Fast particulate nitrate formation via N_2O_5 uptake aloft in winter 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 measurement of NO_x and O_3 by in-situ instruments on a movable carriage on a tower during a winter heavy-haze episode (December 18 to 20, 2016) in urban Beijing, China. Based on the box model simulation at different height, we found that pNO_3^- formation via N_2O_5 heterogeneous uptake was negligible at ground level due to N_2O_5 concentration of near zero controlling by high NO emission and NO concentration. In contrast, the contribution from N_2O_5 uptake was large at high altitudes (e.g., > 150 m), which was supported by the low total oxidant (NO_2 + O_3) level at high altitudes than that 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 μg 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 NO_3-N_2O_5 chemistry was maximized once the N_2O_5 uptake coefficient was over 2×10^{-3} on polluted days with S_a was 3000 μm^2 cm^{-3} in wintertime. The case study

provided a chance to highlight that pNO_3^- formation via N_2O_5 heterogeneous hydrolysis may be an important source of the 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 G 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 $PM_{2.5}$ mass concentration in China (Sun et al., 2013, 2015a, 2015b; 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 NO_2 and (2) N_2O_5 heterogeneous hydrolysis (Seinfeld and Pandis, 2006). The reaction of OH with NO_2 is a daytime pathway, as OH is very low in concentration at night, and N_2O_5 uptake is a nighttime pathway, as NO_3 and N_2O_5 are easily photo-labile.

Particulate nitrate formation via N_2O_5 heterogeneous hydrolysis in summer was proved efficient by ground-based observation in North China (Wang H et al., 2017b; Wang Z et al., 2017), and found comparable to or even higher than the daytime formation. Several studies showed that N_2O_5 hydrolysis is responsible for nocturnal pNO_3^- enhancement in summer Beijing (Pathak et al., 2009, 2011; Wang H et al., 2017a). Although pNO_3^- formation via N_2O_5 uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in N_2O_5 chemistry exist between winter and summer. First, as the key precursor of NO_3 and N_2O_5, O_3 has a much lower concentration in winter than in summer, owing to the short daytime length and weak solar radiation. Second, colder temperature and high NO_2 level favor the partitioning towards N_2O_5. Third, longer nighttime length in winter makes N_2O_5 heterogeneous hydrolysis potentially more important in pNO_3^- formation. Finally, the N_2O_5 uptake coefficient, as an important parameter in N_2O_5

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 N_2O_5 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 N_2O_5 uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences in pNO_3^- formation via N_2O_5 uptake, modeling and field studies showed high levels of NO_3 and N_2O_5 at high altitudes within the nocturnal boundary layer (NBL), owing to the stratification of surface NO and volatile organic compounds (VOCs) 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 N_2O_5 uptake contributes to the gradients in the compounds percentage and size distribution of the particle (Ferrero et al., 2010; 2012). On nights when NO_3 can't accumulate in the surface layer owing to high NO emissions, N_2O_5 uptake can still be active aloft without NO titration. The N_2O_5 uptake aloft leads to elevated pNO_3^- formation in the upper layer as well as effective NO_x removal (Watson et al., 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 of 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 the 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 in Beijing (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), 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, NO_2, and O_3 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 N_2O_5 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 N_2O_5 uptake coefficient was probed.

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, 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 O_3 was measured with a UV photometric O_3 analyzer (Thermo Scientific, TE-49i). Dry-state particle number and size distribution (PNSD) was 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. The data were collected from December 16 to 22, 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 December 18 to 20, 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 NO_2 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 NO_2 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 O_3 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 a NO standard (9.8 ppmv). The O_3 calibration was done with an O_3 calibrator (TE 49i-PS), which was traceable to NIST (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 O_3 monitor was compared to a commercial O_3 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 m during 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 R1–R5) was used in a box model to simulate the

nighttime NO_3 and N_2O_5 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, the physical influence to the model result will be discussed in Sect. 3.4. Here, *f* represents the $ClNO_2$ yield from N_2O_5 uptake. Homogeneous hydrolysis of N_2O_5 and NO_3 heterogeneous uptake reaction were neglected in this analysis because of the low level of absolute humidity and the extremely low NO_3 concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of R1–R3 are those reported by Sander et al. (2011).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad \text{(R2)}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \quad \text{(R3)}$$

$$NO_3 + VOCs \rightarrow Products \quad \text{(R4)}$$

$$N_2O_5 + (H_2O \text{ or } Cl^-) \rightarrow (2\text{-}f)\ NO_3^- + f\ ClNO_2 \quad \text{(R5)}$$

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. Eq. 2 can express the losses of NO_2. The s(t) is between 0 and 1 and expressed as Eq. 5, the physical meaning of s(t) is the ratio of NO_3 production which goes through N_2O_5 (either as N_2O_5 or lost through uptake) to the total NO_3 production (Wagner et al., 2013). The s(t) favors 0 when direct loss of NO_3 dominates and favors 1 when N_2O_5 uptake dominates NO_3 loss. The model calculation has two steps. The first step is calculate the mixing ratio of NO_2 and O_3 at time zero (herein designated as sunset). According to Eqs. 1 and 2, the initial NO_2 (t=0) and O_3 (t=0) concentrations can then be integrated backward in time starting with the measured concentrations of NO_2 and O_3 at each height. During the pollution period in winter in Beijing (NO_2 = 45 ppbv, Temperature = 273 K, S_a = 3000 $\mu m^2\ cm^{-3}$), the ratio of N_2O_5 to NO_3 is large enough, i.e., 450. The pseudo-first-order loss rate of N_2O_5 heterogeneous uptake will be 1×10^{-3} s^{-1}, with a N_2O_5 uptake coefficient of 5×10^{-3}. N_2O_5 uptake would contribute to the NO_3 loss rate of 0.4 s^{-1}, which is much higher than the direct NO_3 loss through the reaction of NO_3 with VOCs. Therefore, N_2O_5 uptake was proposed to be dominantly

responsible for the NO_3 loss and the initial s(t) was set to 1. Eq. 3 can describe the sum concentration of NO_3 and N_2O_5. Assuming the equilibrium between NO_3 and N_2O_5 is maintained after a certain period, based on the temperature-dependent equilibrium rate constant (k_{eq}) and the modeled NO_2 at a certain time, Eq. 4 can be used to determine the ratio of N_2O_5 to NO_3. Combined, Eqs. 1–4 allow for the calculation of NO_3 and N_2O_5 concentrations considering stable NO_3 and N_2O_5 loss rate constants (k_{NO3} and k_{N2O5}, respectively). In the second step, a new s(t) was calculated using the data from the first step (Eq. 5), new initial NO_2 and O_3 concentrations were then approximated, and NO_3 and N_2O_5 values were derived using the same method as used 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 N_2O_5 concentrations and given k_{N2O5} were then used to estimate pNO_3^- formation. The HNO_3 produced in R4 was not considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here, k_{NO3} and k_{N2O5} denote the pseudo-first-order reaction rate constants of the total NO_3 reactivity caused by ambient VOCs and N_2O_5 heterogeneous uptake, respectively. k_{N2O5} is given in Eq. 6. S_a is the aerosol surface area, C is the mean molecular speed of N_2O_5, and γ_{N2O5} is the N_2O_5 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 set to 14.5 h from sunset to sunrise.

$$\frac{\mathrm{d}[O_3]}{\mathrm{d}t} = -k_{NO2+O3}[O_3][NO_2] \quad (1)$$

$$\frac{\mathrm{d}[NO_2]}{\mathrm{d}t} = -(1 + \mathrm{s(t)}) \times k_{NO2+O3}[O_3][NO_2] \quad (2)$$

$$\frac{\mathrm{d}[NO_3+N_2O_5]}{\mathrm{d}t} = k_{NO2+O3}[O_3][NO_2] - k_{N2O5}[N_2O_5] - k_{NO3}[NO_3] \quad (3)$$

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

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

$$k_{N2O5} = \frac{C \times S_a \times \gamma_{N2O5}}{4} \quad (6)$$

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 ~30%, which was associated with the error from dry PNSD measurement (~20%) and the growth factor (~20%). Nighttime averaged S_a on the night of December 19 was about 3000 $\mu m^2\ cm^{-3}$. PM measurements at the National Monitoring Sites proved this heavy haze pollution episode was a typical regional event (Fig. S1). Furthermore, synchronous study on the night of December 19, 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 in 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 (01/01/2017 to 01/07/2017), 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 N_2O_5, i.e., 3.6%–4.2%, and an underestimation of pNO_3^- of 0.2%–2.5% when γ_{N2O5} varied from 1×10^{-3} to 0.05.

The N_2O_5 uptake coefficient and $ClNO_2$ 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) shows the significant pNO_3^- suppression of N_2O_5 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 $ClNO_2$ 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_{ClNO2} to zero. Previous work showed the averaged k_{NO3} was 0.01 - 0.02 s^{-1} in summer Beijing, with BVOCs contributing significantly (Wang H et al., 2017a; Wang et al., 2018). The intensity of BVOCs emissions decreased in wintertime, owing to the lower temperature and weak solar radiation, thus the k_{NO3} should be smaller than it is in summer. In this work, the model input k_{NO3} was set to an arbitrary and relatively high value of 0.02 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 N_2O_5 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, included the test of N_2O_5 uptake coefficient and k_{NO3}. The γ_{N2O5} sensitivity tests were set from 0.001 to 0.05, and the k_{NO3} tests were set to 0.001 s^{-1}, 0.01 s^{-1}, and 0.1 s^{-1}.

In the calculation of the particulate nitration formation by N_2O_5 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 as the degassing of gas phase HNO_3 from particulate nitrate. While in winter Beijing, the mixing ratio of NH_3 was rich to tens of ppbv and always much higher than the nocturnal gas phase HNO_3 (e.g., Liu et al., 2017). The high NH_3 suppressed the degassing of particulate nitrate effectively. The measurement of gas phase HNO_3 and pNO_3^- in the surface layer of Beijing showed the soluble nitrate favor to particle phase in winter, especially in 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 December 16 to 22, 2016, in Beijing. Figure 2a shows the time series of $PM_{2.5}$ and other relevant parameters based on

ground measurements at the PKU site. The mass concentration of $PM_{2.5}$ began to increase from December 16, reaching 480 μg m^{-3} on December 20. A fast PM growth event was captured, with an overall increment of 100 μg m^{-3} on the night of December 19 (Fig. 2a). Throughout the pollution episode, the meteorological conditions included high RH (50% ± 16%) and low temperature (2 ± 3 °C). The slow surface wind speed (< 3 m s^{-1}) implied the atmosphere was stable (Fig. 2c, d). The daytime O_3 concentration was low, owing to high NO emission and weak solar radiation. After sunset, O_3 at surface layer was rapidly titrated to zero by the elevated NO. The presence of high NO concentrations would have strongly suppressed the concentration of NO_3, further suppressing N_2O_5 near the ground. Figure 2b depicts the high amounts of NO and NO_2 that were observed at ground level during the PM pollution episode, suggesting that pNO_3^- production via N_2O_5 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 December 20 (Fig. 3a), the NO_2 and NO from 0 – 240 m were abundant and conservative around 21:00, with concentrations of 80 ppbv and 100 ppbv, respectively. The O_3 concentrations remained zero during the nighttime (Fig. 3b). The vertical profile on December 20 suggests that at least below 240 m, the N_2O_5 chemistry was not important, which is consistent with the results at ground level as mentioned above. The vertical profile on December 19 was different with that on December 20. Figure 4a shows the vertical profiles around 21:00 on December 19; NO was abundant from the ground to 100 m, then gradually decreased to zero from 100 m to 150 m, and remained at zero above 150 m. The observed NO_2 concentration was 85 ± 2 ppbv below 100 m, which gradually decreased from 100 m to 150 m, and was 50 ± 2 ppbv from 150 m to 240 m. The observed O_3 concentrations below 150 m were below the instrumental limit of

detection (Fig. 4b). Above 150 m, the O_3 concentration was 20 ± 2 ppbv, corresponding to zero NO concentration. With respect to O_x, the mixing ratio of O_x was 85 ± 2 ppbv at lower altitudes, whereas the O_x concentration at higher altitudes was 15 ppbv lower than that 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, O_3, and O_x at 09:30 on the morning of December 20, which have similar features to those observed at 21:00 on December 19. The vertical profiles suggested 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 December 19 to 20. Figure S3 shows the vertical profiles of NO, NO_2, O_3, and O_x at ~12:00 on December 18, when solar radiation was strong enough to mix the trace gases well in the vertical direction. NO_x and O_3 were found to be well mixed indeed, with small variation from the ground level to 260 m.

3.3 Particulate nitrate formation aloft.

N_2O_5 uptake is one of the two most important pathways of ambient NO_x loss and pNO_3^- formation (Wagner et al., 2013; Stutz et al., 2010; Tsai et al., 2014). At high altitudes (e.g., > 150 m), NO_3 and N_2O_5 chemistry can be initiated in the co-presence of high NO_2 and significant O_3 levels. Therefore, N_2O_5 uptake could represent a plausible explanation for the O_x observed missing at high altitude on the night of December 19. To explore this phenomenon, a time-step box model was used to simulate the NO_3 and N_2O_5 chemistry based on the observed vertical profiles of NO_2 and O_3 on the night of December 19.

In the base case, the average initial NO_2 and O_3 levels above 150 m at sunset were 61 ± 3 ppbv and 27 ± 6 ppbv, respectively. The measured NO_2 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 rapidly consumption of the formed NO_3. In contrast, the modeled N_2O_5 concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The pNO_3^- formation by N_2O_5 heterogeneous uptake from sunset to the measurement time can be calculated using Eq. 7, which was significant of 24 μg m^{-3} after sunset above 150 m. The pNO_3^- formed in 4.5 hours was equivalent to 13 ppbv O_x loss and consistent with the observation (15 ppbv) (Fig. 6b). Where the 1.5:1 relationship between O_x and pNO_3^- was used to calculate the O_x equivalence (S. S. Brown et al., 2006).

$$\sum \mathrm{pNO_3^-} = \int_0^t (2 - f) \cdot k_{\mathrm{N2O5}} \cdot [\mathrm{N_2O_5}]dt \quad (7)$$

The box model enabled the analysis of the integrated pNO_3^- and $ClNO_2$ via N_2O_5 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 sunrise was equal to the loss of 27 ppbv O_x, showing a good agreement with the observed O_x missing (25 ppbv) aloft in the morning hours. During the nighttime, the pNO_3^- formed aloft via N_2O_5 uptake led to the much higher particle nitrate concentration than that in the surface layer, which has been reported in many field observations (Watson et al., 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 et al., 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 December 19 to 20, 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 m to 340 m is 50 μg m^{-3} during the nighttime and well mixed within the PBL in the next morning, the pNO_3^- enhancement at the surface layer (ΔpNO_3^-) can be simplified to the calculation in Eq. 8 as following:

$$\Delta \mathrm{pNO_3} = \frac{\int_0^{150} P(\mathrm{pNO_3})dH + \int_{150}^{340} P(\mathrm{pNO_3})dH}{340} \quad (8)$$

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 N_2O_5 uptake was zero. The enhancement of pNO_3^- from 150 m to 340 m was calculated as 28 μg m^{-3}, which is in good agreement with the observed PM peak in the morning on December 20, with PM enhancement of ~60 μg m^{-3}. The result demonstrated that the nocturnal N_2O_5 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 H et al., 2016), which is the main source of uncertainties in this model. In the present research, sensitivity studies showed the modeled N_2O_5 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 N_2O_5 concentration is very sensitive to the loss from heterogeneous reactions. Compared to the base case, the accumulated pNO_3^- was evidently lower at $\gamma = 0.001$ (44 μg m^{-3}). Low N_2O_5 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 et al., 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 $ClNO_2$ yield. The conversion of NO_x to pNO_3^- was not limited by the N_2O_5 heterogeneous reaction rate, but limited by the formation of NO_3 via the reaction of NO_2 with O_3 during the polluted night.

For describing the nocturnal NO_x removal capacity and pNO_3^- formation via NO_3 and N_2O_5 chemistry, the overnight NO_x loss efficiency (ε) was calculated using Eq. 9.

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

The case modeled typical winter haze pollution conditions in Beijing from sunset to sunrise, with the initial model values of NO_2 and O_3 set to 60 ppbv and 30 ppbv,

respectively. S_a was set to 3000 μm^2 cm^{-3}, the $ClNO_2$ yield was zero, and k_{NO3} was 0.02 s^{-1}. The reaction time was set to 14.5 h to represent an overnight period in wintertime. The consumed NO_3 by the reaction with VOCs and N_2O_5 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 γ_{N2O5}, which is similar to the result addressed by Chang et al. (2011). The ceiling of overnight NO_x loss via NO_3-N_2O_5 chemistry was fixed when all the NO_x loss was through N_2O_5 uptake in polluted days, which is limited by the reaction time and the formation rate of NO_3 (R1). In this case, the N_2O_5 uptake contributed about 90% of the overnight NO_x loss (50.4%) when γ_{N2O5} was equal to 2×10^{-3}. When γ_{N2O5} was less than 2×10^{-3}, NO_x removal increased rapidly with the increasing of γ_{N2O5}, which was defined as the γ_{N2O5}-sensitive region. When $\gamma_{N2O5} \geq 2\times10^{-3}$, the contribution of N_2O_5 uptake to NO_x loss was over 90% and became insensitive. This region was defined as the γ_{N2O5}-insensitive region. According to Eqs. 3 and 5, high S_a, high NO_x, low k_{NO3} or low temperature allow the N_2O_5 uptake more easily located in the γ_{N2O5}-insensitive region. Here, the critical value of the N_2O_5 uptake coefficient (2×10^{-3}) was relatively low compared with that recommended for the surface of mineral dust (0.013, 290-300K) (Crowley et al., 2010b; Tang et al., 2017) or determined in many field experiments (e.g., S. S. Brown et al., 2006; 2009; Wagner et al., 2013; Morgan et al., 2015; Phillips et al., 2016; Wang Z et al., 2017; Brown et al., 2016; Wang H et al., 2017b; Wang X et al., 2017). This suggests that the NO_x loss and pNO_3^- formation by N_2O_5 uptake were easily maximized in the pollution episode, and further worsening the PM pollution.

In the base case, the modeled pNO_3^- formation via N_2O_5 uptake was an upper limit result, as the $ClNO_2$ 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 chloride-containing aerosols to form $ClNO_2$ via N_2O_5 uptake aloft, implying that significant $ClNO_2$ formed in the upper layer of the NBL (Tham et al.,

2016; Wang Z et al., 2017). Assuming the $ClNO_2$ yield is the average value of 0.28 determined at high altitude in north China (Wang Z et al., 2017), the pNO_3^- produced throughout the night decreased 7 μg m^{-3}. The modeled formation of $ClNO_2$ aloft throughout the night was 2.5 ppbv, which is comparable with the observation in North China (Tham et al., 2016; Wang Z et al., 2017; Wang X et al., 2017). Since the modeled pNO_3^- formation is sensitive to the $ClNO_2$ yield, a higher yield would increase the model uncertainty directly, hence probing the $ClNO_2$ yield is warranted in future studies. As for NO_3 reactivity, Fig. 8 shows the sensitivity tests of the integral pNO_3^- formation for the whole night at k_{NO3} values = 0.001 s^{-1}, 0.01 s^{-1}, 0.02 s^{-1}, and 0.05 s^{-1}. The integral pNO_3^- formation decreased when k_{NO3} varied from 0.001 s^{-1} to 0.1 s^{-1}, but the variation ratio to the base case was within 5%. The result shows the NO_3-N_2O_5 loss via NO_3 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 N_2O_5 uptake was extremely low (e.g., $\gamma_{N2O5} < 10^{-4}$), the uncertainty of NO_3 oxidation would increase significantly.

The uncertainty caused by the physical changes of the air masses were analyzed from two folds, 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 NO_2, O_3, NO_3 and N_2O_5, and leads to a lower contribution to the 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 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 in fact. 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, sensitivities tests of the box model to shorting the duration of 25%, the bias of the integrated pNO_3^- throughout the night was small within 12% relative to 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. Conclusion

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 N_2O_5 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 break-up of the NBL in the morning.

Our result emphasized the importance of the heterogeneous chemistry aloft 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 altitude above urban Beijing, even with 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 probing the ground-level PM pollution problem. In the future, direct observations of N_2O_5 and 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 the

winter haze formation.

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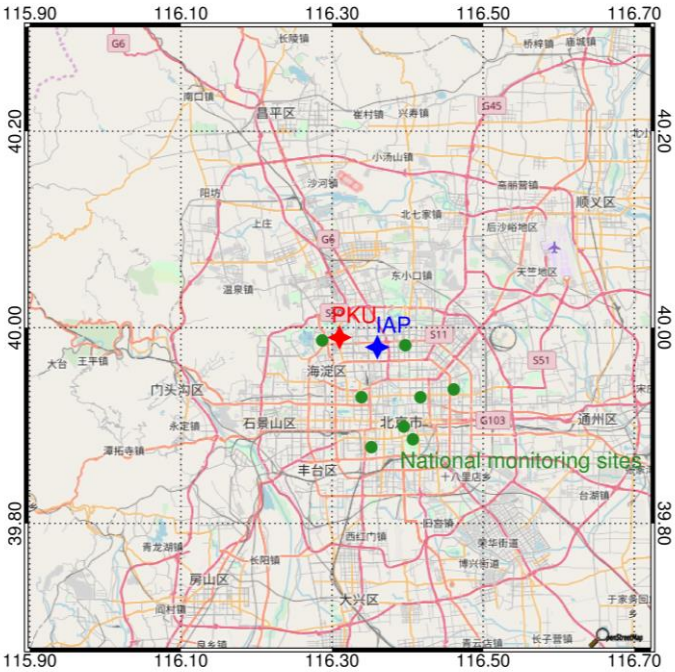
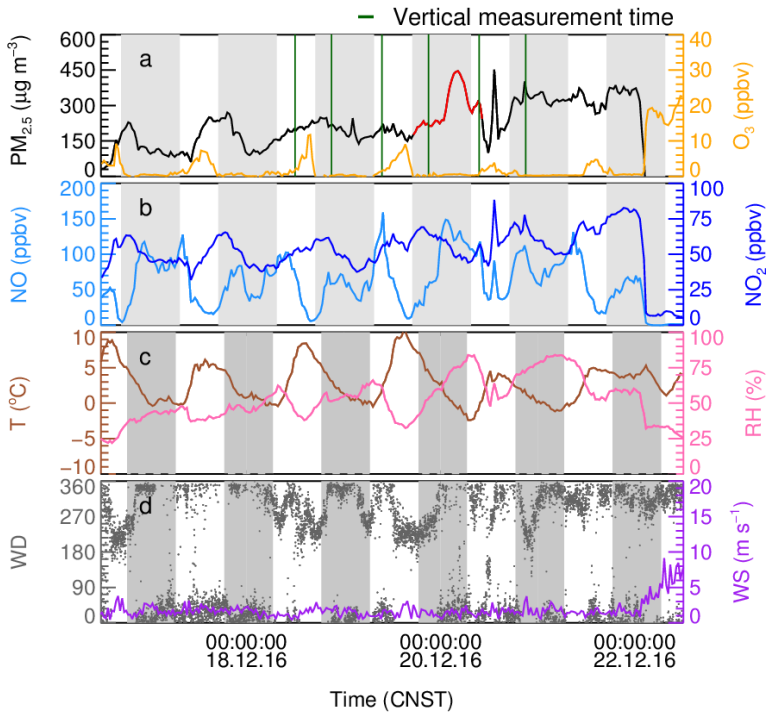
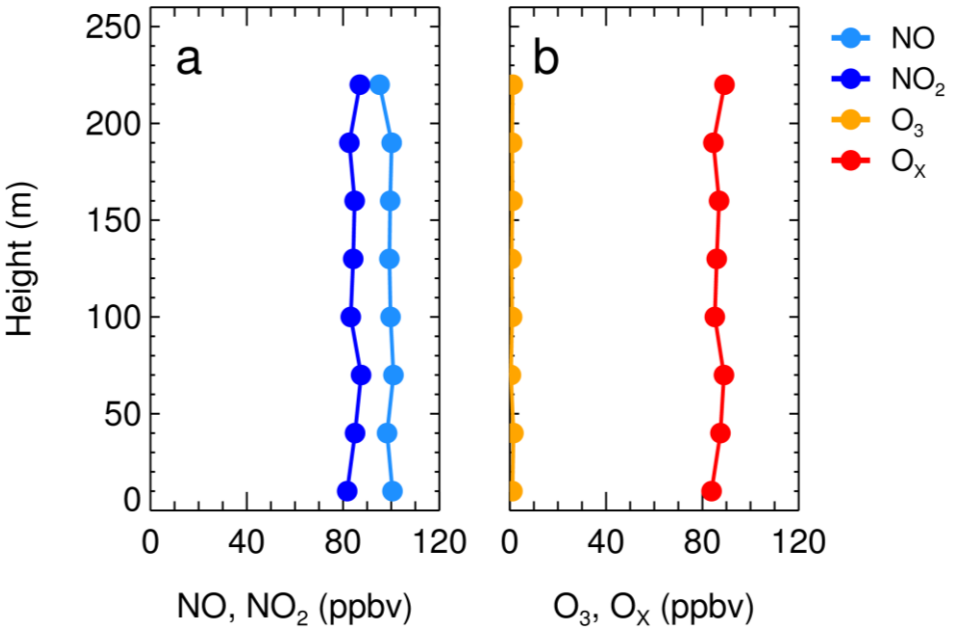


Figure 1. Location of the monitoring sites used in this study, including PKU (red diamond), IAP (blue diamond), and other National Monitoring Sites (green circles). Vertical profiles of NO_x and O_3 were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate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



737

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



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745 **Figure 3.** Vertical profiles of NO and NO_2 (**a**), O_3 and O_x (**b**) at 20:38-21:06 on the
746 night of December 20, 2016.
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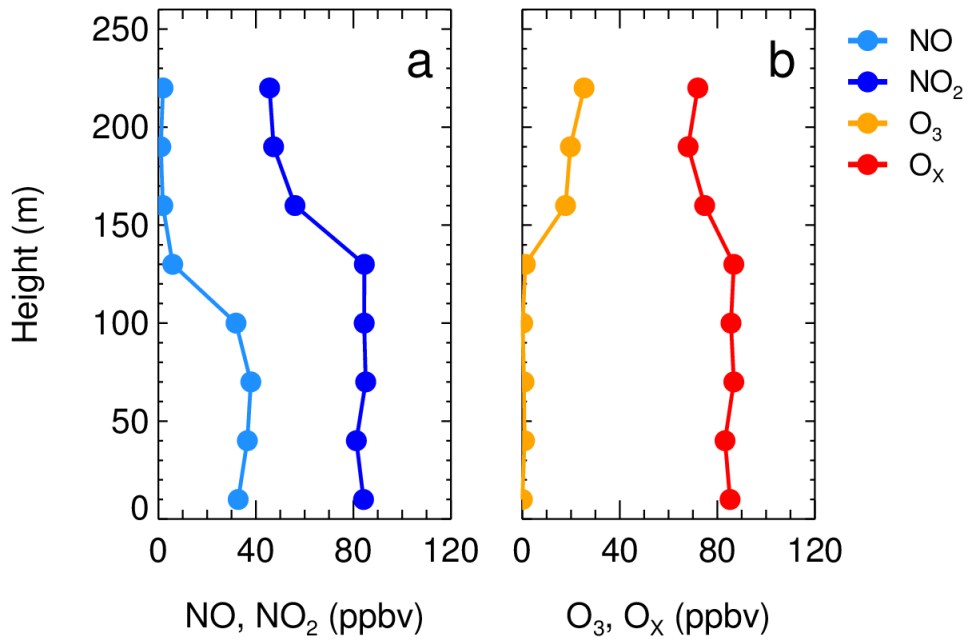

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749 **Figure 4.** O_x missing case presented by the vertical profiles of (**a**) NO and NO_2, (**b**)
750 O_3 and O_x at 20:38-21:13 on the night of December 19, 2016.

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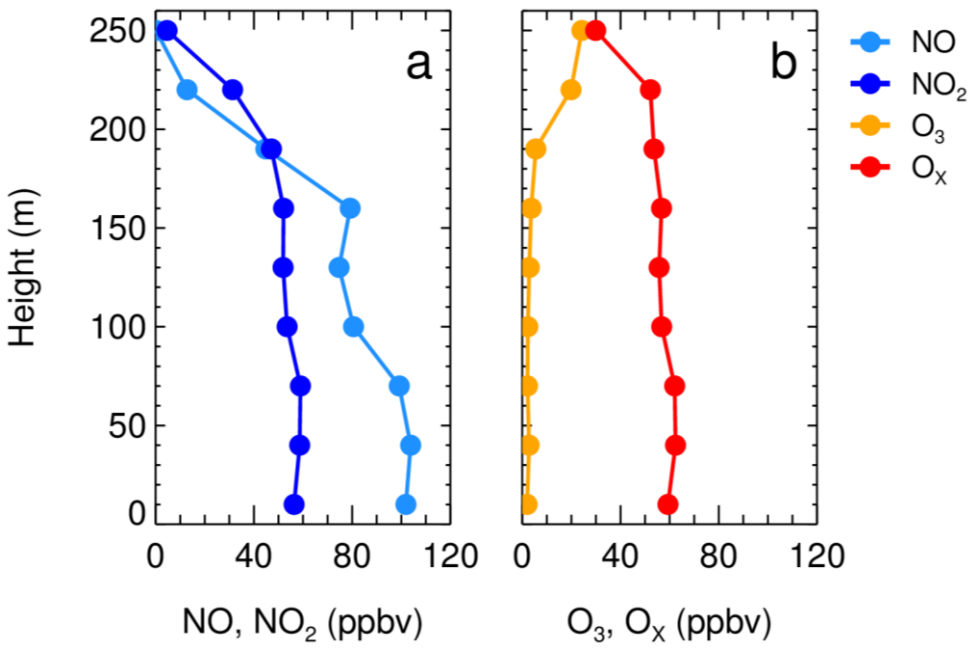

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753 **Figure 5.** Vertical profiles of (**a**) NO and NO_2, (**b**) O_3 and O_x at 09:06-09:34 in the
754 morning of December 20, 2016.

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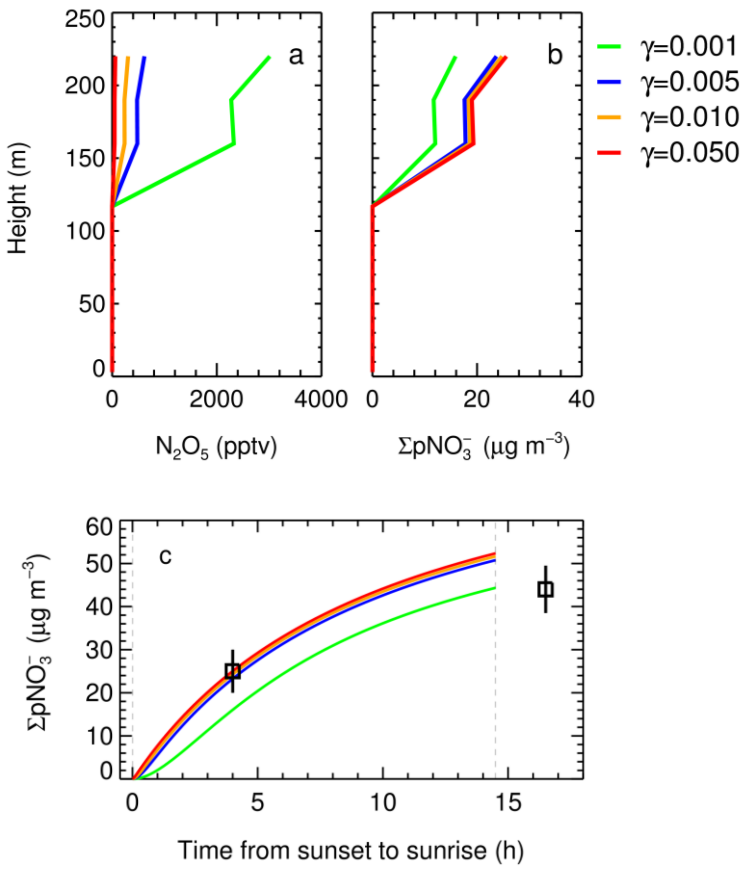
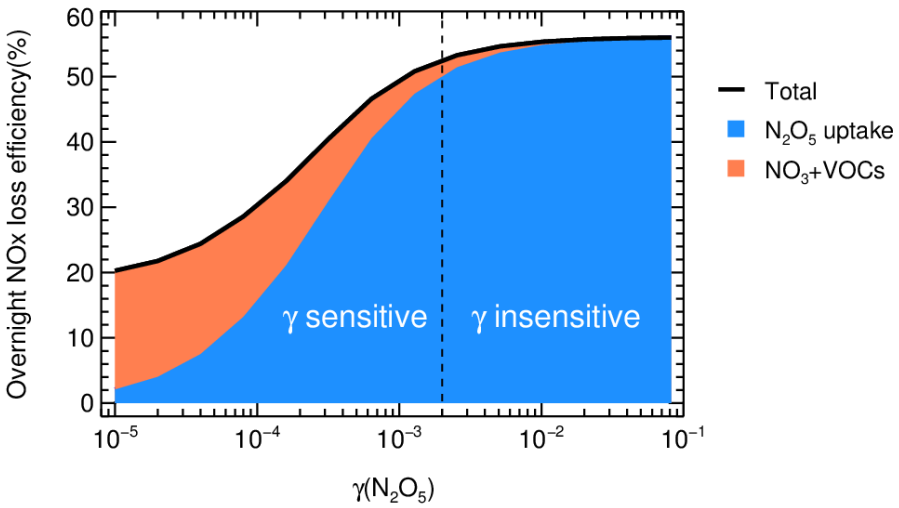


Figure 6. Base case (γ=0.005) and sensitivity tests of the vertical profile on the night of December 19 at different N_2O_5 uptake coefficients, including **(a)** the mixing ratio of N_2O_5 at 21:00, **(b)** the integral pNO_3^- production from sunset to 21:00, **(c)** the time series of the integral pNO_3^- formed at 240 m via N_2O_5 uptake from sunset (17:00) to sunrise (07:30, nighttime length = 14.5 h), the squares represents the pNO_3^- equivalent weight from the observed O_x missing in the two vertical measurements ~21:00 and ~09:30 in the following morning.



766

767 **Figure 7.** The dependence of overnight NO_x loss via N_2O_5 uptake on γ_{N2O5} in a typical
768 winter pollution condition. The initial NO_2 and O_3 were set to 60 ppbv and 30 ppbv,
769 respectively, S_a was set to 3000 μm^2 cm^{-3}, the $ClNO_2$ yield was zero and k_{NO3} was 0.02
770 s^{-1}. The reaction time was set to 14.5 h. The blue and orange zone represent the
771 contribution by NO_3+VOCs and N_2O_5 uptake, the dashed line (γ = 0.002, when N_2O_5
772 uptake contribute to 90% of the maximum NO_x loss) divide the loss into γ sensitive
773 and insensitive region. The maximum nocturnal NO_x loss by NO_3-N_2O_5 chemistry is
774 56%.

775

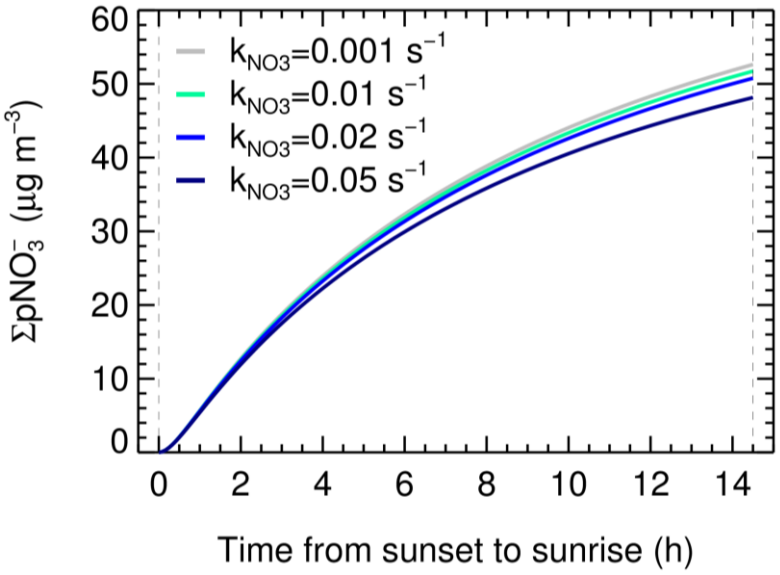


Figure 8. Base case (k_{NO3}=0.02 s^{-1}) and sensitivity tests of the integral pNO_3^- formed at 240 m via N_2O_5 uptake at different NO_3 reactivity (0.001 s^{-1}, 0.01 s^{-1}, 0.05 s^{-1}) on the whole night of December 19, 2016.

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

Cases	k_{NO3} (s^{-1})	γ_{N2O5}
Base case	0.02	0.005
k_{NO3} test 1	0.001	0.005
k_{NO3} test 2	0.01	0.005
k_{NO3} test 3	0.05	0.005
γ_{N2O5} test 1	0.02	0.001
γ_{N2O5} test 2	0.02	0.01
γ_{N2O5} test 3	0.02	0.05

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