and N₂O₅ uptake, and the dashed line ($\gamma = 0.002$ when N₂O₅ uptake contributes to 90% of the maximum NO_x loss) divides the loss into γ -sensitive and γ insensitive regions. The maximum nocturnal NO_x loss by NO₃– N₂O₅ chemistry is 56%.

Eq. (9). $\varepsilon = \frac{\int_0^t 2 \times k_{N2O5} \cdot [N_2O_5] dt + \int_0^t k_{NO3} \cdot [NO_3] dt}{[NO_2](0)}$ (9)

The case modeled typical winter haze pollution conditions in Beijing from sunset to sunrise, with the initial model values of NO₂ and O₃ set to 60 and 30 ppbv, respectively. S_a was set to $3000 \,\mu\text{m}^2 \,\text{cm}^{-3}$, the ClNO₂ yield was zero, and k_{NO_3} was 0.02 s^{-1} . The reaction time was set to 14.5 h to represent an overnight period in wintertime. The consumed NO₃ by the reaction with VOCs and N₂O₅ by uptake reaction were regarded as NO_x removal. Figure 7 shows the dependence of the overnight NO_x loss efficiency on the N_2O_5 uptake coefficient, as it varied from 1×10^{-5} to 0.1. This is an increase from 20 to 56 % with increasing $\gamma_{N_2O_5}$, which is similar to the result addressed by Chang et al. (2011). The ceiling of overnight NO_x loss via NO₃–N₂O₅ chemistry was fixed when all the NO_x loss was through N_2O_5 uptake on polluted days, which is limited by the reaction time and the formation rate of NO₃ (Reaction R1). In this case, the N₂O₅ uptake contributed about 90 % of the overnight NO_x loss (50.4 %) when $\gamma_{N_2O_5}$ was equal to 2×10^{-3} . When $\gamma_{N_2O_5}$ was less than 2×10^{-3} , NO_x removal increased rapidly with increasing $\gamma_{N_2O_5}$, which was defined as the $\gamma_{N_2O_5}$ -sensitive region. When $\gamma_{N_2O_5} \ge 2 \times 10^{-3}$, the contribution of N₂O₅ uptake to NO_x loss was over 90% and became insensitive. This region was defined as the $\gamma_{N_2O_5}$ -insensitive region. According to Eqs. (3) and (5), high S_a , high NO_x, low k_{NO_3} , or low temperature allow the N2O5 uptake to more easily be located in the $\gamma_{N_2O_5}$ -insensitive region. Here, the critical value of the N_2O_5 uptake coefficient (2 × 10⁻³) was relatively low com-



Figure 8. Base case $(k_{NO_3} = 0.02 \text{ s}^{-1})$ and sensitivity tests of the integral pNO_3^- formed at 240 m via N₂O₅ uptake at different NO₃ reactivity (0.001, 0.01, 0.05 s⁻¹) on the whole night of 19 December 2016.

pared with that recommended for the surface of mineral dust (0.013, 290–300 K; Crowley et al., 2010b; Tang et al., 2017) or determined in many field experiments (e.g., S. S. Brown et al., 2006b, 2009; Wagner et al., 2013; Morgan et al., 2015; Phillips et al., 2016; Z. Wang et al., 2017; Brown et al., 2016; Wang et al., 2017b; X. F. Wang et al., 2017). This suggests that the NO_x loss and pNO_3^- formation by N₂O₅ uptake were easily maximized in the pollution episode and further worsened the PM pollution.

In the base case, the modeled pNO_3^- formation via N₂O₅ uptake was an upper limit result, as the ClNO₂ yield was set to zero. High coal combustion emitted chloride into the atmosphere of Beijing during the heating period (Sun et al., 2013), like the emissions from power plants in North China. This enhanced anthropogenic chloride provides abundant chloridecontaining aerosols to form CINO₂ via N₂O₅ uptake aloft, implying that significant ClNO₂ formed in the upper layer of the NBL (Tham et al., 2016; Z. Wang et al., 2017). Assuming the CINO₂ yield is the average value of 0.28 determined at high altitude in North China (Z. Wang et al., 2017), the pNO_3^- produced throughout the night decreased $7 \,\mu g \,m^{-3}$. The modeled formation of ClNO₂ aloft throughout the night was 2.5 ppbv, which is comparable with the observation in North China (Tham et al., 2016; Z. Wang et al., 2017; X. F. Wang et al., 2017). Since the modeled pNO_3^- formation is sensitive to the ClNO₂ yield, a higher yield would increase the model uncertainty directly, and hence investigating the ClNO₂ yield is warranted in future studies. As for NO₃ reactivity, Fig. 8 shows the sensitivity tests of the integral pNO_3^- formation for the whole night at k_{NO_3} values of 0.001, 0.01, 0.02, and 0.05 s^{-1} . The integral pNO_3^- formation decreased when k_{NO_3} varied from 0.001 to 0.1 s⁻¹, but the variation ratio to the base case was within 5%. The result shows that the NO₃-N₂O₅ loss via NO₃ reaction with VOCs during the polluted wintertime was not important, which may only lead to relatively small uncertainties in the integral pNO_3^- formation calculation. Nevertheless, if N₂O₅ uptake was extremely low (e.g., $\gamma_{N_2O_5} < 10^{-4}$), the uncertainty of NO₃ oxidation would increase significantly.

The uncertainty caused by the physical changes in the air masses were analyzed from two angles: one is the dilution and the other is the mixing and exchange of the air mass. With respect to the impact of the dilution process, it would decrease the mixing ratio of NO₂, O₃, NO₃, and N₂O₅ and leads to a lower contribution to particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28 % compared with the base case. With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass. If the warm combustion source emitted NO_x into the air mass after sunset, which would increase the mixing ratio of O_x , and restart the zero time of the model. Accounting for the uncertainties from the mixing and sensitivity tests of the box model to shortening the duration by 25 %, the bias of the integrated pNO_3^- throughout the night was small within 12% relative to the base case. If the air mass was affected by the clean air mass from the north, it would be featured with very low NO_x and about 40 ppbv O_3 (background condition), which was not consistent with our observation.

4 Conclusions

During the wintertime, ambient O_3 is often fully titrated at the ground level in urban Beijing owing to its fast reaction with NO emissions. Consequently, the near-surface air masses are chemically inert. Nevertheless, the chemical information of the air masses at higher altitudes was indicative of a reactive layer above urban Beijing, which potentially drives fast pNO_3^- production via N₂O₅ uptake and contributes to the surface PM mass concentration. In this study, we found a case to show evidence for additional O_x missing (25 ppbv) aloft throughout the night. Based on model simulation, we found that the particulate nitrate formed above 150 m reached 50 µg m⁻³ and enhanced the surface level PM concentration significantly by 28 µg m⁻³ with downward mixing after the breakup of the NBL in the morning.

Our result emphasized the importance of the heterogeneous chemistry aloft over the city through a case study. The model simulation also demonstrated that during the heavy PM pollution period, the particulate nitrate formation capacity via N_2O_5 uptake was easily maximized in the high altitudes above urban Beijing, even with a low N_2O_5 uptake coefficient. This indicates that the mixing ratio of NO_2 aloft was directly linked to nitrate formation, and reduction of NO_x is helpful in decreasing nocturnal nitrate formation. Overall, this study highlights the importance of the interplay between chemical formation aloft and dynamic processes for investigating the ground-level PM pollution problem. In the future, direct observations of N_2O_5 and the associated parameters should be performed to explore the physical and chemical properties of this overhead nighttime reaction layer and to reach a better understanding of winter haze formation.

Data availability. All the observational data used in this study are available from the corresponding author upon request (k.lu@pku.edu.cn).

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