Fast particulate nitrate formation via N₂O₅ uptake aloft in winter Beijing

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Abstract.

Particulate nitrate (pNO₃⁻) 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 NOₓ and O₃ 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 pNO₃⁻ formation via N₂O₅ heterogeneous uptake was negligible at ground level due to N₂O₅ concentration of near zero controlling by high NO emission and NO concentration. In contrast, the contribution from N₂O₅ uptake was large at high altitudes (e.g., > 150 m), which was supported by the low total oxidant (NO₂ + O₃) level at high altitudes than that at ground level. Modeling results show the specific case that the nighttime integrated production of pNO₃⁻ for the high-altitude air mass above urban Beijing was estimated to be 50 μg m⁻³ and enhanced the surface-layer pNO₃⁻ the next morning by 28 μg m⁻³ through vertical mixing. Sensitivity tests suggested that the nocturnal NOₓ loss by NO₃⁻-N₂O₅ chemistry was maximized once the N₂O₅ uptake coefficient was over 2×10⁻³ on polluted days with Sₐ was 3000 μm² cm⁻³ in wintertime. The case study
provided a chance to highlight that pNO$_3^-$ formation via N$_2$O$_5$ 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 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$_2$O$_5$ 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$_2$O$_5$ uptake is a nighttime pathway, as NO$_3$ and N$_2$O$_5$ are easily photo-labile.

Particulate nitrate formation via N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in N$_2$O$_5$ chemistry exist between winter and summer. First, as the key precursor of NO$_3$ and N$_2$O$_5$, 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$_2$O$_5$. Third, longer nighttime length in winter makes N$_2$O$_5$ heterogeneous hydrolysis potentially more important in pNO$_3^-$ formation. Finally, the N$_2$O$_5$ uptake coefficient, as an important parameter in N$_2$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 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 pNO₃⁻ 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 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 pNO₃⁻ formation via N₂O₅ uptake contributes
to the gradients in the compounds percentage and size distribution of the particle
(Ferrero et al., 2010; 2012). On nights when NO₃ can’t 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 pNO₃⁻ formation in the upper layer
as well as effective NOₓ 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 N₂O₅ concentrations aloft. Model
studies showed that pNO₃⁻ 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 pNO₃⁻ 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$_2$O$_5$ 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$_2$O$_5$ 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 NOx and O3 instruments were installed aboard a movable cabin on the tower. NOx and O3 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 O3 (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. NOx calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with a NO standard (9.8 ppmv). The O3 calibration was done with an O3 calibrator (TE 49i-PS), which was traceable to NIST (National Institute of Standards and Technology) standards annually. Before the campaign, the NOx 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 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\textsubscript{3} and N\textsubscript{2}O\textsubscript{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\textsubscript{2} yield from N\textsubscript{2}O\textsubscript{5} uptake. Homogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} and NO\textsubscript{3} heterogeneous uptake reaction were neglected in this analysis because of the low level of absolute humidity and the extremely low NO\textsubscript{3} concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of R1–R3 are those reported by Sander et al. (2011).

\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_2 + \text{NO}_3 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \\
\text{N}_2\text{O}_5 + \text{M} & \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \\
\text{NO}_3 + \text{VOCs} & \rightarrow \text{Products} \\
\text{N}_2\text{O}_5 + (\text{H}_2\text{O} \text{ or Cl}) & \rightarrow (2-f) \text{NO}_3^- + f\text{ClNO}_2
\end{align*}

Following the work of Wagner et al. (2013), the box model can be solved using six equations (Eqs. 1–6). In the framework, O\textsubscript{3} is only lost via the reaction of NO\textsubscript{2} + O\textsubscript{3} and the change in the O\textsubscript{3} concentration can be expressed as Eq. 1. Eq. 2 can express the losses of NO\textsubscript{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\textsubscript{3} production which goes through N\textsubscript{2}O\textsubscript{5} (either as N\textsubscript{2}O\textsubscript{5} or lost through uptake) to the total NO\textsubscript{3} production (Wagner et al., 2013). The \( s(t) \) favors 0 when direct loss of NO\textsubscript{3} dominates and favors 1 when N\textsubscript{2}O\textsubscript{5} uptake dominates NO\textsubscript{3} loss. The model calculation has two steps. The first step is calculate the mixing ratio of NO\textsubscript{2} and O\textsubscript{3} at time zero (herein designated as sunset). According to Eqs. 1 and 2, the initial NO\textsubscript{2} (t=0) and O\textsubscript{3} (t=0) concentrations can then be integrated backward in time starting with the measured concentrations of NO\textsubscript{2} and O\textsubscript{3} at each height. During the pollution period in winter in Beijing (NO\textsubscript{2} = 45 ppbv, Temperature = 273 K, \( S_a = 3000 \text{ \mu m}^2 \text{ cm}^{-3} \)), the ratio of N\textsubscript{2}O\textsubscript{5} to NO\textsubscript{3} is large enough, i.e., 450. The pseudo-first-order loss rate of N\textsubscript{2}O\textsubscript{5} heterogeneous uptake will be \( 1\times10^{-3} \text{ s}^{-1} \), with a N\textsubscript{2}O\textsubscript{5} uptake coefficient of \( 5\times10^{-3} \). N\textsubscript{2}O\textsubscript{5} uptake would contribute to the NO\textsubscript{3} loss rate of 0.4 \text{ s}^{-1}, which is much higher than the direct NO\textsubscript{3} loss through the reaction of NO\textsubscript{3} with VOCs. Therefore, N\textsubscript{2}O\textsubscript{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$_2$O$_5$. Assuming the equilibrium between NO$_3$ and N$_2$O$_5$ 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$_2$O$_5$ to NO$_3$. Combined, Eqs. 1–4 allow for the calculation of NO$_3$ and N$_2$O$_5$ concentrations considering stable NO$_3$ and N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$, and $\gamma_{N2O5}$ is the N$_2$O$_5$ 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.

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

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

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

\[
\frac{[N_2O_3]}{[NO_3]} = k_{eq}[NO_2] \quad (4)
\]
\[
\begin{align*}
s(t) &= \int_{t_0}^{t} k_{N_2O_5} [N_2O_5] \, dt + [N_2O_5](t) (5) \\
k_{N_2O_5} &= \frac{c \times S_a \times \gamma_{N_2O_5}}{4} (6)
\end{align*}
\]

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 \( \mu \text{m}^2 \text{cm}^{-2} \). 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 \( \mu \text{m} \) 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 (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 \( \gamma_{N_2O_5} \) varied from \( 1 \times 10^{-3} \) 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 $f_{CINO2}$ 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 $\gamma_{N2O5}$ 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$_2$O$_5$ 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$_2$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 (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$_2$O$_5$ 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 $20 \pm 2$ ppbv, corresponding to zero NO concentration. With respect to O$_x$, the mixing ratio of O$_x$ was $85 \pm 2$ 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$_2$O$_5$ 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$_2$O$_5$ chemistry can be initiated in the co-presence of high NO$_2$ and significant O$_3$ levels. Therefore, N$_2$O$_5$ 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$_2$O$_5$ 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 $61 \pm 3$ ppbv and $27 \pm 6$ 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$_2$O$_5$ concentration was zero below 150 m, as the high
level of NO made for rapidly consumption of the formed NO\textsubscript{3}. In contrast, the modeled N\textsubscript{2}O\textsubscript{5} concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The pNO\textsubscript{3} formation by N\textsubscript{2}O\textsubscript{5} heterogeneous uptake from sunset to the measurement time can be calculated using Eq. 7, which was significant of 24 μg m\textsuperscript{3} after sunset above 150 m. The pNO\textsubscript{3} formed in 4.5 hours was equivalent to 13 ppbv O\textsubscript{x} loss and consistent with the observation (15 ppbv) (Fig. 6b). Where the 1.5:1 relationship between O\textsubscript{x} and pNO\textsubscript{3} was used to calculate the O\textsubscript{x} equivalence (S. S. Brown et al., 2006).

\[ \sum \text{pNO}_3 = \int_0^t (2 - f) \cdot k_{N_2O_5} \cdot [N_2O_5]dt \quad (7) \]

The box model enabled the analysis of the integrated pNO\textsubscript{3} and ClNO\textsubscript{2} via N\textsubscript{2}O\textsubscript{5} uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO\textsubscript{3} went as high as 50 μg m\textsuperscript{3}. The integrated pNO\textsubscript{3} at sunrise was equal to the loss of 27 ppbv O\textsubscript{x}, showing a good agreement with the observed O\textsubscript{x} missing (25 ppbv) aloft in the morning hours. During the nighttime, the pNO\textsubscript{3} formed aloft via N\textsubscript{2}O\textsubscript{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\textsubscript{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\textsubscript{3} aloft from 150 m to 340 m is 50 μg m\textsuperscript{3} during the nighttime and well mixed within the PBL in the next morning, the pNO\textsubscript{3} enhancement at the surface layer (∆pNO\textsubscript{3}) can be simplified to the calculation in Eq. 8 as following:

\[ \Delta \text{pNO}_3 = \frac{\int_0^{150} P(p\text{NO}_3)dh + \int_{150}^{340} P(p\text{NO}_3)dh}{340} \quad (8) \]

Here, \( P(p\text{NO}_3) \) is the integral production of pNO\textsubscript{3} and \( H \) represents height. Owing
to high NO below 150 m, the pNO$_3^-$ formation via N$_2$O$_5$ 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$_2$O$_5$ uptake aloft and downward transportation were critical for understanding the PM growth process.

### 3.4 Sensitivity studies.

Previous studies have emphasized that the N$_2$O$_5$ 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$_2$O$_5$ concentration dropping from 3 ppbv to 60 pptv when the N$_2$O$_5$ uptake coefficients increased from 0.001 to 0.05 (Fig. 6a), as the N$_2$O$_5$ concentration is very sensitive to the loss from heterogeneous reactions. Compared to the base case, the accumulated pNO$_3^-$ was evidently lower at γ = 0.001 (44 μg m$^{-3}$). Low N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ chemistry, the overnight NO$_x$ loss efficiency (ε) was calculated using Eq. 9.

$$ \varepsilon = \frac{\int_0^t 2xk_{N2O5}[N_2O_5]dt + \int_0^t f_{NO3}[NO_3]dt}{[NO_2](0)} $$

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 $\mu$m$^2$ 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$_2$O$_5$ by uptake reaction were regarded as NO$_x$ removal. Figure 7 shows the dependence of the overnight NO$_x$ loss efficiency on the N$_2$O$_5$ uptake coefficient, as it varied from 1×10$^{-5}$ to 0.1. This is an increase from 20% to 56% with increasing $\gamma$N$_2$O$_5$, which is similar to the result addressed by Chang et al. (2011). The ceiling of overnight NO$_x$ loss via NO$_3$-N$_2$O$_5$ chemistry was fixed when all the NO$_x$ loss was through N$_2$O$_5$ uptake in polluted days, which is limited by the reaction time and the formation rate of NO$_3$ (R1). In this case, the N$_2$O$_5$ uptake contributed about 90% of the overnight NO$_x$ loss (50.4%) when $\gamma$N$_2$O$_5$ was equal to 2×10$^{-3}$. When $\gamma$N$_2$O$_5$ was less than 2×10$^{-3}$, NO$_x$ removal increased rapidly with the increasing of $\gamma$N$_2$O$_5$, which was defined as the $\gamma$N$_2$O$_5$-sensitive region. When $\gamma$N$_2$O$_5$ ≥ 2×10$^{-3}$, the contribution of N$_2$O$_5$ uptake to NO$_x$ loss was over 90% and became insensitive. This region was defined as the $\gamma$N$_2$O$_5$-insensitive region. According to Eqs. 3 and 5, high $S_a$, high NO$_x$, low $k_{NO3}$ or low temperature allow the N$_2$O$_5$ uptake more easily located in the $\gamma$N$_2$O$_5$-insensitive region. Here, the critical value of the N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$, 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$_2$O$_5$ uptake and contributes to the surface PM mass concentration. In this study, we found a case to show evidence for additional O$_3$ 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$_2$O$_5$ uptake was easily maximized in the high altitude above urban Beijing, even with low N$_2$O$_5$ 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$_2$O$_5$ 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.

Acknowledgements.
This work was supported by the National Natural Science Foundation of China (Grant No. 91544225, 41375124, 21522701, 41571130021), the National Key Technology Research and Development Program of the Ministry of Science and Technology of China (Grant No. 2014BAC21B01). The authors gratefully acknowledge the science team of Peking University for their general support, as well as the team running the tower platform, which enabled the vertical profile observations.

References.


Fehsenfeld, F. C., and Ravishankara, A. R.: Reactive uptake coefficients for N\textsubscript{2}O\textsubscript{5} determined
from aircraft measurements during the Second Texas Air Quality Study: Comparison to
High resolution vertical distributions of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} through the nocturnal boundary layer,
Tsui, W., Parrish, D. D., and Wang, T.: Nighttime chemistry at a high altitude site above Hong Kong,
Dube, W. P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.:
Brown, S. S. and Stutz, J.: Nighttime radical observations and chemistry, Chem Soc Rev, 41,
6405-6447, 2012.
Characteristics of vertical profiles and sources of PM\textsubscript{2.5}, PM\textsubscript{10} and carbonaceous species in
Beijing, Atmos Environ, 39, 5113-5124, 2005.
Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous
Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J.,
Crowley, J. N., Schuster, G., Pouvesle, N., Parchatka, U., Fischer, H., Bonn, B., Bingemer, H., and
Lelieveld, J.: Nocturnal nitrogen oxides at a rural mountain-site in south-western Germany,
Ferrero, L., Cappelletti, D., Moroni, B., Sangiorgi, G., Perrone, M. G., Croccianti, S., and
Bolzacchi, E.: Wintertime aerosol dynamics and chemical composition across the mixing
layer over basin valleys, Atmos Environ, 56, 143-153, 2012.
Ferrero, L., Perrone, M. G., Petraccone, S., Sangiorgi, G., Ferrini, B. S., Lo Porto, C., Lazzati, Z.,


Lei, H. and Wuebbles, D. J.: Chemical competition in nitrate and sulfate formations and its effect on air quality, Atmos Environ, 80, 472-477, 2013.


Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn,

Pathak, R. K., Wang, T., and Wu, W. S.: Nighttime enhancement of PM$_{2.5}$ nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of N2O5 and HNO3 partitioning, Atmos Environ, 45, 1183-1191, 2011.


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$_2$O$_5$ 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.
Figure 2. Time series of (a) PM$_{2.5}$ and O$_3$, (b) NO and NO$_2$, (c) temperature (T) and relative humidity (RH), (d) wind direction (WD) and wind speed (WS) from December 16 to 22, 2016 at PKU site in Beijing, China. The shaded region represents the nighttime periods. Red line in panel (a) shows an example of fast PM$_{2.5}$ enhancement on the night of December 19, and the green lines are the time periods when the vertical measurements conducted in IAP site.
Figure 3. Vertical profiles of NO and NO$_2$ (a), O$_3$ and O$_x$ (b) at 20:38-21:06 on the night of December 20, 2016.
Figure 4. $O_3$ missing case presented by the vertical profiles of (a) NO and NO$_2$, (b) O$_3$ and O$_x$ at 20:38-21:13 on the night of December 19, 2016.
Figure 5. Vertical profiles of (a) NO and NO\textsubscript{2}, (b) O\textsubscript{3} and O\textsubscript{x} at 09:06-09:34 in the morning of December 20, 2016.
Figure 6. Base case (γ=0.005) and sensitivity tests of the vertical profile on the night of December 19 at different N$_2$O$_5$ uptake coefficients, including (a) the mixing ratio of N$_2$O$_5$ 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$_2$O$_5$ 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.
Figure 7. The dependence of overnight NO$_x$ loss via N$_2$O$_5$ uptake on $\gamma_{N_2O_5}$ in a typical winter pollution condition. The initial NO$_2$ and O$_3$ were set to 60 ppbv and 30 ppbv, respectively. $S_a$ was set to 3000 $\mu$m$^2$ 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. The blue and orange zone represent the contribution by NO$_3$+VOCs and N$_2$O$_5$ uptake, the dashed line ($\gamma = 0.002$, when N$_2$O$_5$ uptake contribute to 90% of the maximum NO$_x$ loss) divide the loss into $\gamma$ sensitive and insensitive region. The maximum nocturnal NO$_x$ loss by NO$_3$-N$_2$O$_5$ chemistry is 56%.
Figure 8. Base case ($k_{NO3}=0.02 \text{ s}^{-1}$) 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.
Table 1. List of the parameter sets in base case and sensitivity tests.

<table>
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<th>Cases</th>
<th>$k_{NO3}$ (s$^{-1}$)</th>
<th>$\gamma_{N2O5}$</th>
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<tbody>
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<td>Base case</td>
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<tr>
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<td>0.005</td>
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</tr>
<tr>
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<td>0.005</td>
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<td>0.001</td>
</tr>
<tr>
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<td>0.01</td>
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<tr>
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