



# Fast particulate nitrate formation via $\text{N}_2\text{O}_5$ uptake aloft in winter in Beijing

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**Abstract.** Particulate nitrate ( $p\text{NO}_3^-$ ) 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  $\text{NO}_x$  and  $\text{O}_3$  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  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  heterogeneous uptake was negligible at ground level due to  $\text{N}_2\text{O}_5$  concentrations of near zero controlled by high  $\text{NO}$  emissions and  $\text{NO}$  concentration. In contrast, the contribution from  $\text{N}_2\text{O}_5$  uptake was large at high altitudes (e.g.,  $> 150$  m), which was supported by the lower total oxidant ( $\text{NO}_2 + \text{O}_3$ ) level at high altitudes than at ground level. Modeling results show the specific case that the nighttime integrated production of  $p\text{NO}_3^-$  for the high-altitude air mass above urban Beijing was estimated to be  $50 \mu\text{g m}^{-3}$  and enhanced the surface-layer  $p\text{NO}_3^-$  the next morning by  $28 \mu\text{g m}^{-3}$  through vertical mixing. Sensitivity tests suggested that the nocturnal  $\text{NO}_x$  loss by  $\text{NO}_3$ – $\text{N}_2\text{O}_5$  chemistry was maximized once the  $\text{N}_2\text{O}_5$  uptake coefficient was over  $2 \times 10^{-3}$  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  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  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 ( $p\text{NO}_3^-$ ) is an important component of secondary inorganic aerosols and contributes 15–40 % of the  $\text{PM}_{2.5}$  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  $\text{NO}_2$  and (2)  $\text{N}_2\text{O}_5$  heterogeneous hydrolysis (Seinfeld and Pandis, 2006). The reaction of OH with  $\text{NO}_2$  is a daytime pathway, as OH is very low in concentration at night, and  $\text{N}_2\text{O}_5$  uptake is a nighttime pathway, as  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are easily photolabile.

Particulate nitrate formation via  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  hydrolysis is responsible for nocturnal  $p\text{NO}_3^-$  enhancement in summer in Beijing (Pathak et al., 2009, 2011; Wang et al., 2017a). Although  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in  $\text{N}_2\text{O}_5$  chemistry exist between winter and summer. First, as the key precursor of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ ,  $\text{O}_3$  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  $\text{NO}_2$  levels favor partitioning towards  $\text{N}_2\text{O}_5$ . Third, longer nighttime length in winter makes  $\text{N}_2\text{O}_5$  heterogeneous hydrolysis potentially more important in  $p\text{NO}_3^-$  formation. Finally, the  $\text{N}_2\text{O}_5$  uptake coefficient, as an important parameter in  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  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; Grzanic et al., 2015). Several parameterization methods did not have good performance in predicting  $\text{N}_2\text{O}_5$  uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences in  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  uptake, modeling and field studies showed high levels of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  at high altitudes within the nocturnal boundary layer (NBL) owing to the stratification of surface  $\text{NO}$  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  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  uptake contributes to the gradients in the compound percentage and size distribution of the particle (Ferrero et al., 2010, 2012). On nights when  $\text{NO}_3$  cannot accumulate in the surface layer owing to high  $\text{NO}$  emissions,  $\text{N}_2\text{O}_5$  uptake can still be active aloft without  $\text{NO}$  titration. The  $\text{N}_2\text{O}_5$  uptake aloft leads to elevated  $p\text{NO}_3^-$  formation in the upper layer as well as effective  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  concentrations aloft. Model studies showed that  $p\text{NO}_3^-$  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  $p\text{NO}_3^-$  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).

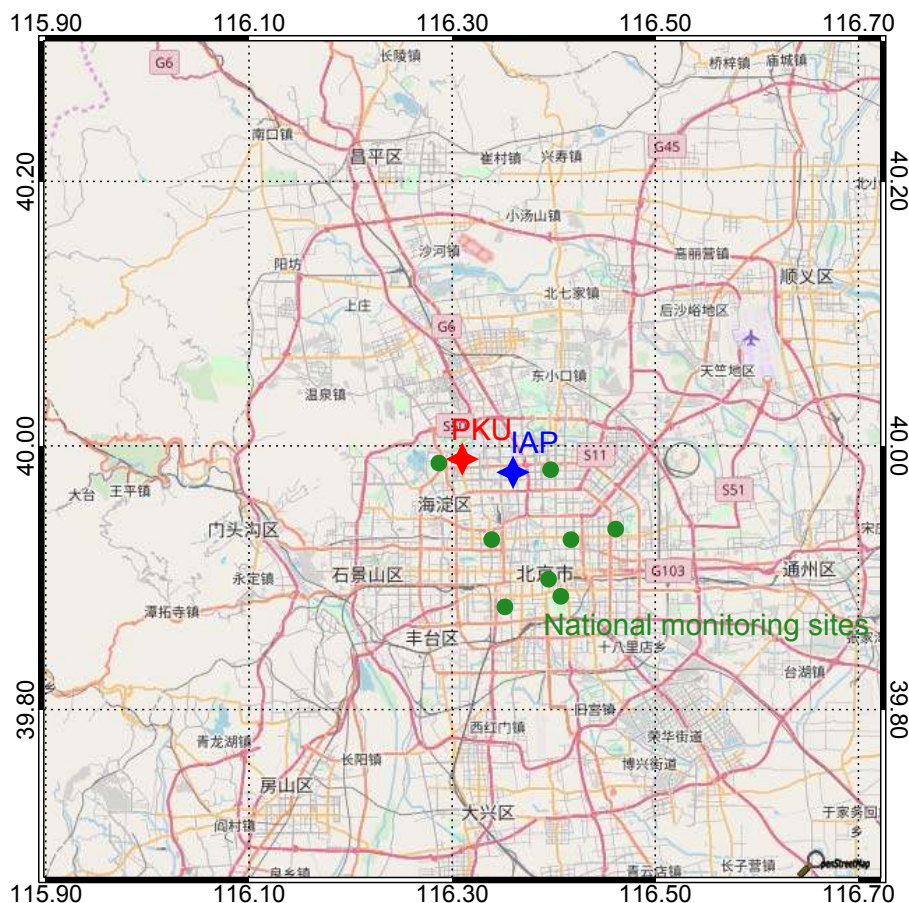
To explore the possible sources of  $p\text{NO}_3^-$  and the dependence of its formation on altitude in wintertime in Beijing, we conducted vertical profile measurements of  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$  with a moving cabin at a tower platform in combination with simultaneous ground measurements of more comprehensive parameters in urban Beijing. A box model was used to investigate the reaction rate of  $\text{N}_2\text{O}_5$  heterogeneous hydrolysis and its impact on  $p\text{NO}_3^-$  formation at different altitudes during a heavy-haze episode over urban Beijing. Additionally, the dependence of  $\text{NO}_x$  removal and  $p\text{NO}_3^-$  formation on the  $\text{N}_2\text{O}_5$  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;  $39^\circ 59' 21''$  N,  $116^\circ 18' 25''$  E) in Beijing, China. The vertical measurements were conducted at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences ( $39^\circ 58' 28''$  N,  $116^\circ 22' 16''$  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  $\text{PM}_{2.5}$  was measured using a TEOM 1400A analyzer.  $\text{NO}_x$  was measured via a chemiluminescence analyzer (Thermo Scientific, TE-42i-TR), and  $\text{O}_3$  was measured with a UV photometric  $\text{O}_3$  analyzer (Thermo Scientific, TE-49i). Dry-state particle number and size distribution (PNSD) were measured from 0.01 to  $0.7\ \mu\text{m}$  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  $\text{NO}_x$  and  $\text{O}_3$  instruments were installed aboard a movable cabin on the tower.  $\text{NO}_x$  and  $\text{O}_3$  were measured with two low-power, lightweight instruments (model 405 nm and model 106-L, 2B Technologies, USA). The model 405 nm instrument measures  $\text{NO}_2$  directly based on the absorbance at 405 nm, and  $\text{NO}$  is measured by adding excess  $\text{O}_3$  (conversion efficiency  $\sim 100\%$ ). The limit of detection of both  $\text{NO}$  and  $\text{NO}_2$  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  $\text{O}_3$  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.  $\text{NO}_x$  calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with an  $\text{NO}$  standard (9.8 ppmv). The  $\text{O}_3$  calibration was done with an  $\text{O}_3$  calibrator (TE 49i-PS), which was traceable to NIST

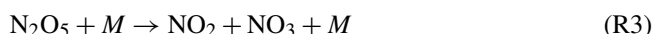
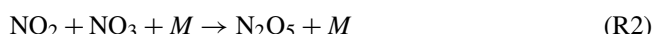


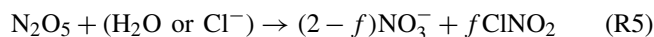
**Figure 1.** Location of the monitoring sites used in this study, including PKU (red diamond), IAP (blue diamond), and other national monitoring sites (green circles). Vertical profiles of  $\text{NO}_x$  and  $\text{O}_3$  were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate  $\text{N}_2\text{O}_5$  and particle nitrate formation) were collected from a ground site at PKU. Additional measurements of  $\text{PM}_{2.5}$  concentrations were continuously taken at national monitoring sites throughout Beijing.

(National Institute of Standards and Technology) standards annually. Before the campaign, the  $\text{NO}_x$  monitor was compared with a cavity attenuated phase shift (CAPS) particle light extinction monitor, and the  $\text{O}_3$  monitor was compared to a commercial  $\text{O}_3$  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  $10 \text{ m min}^{-1}$ , 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 Reactions R1–R5) was used in a box model to simulate the nighttime  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  chemistry under  $\text{NO}$  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  $\text{ClNO}_2$  yield from  $\text{N}_2\text{O}_5$  uptake. Homogeneous hydrolysis of  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  heterogeneous uptake reaction were neglected in this analysis because of the low level of absolute humidity and the extremely low  $\text{NO}_3$  concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of Reactions (R1)–(R3) are those reported by Sander et al. (2011).





Following the work of Wagner et al. (2013), the box model can be solved using six equations (Eqs. 1–6). In the framework,  $\text{O}_3$  is only lost via the reaction of  $\text{NO}_2 + \text{O}_3$  and the change in the  $\text{O}_3$  concentration can be expressed as Eq. (1). Equation (2) can express the losses of  $\text{NO}_2$ . 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  $\text{NO}_3$  production, which goes through  $\text{N}_2\text{O}_5$  (either as  $\text{N}_2\text{O}_5$  or lost through uptake) to the total  $\text{NO}_3$  production (Wagner et al., 2013). The  $s(t)$  favors 0 when direct loss of  $\text{NO}_3$  dominates and favors 1 when  $\text{N}_2\text{O}_5$  uptake dominates  $\text{NO}_3$  loss. The model calculation has two steps. The first step is to calculate the mixing ratio of  $\text{NO}_2$  and  $\text{O}_3$  at time zero (herein designated as sunset). According to Eqs. (1) and (2), the initial  $\text{NO}_2$  ( $t = 0$ ) and  $\text{O}_3$  ( $t = 0$ ) concentrations can then be integrated backward in time starting with the measured concentrations of  $\text{NO}_2$  and  $\text{O}_3$  at each height. During the pollution period in winter in Beijing ( $\text{NO}_2 = 45$  ppbv, temperature = 273 K,  $S_a = 3000 \mu\text{m}^2 \text{cm}^{-3}$ ), the ratio of  $\text{N}_2\text{O}_5$  to  $\text{NO}_3$  is large enough, i.e., 450. The pseudo-first-order loss rate of  $\text{N}_2\text{O}_5$  heterogeneous uptake will be  $1 \times 10^{-3} \text{s}^{-1}$ , with an  $\text{N}_2\text{O}_5$  uptake coefficient of  $5 \times 10^{-3}$ .  $\text{N}_2\text{O}_5$  uptake contributes to the  $\text{NO}_3$  loss rate of  $0.4 \text{s}^{-1}$ , which is much higher than the direct  $\text{NO}_3$  loss through the reaction of  $\text{NO}_3$  with VOCs. Therefore,  $\text{N}_2\text{O}_5$  uptake was proposed to be dominantly responsible for the  $\text{NO}_3$  loss and the initial  $s(t)$  was set to 1. Equation (3) can describe the sum concentration of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ . Assuming that equilibrium between  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  is maintained after a certain period, based on the temperature-dependent equilibrium rate constant ( $k_{\text{eq}}$ ) and the modeled  $\text{NO}_2$  at a certain time, Eq. (4) can be used to determine the ratio of  $\text{N}_2\text{O}_5$  to  $\text{NO}_3$ . Combined, Eqs. (1)–(4) allow for the calculation of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  concentrations considering stable  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  loss rate constants ( $k_{\text{NO}_3}$  and  $k_{\text{N}_2\text{O}_5}$ , respectively). In the second step, a new  $s(t)$  was calculated using the data from the first step (Eq. 5); new initial  $\text{NO}_2$  and  $\text{O}_3$  concentrations were then approximated, and  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  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  $\text{N}_2\text{O}_5$  concentrations and given  $k_{\text{N}_2\text{O}_5}$  were then used to estimate  $p\text{NO}_3^-$  formation. The  $\text{HNO}_3$  produced in Reaction (R4) was not considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here,  $k_{\text{NO}_3}$  and  $k_{\text{N}_2\text{O}_5}$  denote the pseudo-first-order reaction rate constants of the total  $\text{NO}_3$  reactivity caused by ambient VOCs and  $\text{N}_2\text{O}_5$  heterogeneous uptake, respectively.  $k_{\text{N}_2\text{O}_5}$  is given in Eq. (6).  $S_a$  is the aerosol surface area,  $C$  is the mean molecular speed of  $\text{N}_2\text{O}_5$ , and  $\gamma_{\text{N}_2\text{O}_5}$  is the  $\text{N}_2\text{O}_5$  uptake coefficient. Sunset and sunrise times during the mea-

surements 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.

$$\frac{d[\text{O}_3]}{dt} = -k_{\text{NO}_2+\text{O}_3}[\text{O}_3][\text{NO}_2] \quad (1)$$

$$\frac{d[\text{NO}_2]}{dt} = -(1 + s(t)) \times k_{\text{NO}_2+\text{O}_3}[\text{O}_3][\text{NO}_2] \quad (2)$$

$$\frac{d[\text{NO}_3 + \text{N}_2\text{O}_5]}{dt} = k_{\text{NO}_2+\text{O}_3}[\text{O}_3][\text{NO}_2] - k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5] - k_{\text{NO}_3}[\text{NO}_3] \quad (3)$$

$$\frac{[\text{N}_2\text{O}_5]}{[\text{NO}_3]} = k_{\text{eq}}[\text{NO}_2] \quad (4)$$

$$s(t) = \frac{\int_0^t k_{\text{N}_2\text{O}_5} \cdot [\text{N}_2\text{O}_5] dt + [\text{N}_2\text{O}_5]_t}{[\text{O}_3](0) - [\text{O}_3](t)} \quad (5)$$

$$k_{\text{N}_2\text{O}_5} = \frac{C \times S_a \times \gamma_{\text{N}_2\text{O}_5}}{4} \quad (6)$$

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  $\sim 30\%$ , 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  $0.7 \mu\text{m}$  was not valid during the study period, the particles smaller than  $0.7 \mu\text{m}$  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  $\text{N}_2\text{O}_5$ , i.e., 3.6–4.2 %, and an underestimation of  $p\text{NO}_3^-$  of 0.2–2.5 % when  $\gamma_{\text{N}_2\text{O}_5}$  varied from  $1 \times 10^{-3}$  to 0.05.

The  $\text{N}_2\text{O}_5$  uptake coefficient and  $\text{ClNO}_2$  yield are key parameters in the estimation of  $p\text{NO}_3^-$  formation (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016). Wagner et al. (2013) show the significant  $p\text{NO}_3^-$  suppression of  $\text{N}_2\text{O}_5$  uptake aloft in the wintertime in Denver, CO, USA; the uptake coefficient is 0.005 when the percentage of  $p\text{NO}_3^-$  in the  $\text{PM}_{2.5}$  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  $\text{ClNO}_2$

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

Cases	$k_{\text{NO}_3}$ ( $\text{s}^{-1}$ )	$\gamma_{\text{N}_2\text{O}_5}$
Base case	0.02	0.005
$k_{\text{NO}_3}$ test 1	0.001	0.005
$k_{\text{NO}_3}$ test 2	0.01	0.005
$k_{\text{NO}_3}$ test 3	0.05	0.005
$\gamma_{\text{N}_2\text{O}_5}$ test 1	0.02	0.001
$\gamma_{\text{N}_2\text{O}_5}$ test 2	0.02	0.01
$\gamma_{\text{N}_2\text{O}_5}$ test 3	0.02	0.05

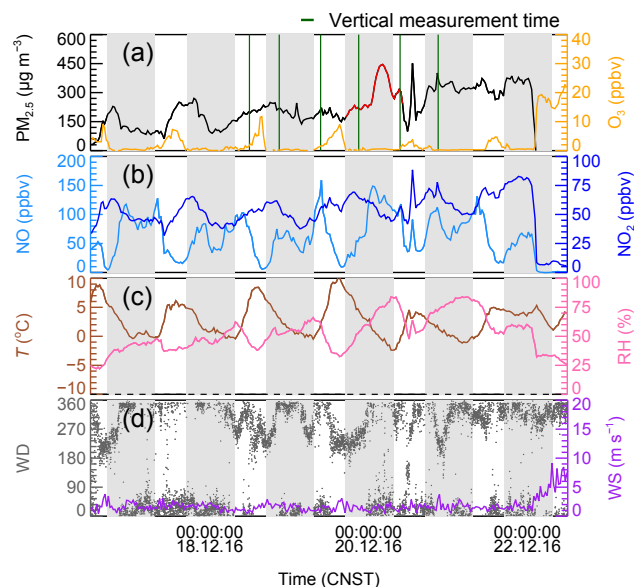
yield only affects the value of produced  $p\text{NO}_3^-$  concentration and would not change the modeled  $\text{N}_2\text{O}_5$  concentration, we set the initial  $f_{\text{ClNO}_2}$  to zero. Previous work showed the averaged  $k_{\text{NO}_3}$  was 0.01–0.02  $\text{s}^{-1}$  in summer in Beijing, 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  $k_{\text{NO}_3}$  should be smaller than it is in summer. In this work, the model input  $k_{\text{NO}_3}$  was set to an arbitrary and relatively high value of 0.02  $\text{s}^{-1}$  (equivalent to 0.2 ppbv isoprene +40 parts per trillion volume (pptv) monoterpene +1.0 ppbv *cis*-2-butene) to constrain the impact of  $\text{N}_2\text{O}_5$  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, including the test of  $\text{N}_2\text{O}_5$  uptake coefficient and  $k_{\text{NO}_3}$ . The  $\gamma_{\text{N}_2\text{O}_5}$  sensitivity tests were set from 0.001 to 0.05, and the  $k_{\text{NO}_3}$  tests were set to 0.001, 0.01, and 0.1  $\text{s}^{-1}$ .

In the calculation of particulate nitration formation by  $\text{N}_2\text{O}_5$  uptake, an assumption is that all soluble nitrate formed from  $\text{N}_2\text{O}_5$  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  $\text{HNO}_3$  from particulate nitrate. While in winter in Beijing, the mixing ratio of  $\text{NH}_3$  was rich to tens of ppbv and always much higher than the nocturnal gas-phase  $\text{HNO}_3$  (e.g., Liu et al., 2017). The high  $\text{NH}_3$  suppressed the degassing of particulate nitrate effectively. The measurement of gas-phase  $\text{HNO}_3$  and  $p\text{NO}_3^-$  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  $p\text{NO}_3^-$  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

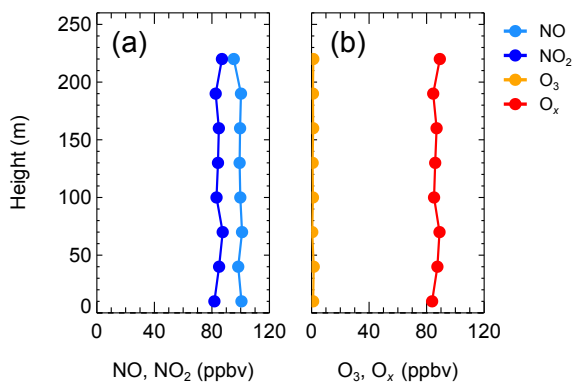


**Figure 2.** Time series of (a)  $\text{PM}_{2.5}$  and  $\text{O}_3$ , (b)  $\text{NO}$  and  $\text{NO}_2$ , (c) temperature ( $T$ ) and relative humidity ( $\text{RH}$ ), and (d) wind direction ( $\text{WD}$ ) and wind speed ( $\text{WS}$ ) from 16 to 22 December 2016 at the PKU site in Beijing, China. The shaded region represents the nighttime periods. The red line in (a) shows an example of fast  $\text{PM}_{2.5}$  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.

$\text{PM}_{2.5}$  and other relevant parameters based on ground measurements at the PKU site. The mass concentration of  $\text{PM}_{2.5}$  began to increase from 16 December, reaching  $480 \mu\text{g m}^{-3}$  on 20 December. A fast PM growth event was captured, with an overall increment of  $100 \mu\text{g m}^{-3}$  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 ( $< 3 \text{ m s}^{-1}$ ) implied the atmosphere was stable (Fig. 2c, d). The daytime  $\text{O}_3$  concentration was low owing to high  $\text{NO}$  emission and weak solar radiation. After sunset,  $\text{O}_3$  at the surface layer was rapidly titrated to zero by the elevated  $\text{NO}$ . The presence of high  $\text{NO}$  concentrations would have strongly suppressed the concentration of  $\text{NO}_3$ , further suppressing  $\text{N}_2\text{O}_5$  near the ground. Figure 2b depicts the high amounts of  $\text{NO}$  and  $\text{NO}_2$  that were observed at ground level during the PM pollution episode, suggesting that  $p\text{NO}_3^-$  production via  $\text{N}_2\text{O}_5$  uptake was not important near the ground during the winter haze episode.

#### 3.2 Tower observations

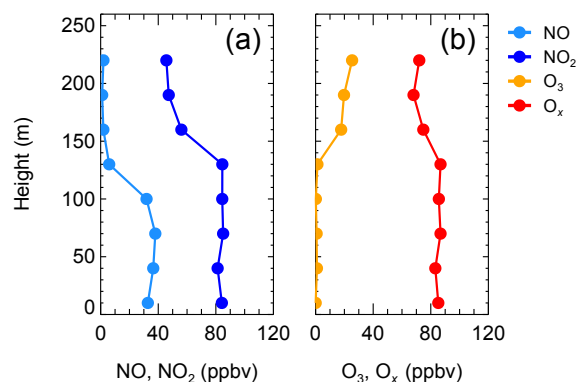
Six vertical measurements of the total oxidants ( $\text{O}_x = \text{O}_3 + \text{NO}_2$ ) below 50 m were consistent with those measured at ground level and are shown in Fig. S2, confirming that the two sites are comparable. On the night of 20 December (Fig. 3a), the  $\text{NO}_2$  and  $\text{NO}$  from 0–240 m were abundant



**Figure 3.** Vertical profiles of NO and NO<sub>2</sub> (a) and of O<sub>3</sub> and O<sub>x</sub> (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 O<sub>3</sub> concentrations remained zero during the nighttime (Fig. 3b). The vertical profile on 20 December suggests that at least below 240 m, the N<sub>2</sub>O<sub>5</sub> 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 NO<sub>2</sub> concentration was  $85 \pm 2$  ppbv below 100 m, which gradually decreased from 100 to 150 m and was  $50 \pm 2$  ppbv from 150 to 240 m. The observed O<sub>3</sub> concentrations below 150 m were below the instrumental limit of detection (Fig. 4b). Above 150 m, the O<sub>3</sub> concentration was  $20 \pm 2$  ppbv, corresponding to zero NO concentration. With respect to O<sub>x</sub>, the mixing ratio of was  $85 \pm 2$  ppbv at lower altitudes, whereas the concentration at higher altitudes was 15 ppbv lower than at lower altitudes (Fig. 4b). The O<sub>x</sub> missing from the higher-altitude air mass indicated an additional nocturnal removal of O<sub>x</sub> aloft.

Figure 5 depicts the vertical profiles of NO<sub>x</sub>, O<sub>3</sub>, and O<sub>x</sub> 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<sub>x</sub> missing aloft in the morning increased to 25 ppbv at 240–260 m, demonstrating that an additional 25 ppbv of O<sub>x</sub> 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, NO<sub>2</sub>, O<sub>3</sub>, and O<sub>x</sub> at ~12:00 on 18 December, when solar radiation was strong enough to mix the trace gases well in the vertical direction. NO<sub>x</sub> and O<sub>3</sub> were found to be well mixed indeed, with small variation from the ground level to 260 m.



**Figure 4.** O<sub>x</sub> missing case presented by the vertical profiles of (a) NO and NO<sub>2</sub> and of (b) O<sub>3</sub> and O<sub>x</sub> at 20:38–21:13 on the night of 19 December 2016.

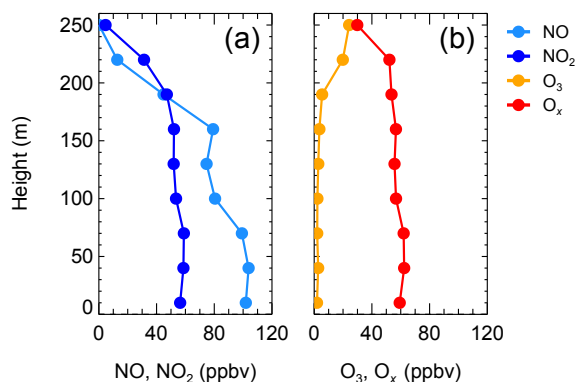
### 3.3 Particulate nitrate formation aloft

N<sub>2</sub>O<sub>5</sub> uptake is one of the two most important pathways of ambient NO<sub>x</sub> loss and pNO<sub>3</sub><sup>-</sup> formation (Wagner et al., 2013; Stutz et al., 2010; Tsai et al., 2014). At high altitudes (e.g., > 150 m), NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> chemistry can be initiated in the co-presence of high NO<sub>2</sub> and significant O<sub>3</sub> levels. Therefore, N<sub>2</sub>O<sub>5</sub> uptake could represent a plausible explanation for the O<sub>x</sub> 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 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> chemistry based on the observed vertical profiles of NO<sub>2</sub> and O<sub>3</sub> on the night of 19 December.

In the base case, the average initial NO<sub>2</sub> and O<sub>3</sub> levels above 150 m at sunset were  $61 \pm 3$  and  $27 \pm 6$  ppbv, respectively. The measured NO<sub>2</sub> 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<sub>2</sub>O<sub>5</sub> concentration was zero below 150 m, as the high level of NO made for rapid consumption of the formed NO<sub>3</sub>. In contrast, the modeled N<sub>2</sub>O<sub>5</sub> concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The pNO<sub>3</sub><sup>-</sup> formation by N<sub>2</sub>O<sub>5</sub> heterogeneous uptake from sunset to the measurement time can be calculated using Eq. (7), which was significant at  $24 \mu\text{g m}^{-3}$  after sunset above 150 m. The pNO<sub>3</sub><sup>-</sup> formed in 4.5 h was equivalent to 13 ppbv O<sub>x</sub> loss and consistent with the observation (15 ppbv; Fig. 6b). The 1.5 : 1 relationship between O<sub>x</sub> and pNO<sub>3</sub><sup>-</sup> was used to calculate the O<sub>x</sub> equivalence (S. S. Brown et al., 2006a).

$$\sum p\text{NO}_3^- = \int_0^t (2 - f) \cdot k_{\text{N}_2\text{O}_5} \cdot [\text{N}_2\text{O}_5] dt \quad (7)$$

The box model enabled the analysis of the integrated pNO<sub>3</sub><sup>-</sup> and ClNO<sub>2</sub> via N<sub>2</sub>O<sub>5</sub> uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO<sub>3</sub><sup>-</sup> went as high as  $50 \mu\text{g m}^{-3}$ . The integrated pNO<sub>3</sub><sup>-</sup> at sunrise was equal to the loss of 27 ppbv O<sub>x</sub>, showing a good agreement with the ob-



**Figure 5.** Vertical profiles of (a) NO and NO<sub>2</sub> and of (b) O<sub>3</sub> and O<sub>x</sub> at 09:06–09:34 on the morning of 20 December 2016.

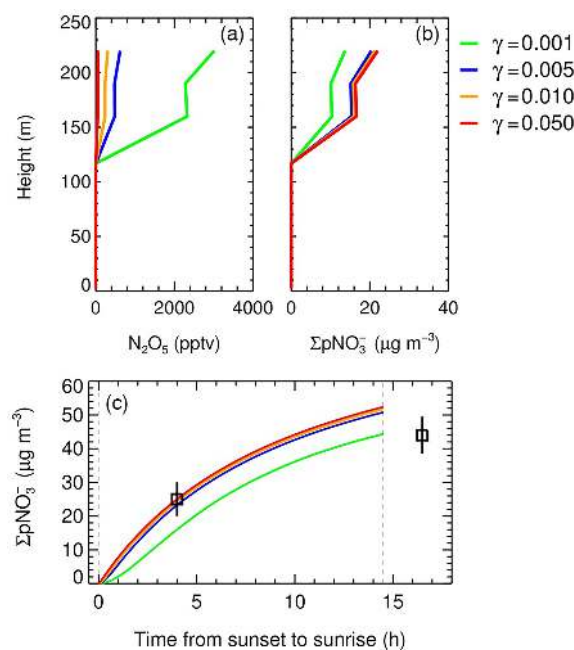
served O<sub>x</sub> missing (25 ppbv) aloft in the morning hours. During the nighttime, the *p*NO<sub>3</sub><sup>-</sup> formed aloft via N<sub>2</sub>O<sub>5</sub> uptake led to a much higher particle nitrate concentration than in the surface layer, which has been reported in many field observations (Watson and Chow, 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Ferrero et al., 2012; Sun et al., 2015b). The elevated *p*NO<sub>3</sub><sup>-</sup> 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 *p*NO<sub>3</sub><sup>-</sup> aloft from 150 to 340 m is 50 μg m<sup>-3</sup> during the nighttime and is well mixed within the PBL the next morning, the *p*NO<sub>3</sub><sup>-</sup> enhancement at the surface layer (Δ*p*NO<sub>3</sub><sup>-</sup>) can be simplified to the calculation in Eq. (8) as follows.

$$\Delta p\text{NO}_3^- = \frac{\int_0^{150} P(p\text{NO}_3^-)dH + \int_{150}^{340} P(p\text{NO}_3^-)dH}{340} \quad (8)$$

Here,  $P(p\text{NO}_3^-)$  is the integral production of *p*NO<sub>3</sub><sup>-</sup> and  $H$  represents height. Owing to high NO below 150 m, the *p*NO<sub>3</sub><sup>-</sup> formation via N<sub>2</sub>O<sub>5</sub> uptake was zero. The enhancement of *p*NO<sub>3</sub><sup>-</sup> from 150 to 340 m was calculated as 28 μg m<sup>-3</sup>, which is in good agreement with the observed PM peak in the morning on 20 December, with PM enhancement of ~60 μg m<sup>-3</sup>. The result demonstrated that the nocturnal N<sub>2</sub>O<sub>5</sub> uptake aloft and downward transportation were critical for understanding the PM growth process.

### 3.4 Sensitivity studies

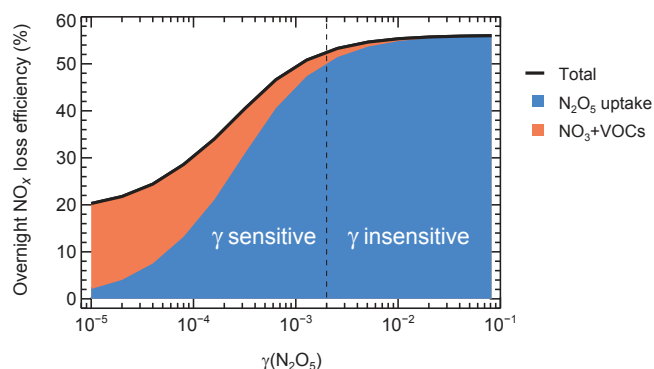
Previous studies have emphasized that the N<sub>2</sub>O<sub>5</sub> uptake coefficient varies greatly (0.001–0.1) in different ambient conditions (Chang et al., 2011; Brown and Stutz, 2012; Wang and Lu, 2016), which is the main source of uncertainties in



**Figure 6.** Base case ( $\gamma = 0.005$ ) and sensitivity tests of the vertical profile on the night of 19 December at different N<sub>2</sub>O<sub>5</sub> uptake coefficients, including (a) the mixing ratio of N<sub>2</sub>O<sub>5</sub> at 21:00, (b) the integral *p*NO<sub>3</sub><sup>-</sup> production from sunset to 21:00, and (c) the time series of the integral *p*NO<sub>3</sub><sup>-</sup> formed at 240 m via N<sub>2</sub>O<sub>5</sub> uptake from sunset (17:00) to sunrise (07:30; nighttime length 14.5 h). The squares represent the *p*NO<sub>3</sub><sup>-</sup> equivalent weight from the observed O<sub>x</sub> 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 N<sub>2</sub>O<sub>5</sub> concentration dropping from 3 ppbv to 60 pptv when the N<sub>2</sub>O<sub>5</sub> uptake coefficients increased from 0.001 to 0.05 (Fig. 6a), as the N<sub>2</sub>O<sub>5</sub> concentration is very sensitive to loss from heterogeneous reactions. Compared to the base case, the accumulated *p*NO<sub>3</sub><sup>-</sup> was evidently lower at  $\gamma = 0.001$  (44 μg m<sup>-3</sup>). Low N<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> uptake coefficient increased from 0.005 to 0.05 (Fig. 6b, c), the increase in integral *p*NO<sub>3</sub><sup>-</sup> was negligible. The conversion capacity of N<sub>2</sub>O<sub>5</sub> uptake to *p*NO<sub>3</sub><sup>-</sup> is maximized for a given fixed value of the ClNO<sub>2</sub> yield. The conversion of NO<sub>x</sub> to *p*NO<sub>3</sub><sup>-</sup> was not limited by the N<sub>2</sub>O<sub>5</sub> heterogeneous reaction rate, but limited by the formation of NO<sub>3</sub> via the reaction of NO<sub>2</sub> with O<sub>3</sub> during the polluted night.

For describing the nocturnal NO<sub>x</sub> removal capacity and *p*NO<sub>3</sub><sup>-</sup> formation via NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> chemistry, the overnight NO<sub>x</sub> loss efficiency ( $\epsilon$ ) was calculated using

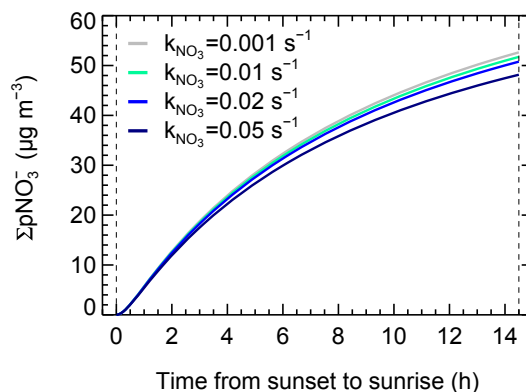


**Figure 7.** The dependence of overnight  $\text{NO}_x$  loss via  $\text{N}_2\text{O}_5$  uptake on  $\gamma_{\text{N}_2\text{O}_5}$  in typical winter pollution conditions. The initial  $\text{NO}_2$  and  $\text{O}_3$  were set to 60 and 30 ppbv, respectively;  $S_a$  was set to  $3000 \mu\text{m}^2 \text{cm}^{-3}$ , the  $\text{ClNO}_2$  yield was zero, and  $k_{\text{NO}_3}$  was  $0.02 \text{s}^{-1}$ . The reaction time was set to 14.5 h. The blue and orange zones represent the contribution by  $\text{NO}_3 + \text{VOCs}$  and  $\text{N}_2\text{O}_5$  uptake, and the dashed line ( $\gamma = 0.002$  when  $\text{N}_2\text{O}_5$  uptake contributes to 90 % of the maximum  $\text{NO}_x$  loss) divides the loss into  $\gamma$ -sensitive and  $\gamma$ -insensitive regions. The maximum nocturnal  $\text{NO}_x$  loss by  $\text{NO}_3$ – $\text{N}_2\text{O}_5$  chemistry is 56 %.

Eq. (9).

$$\varepsilon = \frac{\int_0^t 2 \times k_{\text{N}_2\text{O}_5} \cdot [\text{N}_2\text{O}_5] dt + \int_0^t k_{\text{NO}_3} \cdot [\text{NO}_3] dt}{[\text{NO}_2](0)} \quad (9)$$

The case modeled typical winter haze pollution conditions in Beijing from sunset to sunrise, with the initial model values of  $\text{NO}_2$  and  $\text{O}_3$  set to 60 and 30 ppbv, respectively.  $S_a$  was set to  $3000 \mu\text{m}^2 \text{cm}^{-3}$ , the  $\text{ClNO}_2$  yield was zero, and  $k_{\text{NO}_3}$  was  $0.02 \text{s}^{-1}$ . The reaction time was set to 14.5 h to represent an overnight period in wintertime. The consumed  $\text{NO}_3$  by the reaction with VOCs and  $\text{N}_2\text{O}_5$  by uptake reaction were regarded as  $\text{NO}_x$  removal. Figure 7 shows the dependence of the overnight  $\text{NO}_x$  loss efficiency on the  $\text{N}_2\text{O}_5$  uptake coefficient, as it varied from  $1 \times 10^{-5}$  to 0.1. This is an increase from 20 to 56 % with increasing  $\gamma_{\text{N}_2\text{O}_5}$ , which is similar to the result addressed by Chang et al. (2011). The ceiling of overnight  $\text{NO}_x$  loss via  $\text{NO}_3$ – $\text{N}_2\text{O}_5$  chemistry was fixed when all the  $\text{NO}_x$  loss was through  $\text{N}_2\text{O}_5$  uptake on polluted days, which is limited by the reaction time and the formation rate of  $\text{NO}_3$  (Reaction R1). In this case, the  $\text{N}_2\text{O}_5$  uptake contributed about 90 % of the overnight  $\text{NO}_x$  loss (50.4 %) when  $\gamma_{\text{N}_2\text{O}_5}$  was equal to  $2 \times 10^{-3}$ . When  $\gamma_{\text{N}_2\text{O}_5}$  was less than  $2 \times 10^{-3}$ ,  $\text{NO}_x$  removal increased rapidly with increasing  $\gamma_{\text{N}_2\text{O}_5}$ , which was defined as the  $\gamma_{\text{N}_2\text{O}_5}$ -sensitive region. When  $\gamma_{\text{N}_2\text{O}_5} \geq 2 \times 10^{-3}$ , the contribution of  $\text{N}_2\text{O}_5$  uptake to  $\text{NO}_x$  loss was over 90 % and became insensitive. This region was defined as the  $\gamma_{\text{N}_2\text{O}_5}$ -insensitive region. According to Eqs. (3) and (5), high  $S_a$ , high  $\text{NO}_x$ , low  $k_{\text{NO}_3}$ , or low temperature allow the  $\text{N}_2\text{O}_5$  uptake to more easily be located in the  $\gamma_{\text{N}_2\text{O}_5}$ -insensitive region. Here, the critical value of the  $\text{N}_2\text{O}_5$  uptake coefficient ( $2 \times 10^{-3}$ ) was relatively low com-



**Figure 8.** Base case ( $k_{\text{NO}_3} = 0.02 \text{s}^{-1}$ ) and sensitivity tests of the integral  $p\text{NO}_3^-$  formed at 240 m via  $\text{N}_2\text{O}_5$  uptake at different  $\text{NO}_3$  reactivity (0.001, 0.01,  $0.05 \text{s}^{-1}$ ) 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  $\text{NO}_x$  loss and  $p\text{NO}_3^-$  formation by  $\text{N}_2\text{O}_5$  uptake were easily maximized in the pollution episode and further worsened the PM pollution.

In the base case, the modeled  $p\text{NO}_3^-$  formation via  $\text{N}_2\text{O}_5$  uptake was an upper limit result, as the  $\text{ClNO}_2$  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  $\text{ClNO}_2$  via  $\text{N}_2\text{O}_5$  uptake aloft, implying that significant  $\text{ClNO}_2$  formed in the upper layer of the NBL (Tham et al., 2016; Z. Wang et al., 2017). Assuming the  $\text{ClNO}_2$  yield is the average value of 0.28 determined at high altitude in North China (Z. Wang et al., 2017), the  $p\text{NO}_3^-$  produced throughout the night decreased  $7 \mu\text{g m}^{-3}$ . The modeled formation of  $\text{ClNO}_2$  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  $p\text{NO}_3^-$  formation is sensitive to the  $\text{ClNO}_2$  yield, a higher yield would increase the model uncertainty directly, and hence investigating the  $\text{ClNO}_2$  yield is warranted in future studies. As for  $\text{NO}_3$  reactivity, Fig. 8 shows the sensitivity tests of the integral  $p\text{NO}_3^-$  formation for the whole night at  $k_{\text{NO}_3}$  values of 0.001, 0.01, 0.02, and  $0.05 \text{s}^{-1}$ . The integral  $p\text{NO}_3^-$  formation decreased when  $k_{\text{NO}_3}$  varied from 0.001 to  $0.1 \text{s}^{-1}$ , but the variation ratio to the base case was within 5 %. The result shows that the  $\text{NO}_3$ – $\text{N}_2\text{O}_5$  loss via  $\text{NO}_3$  reaction with VOCs during the polluted wintertime was not important, which may only lead to relatively small uncertainties in the



integral  $p\text{NO}_3^-$  formation calculation. Nevertheless, if  $\text{N}_2\text{O}_5$  uptake was extremely low (e.g.,  $\gamma_{\text{N}_2\text{O}_5} < 10^{-4}$ ), the uncertainty of  $\text{NO}_3$  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  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{NO}_3$ , and  $\text{N}_2\text{O}_5$  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  $\text{NO}_x$  into the air mass after sunset, which would increase the mixing ratio of  $\text{O}_x$ , 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  $p\text{NO}_3^-$  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  $\text{NO}_x$  and about 40 ppbv  $\text{O}_3$  (background condition), which was not consistent with our observation.

## 4 Conclusions

During the wintertime, ambient  $\text{O}_3$  is often fully titrated at the ground level in urban Beijing owing to its fast reaction with  $\text{NO}$  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  $p\text{NO}_3^-$  production via  $\text{N}_2\text{O}_5$  uptake and contributes to the surface PM mass concentration. In this study, we found a case to show evidence for additional  $\text{O}_x$  missing (25 ppbv) aloft throughout the night. Based on model simulation, we found that the particulate nitrate formed above 150 m reached  $50 \mu\text{g m}^{-3}$  and enhanced the surface level PM concentration significantly by  $28 \mu\text{g m}^{-3}$  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  $\text{N}_2\text{O}_5$  uptake was easily maximized in the high

altitudes above urban Beijing, even with a low  $\text{N}_2\text{O}_5$  uptake coefficient. This indicates that the mixing ratio of  $\text{NO}_2$  aloft was directly linked to nitrate formation, and reduction of  $\text{NO}_x$  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  $\text{N}_2\text{O}_5$  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).

*Supplement.* The supplement related to this article is available online at: <https://doi.org/10.5194/acp-18-10483-2018-supplement>.

*Author contributions.* KL and ZW organized the field contributions from the Peking University group for the APHH-Beijing project. KL and HW designed the experiments presented in this study. HW, QZ, and KL analyzed the data. HW wrote the paper and KL revised it. All authors contributed to measurements, discussing results, and commenting on the paper.

*Competing interests.* The authors declare that they have no conflict of interest.

*Special issue statement.* This article is part of the special issue “In-depth study of air pollution sources and processes within Beijing and its surrounding region (APHH-Beijing) (ACP/AMT inter-journal SI)”. It is not associated with a conference.

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