Large particulate nitrate formation from N$_2$O$_5$ uptake in a chemically reactive layer aloft during wintertime in Beijing.

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Abstract.

Particulate nitrate (pNO$_3^-$) is a dominant 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. Simultaneous ground-based and tower-based measurements were conducted during a winter heavy haze episode in urban Beijing, China. We found pNO$_3^-$ formation via N$_2$O$_5$ heterogeneous uptake was negligible at ground level, due to the presence of high NO concentrations limiting the production of N$_2$O$_5$. In contrast, the contribution from N$_2$O$_5$ uptake was larger at higher altitudes (e.g., > 150 m), which was supported by the observed large total oxidant (NO$_2$ + O$_3$) missing aloft compared with ground level. The nighttime integrated production potential of pNO$_3^-$ for the higher altitude air mass overhead urban Beijing was estimated to be 50 μg m$^{-3}$, and enhanced the surface pNO$_3^-$ significantly with 28 μg m$^{-3}$ after nocturnal boundary layer broken in the next morning. In this case, the oxidation of NO$_X$ to nitrate was maximized once N$_2$O$_5$ uptake coefficient over 0.0017, since N$_2$O$_5$ uptake dominated the fate of NO$_3$ and N$_2$O$_5$ with the presence of large aerosol surface concentrations. These results highlight that pNO$_3^-$ formation via N$_2$O$_5$ uptake...
heterogeneous hydrolysis at higher altitude air masses aloft could be an important source for haze formation in the urban airshed during wintertime. Accurately describing the formation and development of reactive air masses aloft is a critical task for improving current chemical transport models.

1. Introduction

Winter particulate matters (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). PM pollution reduced visibility (Lei and Wuebbles, 2013) and had harmful effects on public health (Cao et al., 2012). Particulate nitrate (pNO$_3^-$) is an important component of secondary inorganic aerosols, and contributed to 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 first reaction (OH + NO$_2$) was a daytime pathway since OH is severely limited at night, and N$_2$O$_5$ uptake was refer to a nighttime pathway as NO$_3$ and N$_2$O$_5$ is easily photo-labile.

Nitrate formation via N$_2$O$_5$ heterogeneous hydrolysis was proved efficient by ground based observation in summer in North China (H.C. Wang et al., 2017b; Z. Wang et al., 2017), which is comparable with or even high than the daytime formation. Several model studies showed N$_2$O$_5$ hydrolysis is responsible for nocturnal pNO$_3^-$ enhancement in Beijing (Pathak et al., 2009, 2011; H.C. Wang et al., 2017a). Although the pNO$_3^-$ formation via N$_2$O$_5$ uptake is significant in summertime, the importance of this pathway in wintertime was not well characterized. As there are many differences of N$_2$O$_5$ chemistry between winter and summer. First, as the key precursor of NO$_3$ and N$_2$O$_5$, O$_3$ level are much lower in winter than in summer due to short daytime length and weak solar radiation. Second, colder temperatures and high NO$_2$ levels favor partitioning towards N$_2$O$_5$. Third, nighttime lasts much longer in winter, making N$_2$O$_5$ heterogeneous hydrolysis potentially more important in pNO$_3^-$ formation. Finally,
N\textsubscript{2}O\textsubscript{5} uptake coefficient, the most important parameter in N\textsubscript{2}O\textsubscript{5} heterogeneous hydrolysis, is likely very different from that in summer. Since the particle characteristics and meteorological conditions (e.g. organic compounds, particle nitrate, liquid water contents, solubility, viscosity and relative humidity) are different in summer and winter (Chen et al., 2015; Zhang et al., 2007). These differences would result in the N\textsubscript{2}O\textsubscript{5} uptake coefficient has large variation (Wahner et al., 1998; Mentel et al., 1999; Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003; Bertram and Thornton, 2009; Grzinic et al., 2015; Wagner et al., 2013).

In addition to seasonal differences, previous studies have also shown a potential altitude dependence in pNO\textsubscript{3} production. In the evening, vertical mixing is strong suppressed in nocturnal boundary layer (NBL) due to the reduction of sunlight diminishes the heating of the earth’s surface, leading to vertical layer occur with NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} gradient (Brown et al., 2007), as well as the particle compounds percentage and size distribution (Ferrero et al., 2010; 2012). On nights when NO\textsubscript{3} radical production in the surface layer is negligible due to high NO emissions, N\textsubscript{2}O\textsubscript{5} uptake may still be active aloft without NO titration (Pusede et al., 2016; Baasandorj et al., 2017). The N\textsubscript{2}O\textsubscript{5} uptake aloft leads to elevated pNO\textsubscript{3} \textsuperscript{-} formed in the upper layer with effective NO\textsubscript{X} removal (Watson et al., 2002; S.G. Brown et al., 2006; Lurmann et al., 2006), which was reported with field observations at a high altitude site in Kleiner Feldberg, Germany (Crowley et al., 2010a), London British Telecommunications tower, UK (Benton et al., 2010), Boulder Atmospheric Observatory (BAO) tower in Colorado, USA (Wagner et al., 2013) and so on. Model studies also proposed nitrate formation varied in different height (Kim et al., 2014; Ying, 2011; Su et al., 2017). The mass fraction and concentration of pNO\textsubscript{3} in Beijing was reported higher aloft (260 m) than at the ground in Beijing (Chan et al., 2005; Sun et al., 2015b), and they explained the favorable gas–particle partitioning aloft under lower temperature conditions.

To explore the possible sources of pNO\textsubscript{3} and the dependence of altitude in wintertime, we conducted vertical profile measurements of NO, NO\textsubscript{2}, and O\textsubscript{3} with a tower platform in combination with simultaneous ground measurements of these
parameters in urban Beijing. A box model was used to investigate the reaction rate of 
N$_2$O$_5$ heterogeneous hydrolysis and impact on pNO$_3^-$ formation at different altitudes 
during a heavy haze episode over urban Beijing. Additionally, the dependence of 
pNO$_3^-$ formation on the N$_2$O$_5$ uptake coefficient was probed.

2. Methods

2.1 Field measurement

Ground measurement (15 m above the ground) was carried out in the campus of 
Peking University (PKU, 39°59'21"N, 116°18'25"E) in Beijing, China. The location 
of the PKU site was shown in Fig. 1, as well as the vertical measurement site (IAP, 
introduced below). At PKU site, dry-state mass concentration of PM$_{2.5}$ was measured 
by a TEOM 1400A analyzer. NOx was measured by chemiluminescence analyzer 
(Thermo Scientific, TE-42i-TR) and O$_3$ was measured by a UV photometric O$_3$ 
analyzer (Thermo Scientific, TE-49i). Dry state particle number and size distribution 
(PNSD) was measured from 0.01 to 0.6 µm with a Scanning Mobility Particle Sizer 
(SMPS, TSI Inc. 3010). These parameters were listed in Table S1. The data were 
collected from December 16 to 22, 2016. Additionally, relative humidity (RH), 
temperature (T), wind direction and speed were available during the measurement 
period.

Vertical profile measurements were conducted from December 18 to 20, 2016 at the 
tower-based platform (maximum height: 325 m) on the campus of the Institute of 
Atmospheric Physics, Chinese Academy of Sciences (IAP, 39°58'28"N, 116°22'16"E), 
during a heavy PM pollution episode. The IAP site is just with 4 km distance from the 
PKU site. The measurement instruments were installed on board a movable cabin on 
the tower. The ambient NOx and O$_3$ concentrations were measured with two 
low-power, light-weight instruments (Model 405 nm and Model 106-L; 2B 
Technologies, USA). The Model 405 nm instrument measures NO$_2$ directly based on 
the absorbance at 405 nm, and NO is measured by adding excess O$_3$ (conversion 
efficiency ~100%). The limit of detection of both NO and NO$_2$ is 1 part per billion
volume (ppbv), with an accuracy of 2 ppbv or 2% of the reading, and the time resolution is 10 s. The Model 106-L instrument measures O_3 based on the absorbance at 254 nm with a precision of 1 ppbv or 2% of the reading and a limit of detection of 3 ppbv. Height information was retrieved from the observed atmospheric pressure measured by Model 405 nm instrument. The cabin ascended and descended at a rate of 10 m min^{-1}, with a height limit of 260 m at daytime and 240 m at night. The cabin stopped after reaching the peak and parameters were measured continually for 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.

2.2 Box model simulation

A box model was used to model the NO_3 and N_2O_5 mixing ratios and the nitrate formation potential in vertical scale at IAP site. A simple chemical mechanism (see R1-R5) is used to model the nighttime NO_3 and N_2O_5 chemistry in NO free air masses, and the physical mixing, dilution, deposition, or interruption during the transport of the air mass were not considered. Here f represents the ClNO_2 yield from N_2O_5 uptake. Homogeneous hydrolysis of N_2O_5 and NO_3 heterogeneous are neglected in this analysis because there is little absolute humidity and extremely low NO_3 concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of R1- R3 are those reported by Sander et al., (2011).

\begin{align*}
    (R1) & \quad \text{NO}_2 + O_3 \rightarrow \text{NO}_3 + O_2 \\
    (R2) & \quad \text{NO}_2 + \text{NO}_3 + M \rightarrow \text{N}_2\text{O}_5 + M \\
    (R3) & \quad \text{N}_2\text{O}_5 + M \rightarrow \text{NO}_2 + \text{NO}_3 + M \\
    (R4) & \quad \text{NO}_3 + \text{VOCs} \rightarrow \text{Products} \\
    (R5) & \quad \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 by four equations (Eq. 1-4). In the framework, O_3 only losses via the reaction of NO_2+O_3 and the change of the O_3 concentration can express as Eq. 1. Since the ratio of N_2O_5 to NO_3 was calculated to be larger than 150:1 in a typical urban region in wintertime...
(NO₂ = 15 ppbv, nighttime temperature = 0°C), N₂O₅ is proposed to be dominate the NO₃ loss, than means two molecules of NO₂ lost (convert to nitrate or ClNO₂) for one molecule NO₃ formed (Eq. 2). In the model we need to know the mixing ratio of NO₂ and O₃ at time zero (here set to sunset). According to Eq. 1 and Eq. 2, the NO₂ (t=0) and O₃ (t=0) concentration can derived from the duration time and the vertical measured NO₂ and O₃ at each height. Assuming the equilibrium between NO₃ and N₂O₅ is maintained after a time period, the sum concentration of NO₃ and N₂O₅ can be described by Eq. 3. Using the temperature dependent equilibrium rate constant (kₜ) and the modeled NO₂ at a certain time, Eq. 4 can be used to determine the ratio of N₂O₅ and NO₃. Combined, Eq. 1-4 allow for the calculation of N₂O₅ concentrations, given a constant of NO₃ and N₂O₅ rate constant (k_NO₃ and k_N₂O₅). Modeled N₂O₅ concentrations and given k_N₂O₅ are then used to estimate pNO₃⁻ formation, here the HNO₃ produced in R4 is not accounted, as a large part of the products are organic nitrates (Brown and Stutz, 2012). Here k_NO₃ and k_N₂O₅ denotes the pseudo first order reaction rate constant of the total NO₃ reactivity caused by ambient volatile organic compounds (VOCs) and N₂O₅ heterogeneous uptake, respectively. k_N₂O₅ is given in Eq. 5. Sₐ is aerosol surface area, C is the mean molecular speed of N₂O₅, and γ_N₂O₅ is N₂O₅ uptake coefficient. The model is run from sunset to sunrise, where the length of night was about 14.5 h.

\[
\frac{d[O_3]}{dt} = -k_{NO_2+O_3}[O_3][NO_2]
\]

\[
\frac{d[NO_2]}{dt} = -2 \times k_{NO_2+O_3}[O_3][NO_2]
\]

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

\[
\frac{[N_2O_5]}{[NO_3]} = k_{eq}[NO_2]
\]

\[
k_{N_2O_5} = \frac{C \times S_a \times \gamma_{N_2O_5}}{4}
\]

Dry-state Sₐ at PKU site was calculated based on the PNSD measurement, which was corrected to ambient (wet) Sₐ for particle hygroscopicity by a growth factor (Liu et al., 2013). The uncertainty of the wet Sₐ was estimated to be ~30%, which was associated from the error from dry PNSD measurement (~20%) and the growth factor.
(~20%). Nighttime averaged $S_a$ on the night of December 19 is about 3000 μm$^2$ cm$^{-3}$. PM measurements by 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 shown small variation of vertical particle number concentration, with the boundary layer height below 340 m (Zhong et al., 2017). Therefore, the $S_a$ at PKU site is representative to the urban Beijing conditions and applied in the model is reasonable.

$N_2O_5$ uptake coefficient was regard as the main uncertainty of the $N_2O_5$ loss, along with the ClNO$_2$ yield lead to the uncertainties in the estimation of particulate nitrate formation (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016). Wagner et al., (2013) shows the significant particular nitrate suppression aloft in the wintertime in Denver, USA, with the uptake coefficient of about 0.005 when particulate nitrate fraction in the PM$_{2.5}$ mass concentration about 40%. Considered the high particle nitrate content in North China in wintertime is similar to that in Denver (Sun et al., 2013, 2015a; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015), here we used a constant uptake coefficient of 0.005 as the model initial input in the base case, and the uncertainty of $N_2O_5$ uptake coefficients will be discussed later. Since the model input of ClNO$_2$ yield only affect the value of produced particulate nitrate concentration, and would not change the modeled $N_2O_5$ concentration, here we set the initial $f_{ClNO2}$ to zero. The impact of ClNO$_2$ yield will be further discussed later.

Respect to $k_{NO3}$, the average value in summertime was estimated to be 0.024 s$^{-1}$ in 2006 (H.C. Wang et al., 2017a). While in wintertime, the $k_{NO3}$ should be smaller as the intensity of plant emissions reduced in the lower temperature and weak solar radiation. The model input $k(NO_3)$ was set to an relative moderate value of 0.02 s$^{-1}$ (equivalent to 0.2 ppbv isoprene + 40 pptv monoterpen + 1.0 ppbv cis-2-butene). A series of sensitivity tests were conducted to study the uncertainties to the model simulation, and the detailed test set were listed in Table 1, included the test of $N_2O_5$ uptake coefficient and $k_{NO3}$. The $\gamma_{N2O5}$ sensitivity tests were set to a lower limit of 0.001 to a upper limit of 0.05, as well as the $k_{NO3}$ set to 0.001, 0.01 and 0.1 s$^{-1}$. 


3. Results and discussion

3.1 Ground-based observations.

A severe winter PM pollution event was captured from the ground observations from December 16 to 22, 2016 in Beijing. Figure 2a shown the mass concentration of PM$_{2.5}$ began to increase on December 16 and reached the maximum value of 480 μg m$^{-3}$ on December on 20. A fast PM growth event happened on the night of December 19–20 (colored red in Fig. 2a), the PM$_{2.5}$ mass concentration increased continuously throughout the night, with an overall increment of 100 μg m$^{-3}$. During the episode, the meteorological condition is featured with high RH (50% ± 16%) and low temperature (2 ± 3 °C). The slow surface wind (< 3 m s$^{-1}$) indicated the atmosphere was static stabilized (Fig. 2c, 2d). The daytime O$_3$ concentration was low due to high NO emission and weak solar radiation. After sunset, O$_3$ was rapidly titrated to zero by the elevated NO. The presence of high NO concentrations would have strongly suppressed the concentration of NO$_3$, and further suppressed N$_2$O$_5$ near the ground. Figure 2b depicted large amounts of NO and NO$_2$ were observed throughout the whole 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 Ox (< 50 m) was consist with that measured at ground level and shown in Fig. S2, confirmed the two sites are comparable at ground level at last. 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 the concentration of 80 ppbv and 100 ppbv, respectively. The O$_3$ concentrations keep 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 is also not important like ground level as mentioned above. The case on the night of December 18 is similar to the night of December 20.

The vertical measurement on December 19 did not like those happened on
December 18 and 20. Figure 4a shows the vertical profiles around 21:00 on December 19 that NO was abundant from the ground to 100 m, then gradually decreased to zero from 100 m to 150 m, and stay zero above 150 m. The observed NO\textsubscript{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\textsubscript{3} concentrations were below the instrument limit of detection below 150 m (Fig. 4b). Above 150 m, the O\textsubscript{3} concentration was 20 ± 2 ppbv, corresponding to the greatly diminished NO\textsubscript{2} concentration. With respect to the total oxidants (O\textsubscript{x} = O\textsubscript{3} + NO\textsubscript{2}), the mixing ratio of O\textsubscript{x} was 85 ± 2 ppbv at lower altitudes, while the O\textsubscript{x} concentration at higher altitudes was 15 ppbv lower than that at lower altitude (Fig. 4b). The O\textsubscript{x} missing at the higher altitude air mass indicated an additionally nocturnal removal of O\textsubscript{x} aloft.

Figure 5 depicted the vertical measurement at 09:30 on the morning of December 20 has similar features with those observed at 21:00 on December 19, and the NBL still not be broken. The O\textsubscript{x} missing aloft in the morning increased to 25 ppbv at 240–260 m, demonstrated that an additional 25 ppbv of O\textsubscript{x} was removed or converted to other compounds at higher altitudes than surface layer on the night of December 19-20. Figure S3 shows the vertical profiles of NO, NO\textsubscript{2}, O\textsubscript{3} and O\textsubscript{x} at ~12:00 on December 18, when the solar radiation is strong enough to drive the trace gas mixing well in vertical direction. NO\textsubscript{x} and O\textsubscript{3} were observed well mixed indeed, with small variation from ground level to 260 m.

### 3.3 Particulate nitrate formation aloft.

N\textsubscript{2}O\textsubscript{5} uptake is one of the two most important pathways of the ambient NO\textsubscript{x} losses, and is consequently an important pathway of pNO\textsubscript{3} formation (Wagner et al., 2013; Stutz et al., 2010; Tsai et al., 2014). At higher altitudes (e.g. > 150 m), NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} chemistry can be initiated in the co-presence of high NO\textsubscript{2} and significant O\textsubscript{3} levels. Therefore, N\textsubscript{2}O\textsubscript{5} uptake could represent a plausible explanation for the observed O\textsubscript{x} missing in the higher-altitude air masses on the night of December 19. To explore this phenomenon, a time-step box model was used to simulate the NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{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 modeled N$_2$O$_5$ concentration is zero below 150 m, as the high level NO consumed NO$_3$ formation fast. While the modeled N$_2$O$_5$ concentrations at 21:00 were in the range of 400-600 parts per trillion volume (pptv) above 150 m (Fig. 5a). pNO$_3^-$ accumulation via N$_2$O$_5$ heterogeneous hydrolysis from sunset to the measurement time was significant, yielding a maximum of 24 μg m$^{-3}$ within 4.5 hours after sunset (Fig. 5b)).

The box model enabled the analysis of the integrated pNO$_3^-$ and ClNO$_2$ via N$_2$O$_5$ uptake over the whole night. As shown in Fig. 5c, the modeled integrated pNO$_3^-$ went up to as high as 50 μg m$^{-3}$. The integrated pNO$_3^-$ at sunrise was equal to the loss of 27 ppbv OX, shows a good agreement with the observed OX missing aloft at the morning hours. During the nighttime, the formed pNO$_3^-$ aloft via N$_2$O$_5$ uptake would lead to the particle nitrate concentration much higher than that in the surface layer, which has been reported 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). In addition, during the morning time when NBL was broken, the elevated pNO$_3^-$ aloft will vertically mixed and enhanced the PM concentration at surface layer, this phenomenon also been observed in previous studies (Watson et al., 2002; S.G. Brown et al., 2006; Lurmann et al., 2006). In this case, the planetary boundary layer (PBL) height during the daytime is about 340 m on December 20 (Zhong et al., 2017). Assuming that the height of NBL and planetary boundary layer (PBL) are the same, and the air mass was well mixed in the following morning in the PBL. The nighttime N$_2$O$_5$ uptake aloft would be enhanced the ground pNO$_3^-$ mass concentration significantly with 28 μg m$^{-3}$ in the morning, which is in good agreement with the observed PM peak in the morning on December 20, with the PM enhancement of ~60 μg m$^{-3}$. The result demonstrated that the nocturnal N$_2$O$_5$ uptake aloft and downward transportation are really importance in 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 (Brown and Stutz, 2012; H.C. Wang et al., 2016), which is the main source of uncertainties in the model. Sensitivity tests illustrate that the modeled N$_2$O$_5$ concentration varied from 3 ppbv to 60 pptv when the N$_2$O$_5$ uptake coefficients were varied from 0.001 to 0.05 (Fig. 6a), the N$_2$O$_5$ concentration is very sensitivity to the loss from heterogeneous reaction. Compared with the base case, the accumulated pNO$_3^-$ is evidently lower at γ = 0.001 with the accumulated pNO$_3^-$ of 44 μg m$^{-3}$, the low N$_2$O$_5$ uptake coefficient condition is corresponding to several kinds of aerosols, such as secondary organic aerosol (Gross et al., 2009), humic acid (Badger et al., 2006)) and certain solid aerosols (Gross et al., 2008). When the N$_2$O$_5$ uptake coefficient enlarges from 0.005 to 0.05 (Fig. 6b, c), the integral pNO$_3^-$ almost not change with negligible increasing, indicating that the conversion capacity of N$_2$O$_5$ uptake to pNO$_3^-$ was almost maximized at certain ClNO$_2$ yield, the convert capacity of NOx to nitrate was not limited by N$_2$O$_5$ heterogeneous reaction rate, but the formation of NO$_3$ by the reaction of NO$_2$ with O$_3$.

For describing the nocturnal NOx convert capacity to particulate nitrate via N$_2$O$_5$ uptake coefficient, here we defined the particle nitrate convert efficiency (ε) as Eq. 6. The Δt represents the time duration from time zero at sunset till the ending time at sunrise.

(Eq. 6) \[ \varepsilon = \frac{\sum_{i=1}^{n} k_{N_2O_5}[N_2O_4]}{\sum_{i=1}^{n} 2\times k_{NO_2+O_3}[O_3][NO_2]} \]

In the case, $S_a$ is set to 3000 μm$^2$ cm$^{-3}$, the ClNO$_2$ yield is zero and $k_{NO_3}$ is 0.02 s$^{-1}$. Figure 7 shows the dependence of the particle nitrate convert efficiency varied from 10$^{-5}$ to 0.1. When $\gamma_{N_2O_5}$ is lower than 0.0017, the particle nitrate formation enhanced rapidly with the increasing of N$_2$O$_5$ uptake coefficient, here we defined as the $\gamma_{N_2O_5}$ sensitive region when $\gamma_{N_2O_5} < 1.7 \times 10^{-3}$. While $\gamma_{N_2O_5} \geq 1.7 \times 10^{-3}$ is defined as $\gamma_{N_2O_5}$ insensitive region, since the convert efficient is over 90% and not sensitive to the variation of N$_2$O$_5$ uptake coefficient. According to Eq. 3 and Eq. 5, higher aerosol surface concentration, higher NOx, lower $k_{NO_3}$ and temperature would further
enlarging the insensitivity region with lower $\gamma_{N2O5}$ value, and make the N$_2$O$_5$ uptake
more easily located in the $\gamma_{N2O5}$ insensitive region. Here the critical value of the N$_2$O$_5$
utake coefficient (1.7×10$^{-3}$) is relative low compared with that IUPAC (International
Union of Pure and Applied Chemistry) recommended on the surface of mineral dust
(0.013, 290-300K) (Crowley et al., 2010b) 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; Z. Wang et al., 2017; Brown et al., 2016; H.C. Wang et al., 2017b; X.F.
Wang et al., 2017), suggesting the particulate nitrate formation via N$_2$O$_5$ uptake was
easily maximized in polluted episode, and further worsen the PM pollution.

In the base case, the modeled particulate nitrate formation via N$_2$O$_5$ uptake is an
upper limit result, as the ClNO$_2$ yield set to zero. Since large coral combustion
emitted chloride into the atmosphere in the heating period in Beijing (Sun et al., 2013),
associated with the emission by power plants in North China. The enhanced
anthropogenic emission of chloride provides abundant chloride-containing aerosol to
form ClNO$_2$ via N$_2$O$_5$ uptake aloft, implying that significant ClNO$_2$ formed in the
upper layer of NBL (Tham et al., 2016; Z. Wang et al., 2017). Assuming the ClNO$_2$
yield is the average value of 0.28 determined at high altitude in North China (Z. Wang
et al., 2017), the produced pNO$_3^-$ throughout the whole night will decreased 7 µg m$^{-3}$.
The ClNO$_2$ formation aloft throughout the night reach up to 2.5 ppbv, which is
comparable with that observed in the field measurement in North China (Tham et al.,
2016; Z. Wang et al., 2017; X.F. Wang et al., 2017). As the error of pNO$_3^-$ formation
simulation was subject to the ClNO$_2$ yield, higher yield would increase the model
uncertainty directly, probing the ClNO$_2$ yield are warranted in future studies. As for
NO$_3$ reactivity, Figure 7 shows sensitivity tests of the integral pNO$_3^-$ formation in the
whole night at $k_{NO3} = 0.001$ s$^{-1}$, 0.01 s$^{-1}$, 0.02 s$^{-1}$, 0.05 s$^{-1}$. The integral pNO$_3^-$
formation was decreased when $k_{NO3}$ vary from 0.001 s$^{-1}$ to 0.1 s$^{-1}$, but the variation
ratio to base case was within ±5%. The result shows the NO$_3$-N$_2$O$_5$ loss via NO$_3$ react
with VOCs in polluted wintertime is not important, which may only lead to relative
small uncertainties to the integral pNO$_3^-$ formation calculation. Nevertheless, if N$_2$O$_5$
uptake was extremely low (e.g. $\gamma_{N2O5} < 10^{-4}$), the uncertainty cased by NO$_3$ oxidation
will be enlarged significantly.

4. Conclusion

During the wintertime, ambient O$_3$ is often fully titrated to be zero at the ground of urban Beijing due to fast reaction with NO emissions. Consequently, the near surface air masses were 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. In this study, we evidenced of an additional Ox missing aloft with 25 ppb throughout the night. Based on model simulation, we found the particulate nitrate formed above 150 m can reach up to 50 $\mu$g m$^{-3}$, and enhance the surface level PM concentration significantly with 28 $\mu$g m$^{-3}$ after NBL breaking. Our study also demonstrated that during heavy PM pollution period, the particulate nitrate formation capacity via N$_2$O$_5$ uptake is easily maximized in the upper layer, even N$_2$O$_5$ uptake is as low as 1.7×10$^{-3}$, indicating the mixing ratio of NO$_2$ aloft are directly linked to nitrate formation, and reduction of NOx is helpful to decrease 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 reached a better understanding of the winter haze formation.

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References.


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 NOx and O3 were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate N2O5 and particle nitrate formation) were collected from a ground site at PKU. Additional measurements on PM2.5 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 (CNST, Chinese National Standard Time) 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 Ox (b) at 20:38-21:06 on the night of December 20, 2016.
Figure 4. OX missing case presented by the vertical profiles of (a) NO and NO$_2$, (b) O$_3$ and OX at 20:38-21:13 on the night of December 19, 2016.
Figure 5. Vertical profiles of (a) NO and NO$_2$, (b) O$_3$ and O$_x$ 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 pNO$_3^-$ convert efficiency by N$_2$O$_5$ uptake on $\gamma_{N_2O_5}$. The initial $S_o$ set to 3000 $\mu$m$^2$ cm$^{-3}$, the ClNO$_2$ yield is zero and $k_{NO3}$ is 0.02 s$^{-1}$. The orange region shows the convert efficiency is sensitive when $\gamma < 0.0017$, while the blue region shows the convert efficiency is over 90% and insensitive when $\gamma \geq 0.0017$. 
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$_2$O$_5$ uptake at different NO$_3$ reactivity ($0.001 \text{ s}^{-1}$, $0.01 \text{ s}^{-1}$, $0.05 \text{ s}^{-1}$) 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>
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</tr>
<tr>
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