Response to Reviewers

We thank the reviewers for their careful reading and their constructive comments on our manuscript. As detailed below, the reviewer's comments are shown as italicized font, our response to the comments are normal font. New or modified text is in blue. All of the line numbers refer to Manuscript ID: acp-2017-1217.

Reviewer: #1

The topic of the heterogeneous process of NOx is of interest to the community, and the vertical measurements of chemical composition in winter haze are particularly valuable. My main concern, however, on the present work is that the model was poorly constrained by observations and had to reply on too many assumptions. The vertical measurements only included O_3, NO, and NO_2 which enabled calculation of NO_3 production, but several key parameters, such as N_2O_5, VOCs and aerosol surface area density, for loss of NO_3, N_2O_5 production and subsequent loss to nitrate were not measured, making it very difficult, if not impossible, to evaluate nighttime reactions of NOx and for nitrate formation. In addition, the analysis was only based on one profile measured in the early evening, and too many assumptions in the model calculations were not well justified. All these make it very difficult to judge the validity of the conclusions drawn from the analysis. The authors are advised to carefully consider and reduce these uncertainties which could lead to large bias and possible errors.

1). *L16. Please elaborate what the simultaneous measurements were conducted.*

Changed as following: "Simultaneous ground-based and tower-based measurements of NO_x and O_3 were conducted…"

2). *L22. Please define the potential of pNO_3^- .*

This sentence change to: "The nighttime integrated production of pNO_3^- for …"

Here we deleted "potential".

3). *L57-58. It is not clear how the N_2O_5 uptake coefficient in winter will be different from summer.*

Since the properties of the aerosol particles (e.g., organic compounds, particle nitrate, liquid water contents, solubility, viscosity, etc.) and meteorological conditions and (e.g. temperature, relative humidity etc.) are different in summer and winter, these differences will led to changes of the N_2O_5 uptake coefficient. The explanation was added in Line 57-58: "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)."

4). *L96. The abbreviation of 'IAP' should be spelled out upon the first mention in the text.*

Changed accordingly.

5). *L110. Please specify which instruments were installed on board a movable cabin.*

Specified in the Line 110: "NO_x and O_3 instruments were installed on board a movable cabin on the tower…"

6). *L111-113. Describe in more detail about the two light-weight instruments for vertical measurements of O_3, NO and NO_2. How were they calibrated, was there any intercomparison with conventional monitors?*

The detailed description after Line 113 was added: "NO_x calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with a NO standard (9.8 ppmv). The O_3 calibration was done with an O_3 calibrator (TE 49i-PS), which was traceable to NIST (National Institute of Standards and Technology) standards annually. Before the campaign, the NO_x monitor was compared with a Cavity Attenuated Phase Shift (CAPs) Particle Light Extinction Monitor, and the O_3 monitor was compared to a commercial O_3 analyzer (TE-49i, Thermo Electron, USA). Good agreement was found between the portable instruments and the conventional monitors."

7). *L124. Were the daily cycles conducted in the same time periods for every day?*

Yes, we conducted the daily cycle measurement in the similar time periods for the three days.

8). L129-131. The assumptions of no NO influence, no physical mixing, and no transport of the air mass may not be valid here. Without continuous or intermittent measurement as constraints, it is difficult to know the evolution of the air masses, as such one cannot testify the validity of these assumptions.

Since high O_3 concentrations (20 ppbv) at the high altitude (>150 m) were observed at night, the NO concentrations have to be zero for this kind of condition. We were using a box model for the interpretation of the observed dataset. In the framework of box model analysis, the assumption is the analyzed air mass were well mixed. The assumption of well mixing is plausible since the influence of physical mixing on the reaction rate of NO + O_3 could be neglected.

9). *L143-147. The low theoretical equilibrium ratio of NO_3 to N_2O_5 at the low-temperature condition may not necessarily mean that the N_2O_5 formation dominates the NO_3 loss. More evidence is needed here. The kNO_3 value of 0.02 s^{-1} assumed in the present study was much higher than other studies, for example, Brown et al., 2016, in which the NO_3 reaction with VOC contributes more than half of the total NO_3 loss.*

Yes, high N_2O_5/NO_3 is not means N_2O_5 heterogeneous uptake dominate the NO_3 loss. While during the polluted period in winter Beijing (NO_2 = 45 ppbv, Temperature = 273 K, Sa = 3000 $\mu m^2\ cm^{-3}$), the pseudo first order loss rate of N_2O_5 heterogeneous uptake will be $1\times10^{-3}\ s^{-1}$, corresponding to the N_2O_5 uptake coefficient of 5×10^{-3}, and contributed to NO_3 loss rate of 0.4 s^{-1}, which is much higher than the direct NO_3 loss by the reaction of NO_3 with VOCs, even the k_{NO3} set to a high value of 0.02 s^{-1}. Therefore we believe the N_2O_5 formation dominates the NO_3 loss in this study. With respect to k_{NO3}, Brown et al., (2016) shows the wintertime average k_{NO3} in Hong Kong was about $6\times10^{-3}\ s^{-1}$, and dominated by monoterpenes. Previous work showed the average kNO_3 is about 0.011 s^{-1} in rural Beijing in summertime, and BVOCs is the dominating part (Wang et al., 2017; Wang et al., 2018). During wintertime, the BVOCs emission would decrease due to lower temperature and weak solar radiation, the k_{NO3} set to 0.02 s^{-1} in this study represents an upper value to some extent. The differences of this study with the campaign conducted in Hong Kong (Brown et al., 2016) may cause by the higher temperature and much lower aerosol surface area in Hong Kong (Temperature = 285 K, Sa ≈ 200 $\mu m^2\ cm^{-3}$).

In Line 145, we rewrite the part as following: "During the polluted period in winter Beijing (here NO_2 = 45 ppbv, Temperature = 273 K, Sa = 3000 $\mu m^2\ cm^{-3}$), the ratio of N_2O_5 to NO_3 is large enough, i.e., 450, the pseudo first order loss rate of N_2O_5 heterogeneous uptake will be $1\times10^{-3}\ s^{-1}$ with the N_2O_5 uptake coefficient of 5×10^{-3}. N_2O_5 uptake would contribute an NO_3 loss rate of 0.4 s^{-1}, and much higher than the direct NO_3 loss by the reaction of NO_3 with VOCs, even the k_{NO3} set to a high value of 0.02 s^{-1}. Therefore, N_2O_5 uptake was proposed to be dominantly responsible for the NO_3 loss and the initial s(t) was set to 1"

10). *L148-150. It is not clear how the author determined the initial concentration of NO_2 and O_3, which could affect the integrated concentrations. Were you using the* *iterative method suggested by Wagner et al., 2013? The retrieved results should be included in the supplementary. Any measurement constraints were used to validate this calculation?*

Yes, we used the iterative method suggested by Wagner et al., 2013. The initial NO_2 and O_3 concentration were derived according to Eq. 1 and Eq. 2, O_3 and NO_2 are integrated backward in time to sunset. The average initial NO_2 and O_3 above 150 m at sunset time is about 61 ± 3 ppbv and 27 ± 6 ppbv, respectively. The measured NO_2 concentration in PKU site at sunset time (local time, 16:55) is 61 ppbv and show good consistent with the model result.

Changed as following in Line 299: "The average initial NO_2 and O_3 above 150 m at sunset time is about 61 ± 3 ppbv and 27 ± 6 ppbv, respectively. The measured NO_2 concentration in PKU site at sunset time (local time, 16:55) is 61 ppbv and show good consistent with the model result."

11). *L146. "than" should be "that".*

Corrected accordingly.

12). *L162. Please clarify the exact time period for the model running from sunset to sunrise.*

Here we clarified as: "Sunset and sunrise time during the measurement is 16:55 and 07:30 (Chinese National Standard Time, CNST) and the length of night was about 14.5 h, the model is run from sunset to sunrise with the running time set to 14.5 h."

13). *L164-168. There are some flaws in the Eq.1 to 5 of the box model. To simplify the differential equation, the author assumes an equilibrium between NO_3 and N_2O_5 in Eq. 3 and 4, which means the loss rate of NO_2 through R2 and production rate from R3 should be equal. Therefore, the NO_2 loss rate will equal to the reaction rate of R1, which contradicts Eq. 2. As suggested by Wagner et al., 2013, "the assumption of equilibrium leads to an error which accumulates as the equations are integrated". This could affect the results when retrieving the initial NO_2 concentration and subsequent model simulation. To be more accurate, I suggest the author use the explicit equations suggested by Wagner et al., 2013.*

Thanks for the suggestion, we corrected these equations accordingly, and the fixed k_{NO3} and k_{N2O5} first, set s(t) to 1 in the first step and then iterate the s(t) till the difference between two iteration less than 0.005. The explicit equations changed as:

"(Eq. 1) $\frac{d\,[O_3]}{dt} = -k_{NO2+O3}[O_3][NO_2]$

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

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

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

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

(Eq. 6) $\mathrm{k}_{\mathrm{N2O5}} = \frac{C \times S_a \times \gamma_{\mathrm{N2O5}}}{4}$ ”

14). *L169-L179. The surface area was calculated based on the measurement of particle size distribution from 0.01 to 0.6 μm and could be underestimated due to the lack of information of larger particles, resulting in large uncertainty in the calculated uptake coefficients. It is necessary to provide an uncertainty estimation of how much this will affect the results.*

During the study period, the particle number and size distribution (PNSD) larger than 0.7 μm is unavailable, it is different to quantify the contribution from lager particles. While during the following polluted episode (2017-01-01 to 2017-01-07), PNSD of $PM_{2.5}$ data are available, we found particle smaller than 0.7 μm dominated more than 95% aerosol surface area, the similar result also represented in Germany and summer Beijing (Crowley et al., 2010; Wang et al., 2018). The underestimation of S_a in this study (5%) could lead to the overestimation of N_2O_5 3.6% - 4.2%, and underestimation of pNO_3^- with 0.2% - 2.5% considering the N_2O_5 uptake coefficient varied from 1×10^{-3} to 0.05.

We added the description in Line 179: “Although the PNSD information for particles larger than 0.7 μm was not valid during the study period, the particles smaller than 0.7 μm dominated more than 95% of the aerosol surface area in a subsequent pollution episode (01/01/2017 to 01/07/2017), and similar results also were reported in other studies (e.g., Crowley et al., 2010a; Wang et al., 2018). The possible lower bias of S_a (5%) only led to a small overestimation of N_2O_5, i.e., 3.6%–4.2%, and an underestimation of pNO_3^- of 0.2%–2.5% when γ_{N2O5} varied from 1×10^{-3} to 0.05.”

15). *L240-241, L245-247, L257-258. The author attributed the lower Ox level at high altitude on the night of December 19 to missing sinks of Ox with high N_2O_5 uptake, but it could also be a result of the continuous emissions of NOx near the ground leading to accumulation of NO_2 within the nocturnal boundary layer with a height around 100m. So the Ox level in the residual layer and surface doesn't have to be conserved. Here it would be good to show vertical information on meteorological parameters.*

The emission of NO would not influence the sum of Ox (= O_3 + NO_2). The emission of NO_2 would led to higher O_x at the surface layer. Nevertheless, the vertical profile measurement showed no vertical gradient of NO_2 lower than 150 m so that we do not think there could be a significant emission of NO_2. And therefore, the O_x level shall be conserved between the nocturnal boundary layer and the residual layer since no O_3 is produced at night. In addition, the nocturnal boundary layer is determined to be about 340 m through the vertical profile of temperature during the same period in Beijing (Zhong et al., 2017).

16). *L264-265, Wrong figure number referenced here.*

Corrected accordingly.

17). *L265. Please explicitly define the equation used for calculating the nitrate accumulation.*

We listed the calculation equation as following:

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

18). *L262-267. This model simulation assumes an ideal condition with no NO concentration above 150 m from the sunset to 21:00, which cannot be substantiated. Thus the calculated accumulation of nitrate is questionable.*

Due to the strong thermal inversion during winter haze episode (e.g. Zhong et al., 2017), the isolation is existed more easily in vertical scale in urban Beijing, the air mass in upper layer is not easily affected by surface NO emission. The theoretical framework of the box model we used is same as Wagner et al., (2013) and Yun et al., (2018). The model allow us to accumulate the pNO_3^- till sunrise, which shows an upper limit of the nitrate production via N_2O_5 uptake in the upper layer. In addition, at sunset time, we observed significant O_3 presented at the near surface layer. Before O_3 is fully titrated away, the NO concentrations shall be zero for the sunset time.

19). *L281-282. Please elaborate how to deal with calculations of mixing.*

We rewrite the vertical mixing in L279-283 as following: “Zhong et al. (2017) showed that the NBL and PBL both were at 340 m from December 19 to 20, 2016 in Beijing. Daytime vertical downward transportation was helpful in mixing the air mass within the PBL. Assuming the newly formed pNO_3^- aloft from 150 m to 340 m is 50 $\mu g\ m^{-3}$ during the nighttime and well mixed within the PBL by the next morning, the enhancement to the surface layer (ΔpNO_3^-) can be simplified to the calculation in

Eq. 8 as following:

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

Here, $P(\mathrm{pNO_3^-})$ is the integral production of $\mathrm{pNO_3^-}$ and H represents height. Owing to high NO below 150 m, the $\mathrm{pNO_3^-}$ formation via N_2O_5 uptake was zero. The enhancement of $\mathrm{pNO_3^-}$ from 150 m to 340 m was calculated as 28 μg m^{-3},"

20). L282-285. *If the author's hypothesis is true, it should be able to observe a sharp increase of particulate nitrate at the ground site in the morning of December 20. Any evidence on that?*

The particulate nitrate measurement is not available in this study, but as labelled in Figure 2(a), the red line showed PM concentration had a sharp increase of ~60 μg m^{-3}, which was purposed to be consist with the result considering a large proportion of particulate nitrate in PM mass concentration, especially during winter polluted episode in Beijing (e.g., Zheng et al., 2015).

21). L309. *Eq.6 is incorrect. The particle nitrate formation is twice of N_2O_5 loss if assuming $ClNO_2$ yield is zero.*

Thanks, we corrected accordingly.

22). *L328, "coral" should be "coal".*

Corrected accordingly.

23). L342-343. *A possible reason for the small difference on kNO_3 variation could be the NO_3 change (via VOC loss) were unaccounted for in Eq.2 that used to retrieve the initial concentration. Comparison between the full differential equations and simplified calculation is required to validate the results.*

The full differential equations was used to recalculate the $\mathrm{pNO_3^-}$ variation on k_{NO3}. The s(t) decreased from 1 to 0.99 even k_{NO3} set to 0.05, and the difference between the full differential equations and simplified calculation is negligible, suggested that the calculation result is valid.

24). *L351, delete "to be zero".*

Corrected accordingly.

25). *L357, add "that" after "found".*

Corrected accordingly.

Reviewer: #2

The authors explore the mechanisms for particulate nitrate (pNO_3^-) during wintertime haze events in Beijing, China. Comparing simultaneous ground-based and tower-based observations, the authors investigated the significance of pNO_3^- via N_2O_5 heterogeneous uptake as a function of altitude. The work shows the effects of the pNO_3^- formed aloft on the surface $PM_{2.5}$ the following the morning. Given the significance of this work, I recommend this manuscript for publication after significant revisions.

We thank for the Reviewer #2's constructive comments and suggestions to improve the quality of our manuscript.

1). *although the experiment design is well thought and the analysis appears to be solid, the technical writing needs significant improvement. I recommend the authors to use professional technical writing services in English to improve the penmanship and eliminate any grammatical errors. Example sentences to be reviewed carefully and reformulated are line 66-70, line 178-179, 180-183, 186-190, 194-195, 205-213, 242-244, 275-278, 292-295 etc.*

The resubmitted manuscript has been edited by a professional service in English.

2). *I am assuming eq.1 (line 164) is for the nitrate radical production rate (PNO_3), not the rate of change in O_3. As the authors mentioned the availability of O_3 is driven by its reaction with NO.*

Yes, Eq. 1 is the production of nitrate radical, but O_3 is also one reactant of this reaction. As the production of NO_3 takes place, the O_3 is consumed. This reaction is more important for O_3 losses for the conditions of the high-altitude (>150 m) air masses of which the reaction pathway of O_3 + NO is negligible due to the presence of zero NO.

3). *Use subscript for Ox throughout the text*

Corrected accordingly.

***4).** the authors define and discuss "particle nitrate convert efficiency" (sigma) in line 305- 310. Chang et al. 1 gives an excellent review of N_2O_5 chemistry and I suggest the authors read this as they discuss and introduce parameters regarding N_2O_5 conversion. I do not believe it is necessary to introduce a new parameter "particle nitrate convert efficiency" in this case.*

Thanks for your suggestion, Chang et al. (2011) reviewed the N_2O_5 chemistry systematically and comprehensively. With respect to N_2O_5 conversion, Chang et al., focused on the contribution to overnight NO_x loss. Here we revised the parameter to "Overnight NO_x loss efficiency (ε)", which also indicates the nitrate formation capacity. The equation changed as following:

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

Here the consumed NO_3 with VOCs and N_2O_5 uptake regarded as the effective NO_x loss. The Figure 7 changed the Y-axis and we did not normalize the loss efficiency, which shows the similar result with previous figure version."

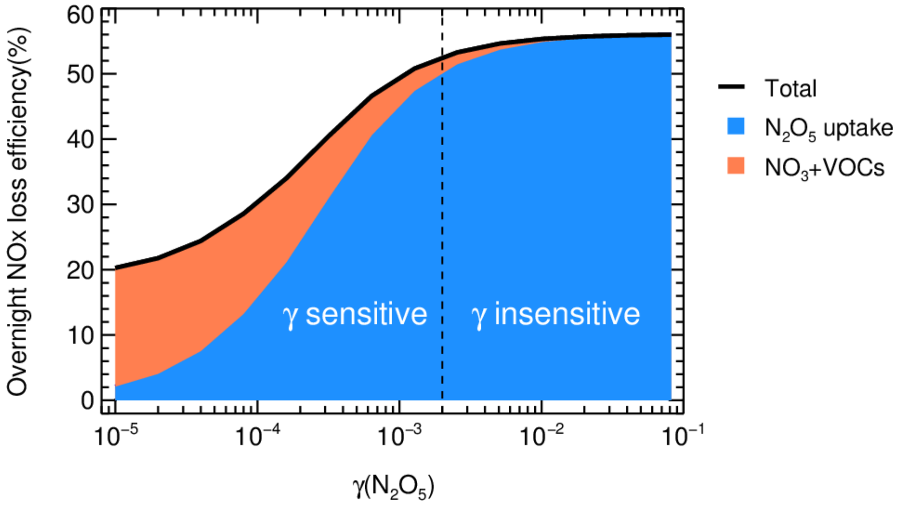

Figure 7. The dependence of overnight NO_x loss on N_2O_5 uptake on γ_{N2O5} in a typical winter pollution condition. The initial NO_2 and O_3 set to 60 ppbv and 30 ppbv, respectively, S_a set to 3000 μm^2 cm^{-3}, the $ClNO_2$ yield is zero and k_{NO3} is 0.02 s^{-1}. The reaction time set to 14.5 h.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

***5).** In that regard, the authors need to extend the literature search and include more references on N_2O_5 heterogeneous uptake and wintertime haze events outside the Beijing area. For more references on relevant topic, review publications of Chang et* *al. 1-2 , Lurmann et al. 3 , Brown et al. 4 , Green et al. 5 , Wang et al. 6 , Prabhakar et al. 7 etc.*

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Thanks for the suggestion and we compared our results with these references that concern the winter haze event in other region, and cited these work in the revised manuscript.

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~~Large~~High particulate nitrate formation ~~from~~via N_2O_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 of NO_x and O_3 were conducted during a winter heavy~~-~~haze episode (December 18 to 20, 2016) in urban Beijing, China. We found that pNO_3^- formation via N_2O_5 heterogeneous uptake was negligible at ground level, ~~due~~owing to the presence of high NO concentrations~~ limiting~~, which limited the production of N_2O_5. In contrast, the contribution from N_2O_5 uptake was larger at higher altitudes (e.g., > 150 m), which was supported by the ~~observed large~~low total oxidant (NO_2 + O_3) ~~missing aloft compared with~~level at higher altitudes than at ground level. ~~The~~ Modeling results show that the nighttime integrated production ~~potential~~ of pNO_3^- for the higher altitude air mass ~~overhead~~above urban Beijing was estimated to be 50 μg m^{-3}~~,~~ and enhanced the surface-layer pNO_3^- the next morning significantly ~~with~~by 28 μg m^{-3} ~~after~~through

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vertical mixing. The overnight NO_x loss via NO_3-N_2O_5 chemistry was efficient aloft (> 50%). The nocturnal ~~boundary layer broken in the next morning. In this case, the oxidation of NO_X to nitrate was~~ NO_x loss was easily maximized once the N_2O_5 uptake coefficient was over ~~0.0017, since N_2O_5 uptake dominated the fate of NO_3 and N_2O_5 with the presence of large aerosol surface concentrations.~~2×10^{-3} on polluted days in wintertime. These results highlight that pNO_3^- formation via N_2O_5 heterogeneous hydrolysis ~~at~~in 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.

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1. Introduction

Winter particulate ~~matters~~matter (PM) pollution events occur frequently in China~~,~~ and have drawn widespread and sustained attention in recent years (Guo et al., 2014; Zhang et al., 2015; Huang et al., 2014~~).~~; Wang G et al., 2016). PM pollution ~~reduced~~reduces visibility (Lei and Wuebbles, 2013) and ~~had~~has harmful effects on public health (Cao et al., 2012). Particulate nitrate (pNO_3^-) is an important component of secondary inorganic aerosols~~,~~ and ~~contributed to~~contributes 15%–40% of the $PM_{2.5}$ mass concentration in China (Sun et al., 2013, 2015a, 2015b; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015). The main atmospheric pathways of nitrate formation are (1) the reaction of OH with NO_2 and (2) N_2O_5 heterogeneous hydrolysis (Seinfeld and Pandis, 2006). The ~~first~~ reaction ~~(~~of OH ~~+~~with NO_2~~) was~~ is a daytime pathway ~~since~~, as OH is severely limited at night, and N_2O_5 uptake ~~was refer to~~is a nighttime pathway, as NO_3 and N_2O_5 ~~is~~are easily photo-labile.

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~~Nitrate~~Particulate nitrate formation via N_2O_5 heterogeneous hydrolysis in summer in north China was proved efficient by ground~~-~~-based observation ~~in summer in North China (H.C.~~ (Wang H et al., 2017b; ~~Z.~~ Wang Z et al., 2017~~), which is~~) and found comparable ~~with~~to or even ~~high~~higher than the daytime formation. Several ~~model~~ studies showed that N_2O_5 hydrolysis is responsible for nocturnal pNO_3^- enhancement

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in summer Beijing (Pathak et al., 2009, 2011; ~~H.C.~~ Wang H et al., 2017a). Although ~~the~~ pNO_3^- formation via N_2O_5 uptake is significant in summertime, the importance of this pathway in wintertime ~~was~~is not well characterized. ~~As there are many~~Many differences ~~of~~in N_2O_5 chemistry exist between winter and summer. First, as the key precursor of NO_3 and N_2O_5, O_3 ~~level are~~has a much lower concentration in winter than in summer ~~due~~, owing to the short daytime length and weak solar radiation. Second, colder temperatures and high NO_2 levels favor partitioning towards N_2O_5. Third, nighttime lasts much longer in winter, making N_2O_5 heterogeneous hydrolysis potentially more important in pNO_3^- formation. Finally, the N_2O_5 uptake coefficient, the most important parameter in N_2O_5 heterogeneous hydrolysis, is likely very different from that in summer. ~~Since~~This is because the ~~particle characteristics and meteorological conditions (e.g.~~properties of aerosol particles (e.g., organic compounds, ~~particle~~particulate nitrate, liquid water contents, solubility, and viscosity) and meteorological conditions (e.g., temperature and relative humidity) ~~are different in~~differ between summer and winter (Chen et al., 2015; Zhang et al., 2007). These ~~differences~~effects would result in large variations in the N_2O_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~~Wagner et al., 2013; Grzinic et al., 2015). Several parameterization methods have been unsuccessful in predicting N_2O_5 uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences~~, previous studies have also shown a potential altitude dependence~~ in pNO_3^- ~~production. In the evening, vertical mixing is strong suppressed in~~ formation via N_2O_5 uptake, modeling and field studies showed greater levels of NO_3 and N_2O_5 at higher altitudes within the nocturnal boundary layer (NBL~~) due~~), owing to the ~~reduction of sunlight diminishes the heating~~stratification of ~~the earth's~~ surface~~, leading to vertical layer occur with NO_3 and N_2O_5 gradient (~~ 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~~), as well as the particle~~; Geyer and Stutz, 2004; Stutz et al., 2004). The pNO_3^- formation via N_2O_5

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uptake contributes to the gradients in the compounds percentage and size distribution of the particle (Ferrero et al., 2010; 2012). On nights when NO_3 ~~radical~~ production in the surface layer is negligible ~~due~~owing to high NO emissions, N_2O_5 uptake ~~may~~can still be active aloft without NO titration ~~(Pusede et al.,~~ . ~~2016; Baasandorj et al., 2017).~~ The N_2O_5 uptake aloft leads to elevated pNO_3^- ~~formed~~formation in the upper layer ~~with~~as well as effective ~~NO_x~~NO_x removal (Watson et al~~.,~~., 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Pusede et al., 2016; Baasandorj et al., 2017). ~~), which was reported with field~~ Field observations at ~~a~~ high altitude ~~site in~~sites of Kleiner Feldberg, Germany (Crowley et al., 2010a~~),~~); the London British Telecommunications tower, UK (Benton et al., 2010~~),~~); and Boulder ~~Atmospheric Observatory (BAO) tower in Colorado~~, CO, USA (Wagner et al., 2013) ~~and so on.~~showed the elevated N_2O_5 concentrations aloft. Model studies ~~also proposed nitrate formation~~ showed that pNO_3^- varied ~~in~~at different ~~height~~heights and stressed the importance of the heterogeneous formation mechanism (Kim et al., 2014; Ying, 2011; Su et al., 2017). The mass fraction and concentration of pNO_3^- in Beijing was reported higher aloft (260 m) than at the ground level in Beijing (Chan et al., 2005; Sun et al., 2015b), ~~and they~~which was explained ~~the~~by favorable gas~~-~~ particle partitioning aloft under lower temperature conditions. 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), especially in valley terrain regions coupled with 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 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_2O_5 heterogeneous hydrolysis and its impact on pNO_3^- formation at different altitudes during a heavy haze episode over urban Beijing. Additionally, the dependence of NO_x removal and pNO_3^- formation on the N_2O_5 uptake coefficient was probed.

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2. Methods

2.1 Field measurement

Ground ~~measurement~~measurements (15 m above the ground) ~~was~~were carried out ~~in~~on the campus of Peking University (PKU~~,~~; 39°59'21"N, 116°18'25"E) in Beijing, China. The ~~location~~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~~ was~~. The locations of the PKU and IAP sites are shown in Fig. 1~~, as well as the vertical measurement site (IAP, introduced below). At~~. At the PKU site, dry-state mass concentration of $PM_{2.5}$ was measured ~~by~~using a TEOM 1400A analyzer. NO_x was measured ~~by~~via a chemiluminescence analyzer (Thermo Scientific, TE-42i-TR~~)~~), and O_3 was measured ~~by~~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.~~6~~7 μm with a Scanning Mobility Particle Sizer (SMPS~~,~~; TSI Inc. 3010). ~~These~~The instrumental parameters ~~were listed~~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~~ at~~, from the tower-based platform (maximum height: 325 m) on the IAP 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 ~~NO_x and O_3 instruments were installed ~~on board~~aboard a movable cabin on the tower. ~~The ambient ~~NO_x and O_3~~ concentrations~~ were measured with two low-power, ~~light-weight~~lightweight instruments (Model 405 nm and Model 106-L~~;~~, 2B Technologies, USA). The Model 405 nm instrument measures NO_2 directly based on the absorbance at 405 nm, and NO is measured by adding excess O_3 (conversion efficiency ~100%). The limit of detection of both NO and NO_2 is 1 part per billion volume (ppbv), with an accuracy of 2 ppbv or 2% of the reading, and the time resolution is 10 s~~.~~ (Birks et al., 2018). The Model 106-L

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instrument measures O_3 based on the absorbance at 254 nm, with a precision of 1 ppbv, or 2% of the reading, and a limit of detection of 3 ppbv. NO_x calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with a NO standard (9.8 ppmv). The O_3 calibration was done with an O_3 calibrator (TE 49i-PS), which was traceable to NIST (National Institute of Standards and Technology) standards annually. Before the campaign, the NO_x monitor was compared with a Cavity Attenuated Phase Shift (CAPs) Particle Light Extinction Monitor, and the O_3 monitor was compared to a commercial O_3 analyzer (TE-49i, Thermo Electron, USA). Good agreement was found between the portable instruments and the conventional monitors. Height information was retrieved ~~from~~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 ~~at~~during the daytime and 240 m at night. The cabin stopped after reaching the peak, and parameters were measured continually ~~for~~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, with six measurement cycles conducted in total during the campaign.

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 the IAP site. A simple chemical mechanism (see R1~~-~~–R5) ~~is~~was used to model the nighttime NO_3 and N_2O_5 chemistry ~~in~~under NO free -air~~ masses, and the physical-~~mass conditions. Physical mixing, dilution, deposition, or interruption during the transport of the air mass ~~were~~was 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~~uptake reaction were neglected in this analysis because ~~there is little~~of the low level of absolute humidity and the extremely low NO_3 concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of R1~~–~~–R3 are those reported by Sander et al~~.,~~. (2011).

~~(R1)~~ $NO_2 + O_3 \rightarrow NO_3 + O_2$ (R1)

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~~(R2)~~ $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$ (R2)

~~(R3)~~ $N_2O_5 + M \rightarrow NO_2 + NO_3 + M$ (R3)

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

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

Following the work of Wagner et al~~.,~~., (2013), the box model can be solved ~~by four~~using six equations (~~Eq~~Eqs. 1~~-4~~-6). In the framework, O_3 is only ~~losses~~lost via the reaction of NO_2~~+~~ + O_3 and the change ~~of~~in the O_3 concentration can ~~express as Eq. 1. Since the ratio~~be expressed as Eq. 1. Eq. 2 can express the losses of NO_2. Here, the s(t) is between 0 and 1 and expressed as Eq. 5. The s(t) favors 0 when direct loss of NO_3 dominates and favors 1 when N_2O_5 ~~to NO_3 was calculated to be larger than 150:1 in a typical urban region in wintertime (NO_2 = 15 ppbv, nighttime temperature = 0°C), N_2O_5 is proposed to be dominate the~~ uptake dominates NO_3 loss~~, than means two molecules of NO_2 lost (convert to nitrate or $ClNO_2$) for one molecule NO_3 formed (Eq. 2). In the~~. The model ~~we need to know~~calculation had two steps. The first step was to calculate the mixing ratio of NO_2 and O_3 at time zero (~~here~~herein designated as sunset). According to Eqs. 1 and 2, the initial NO_2 (t=0) and O_3 (t=0) concentrations can then be integrated backward in time starting with the measured concentrations of NO_2 and O_3 at each height. During the pollution period in winter in Beijing (NO_2 = 45 ppbv, Temperature = 273 K, $S_a = 3000\ \mu m^2\ cm^{-3}$), the ratio of N_2O_5 to NO_3 is large enough, i.e., 450. The pseudo-first-order loss rate of N_2O_5 heterogeneous uptake will be $1\times10^{-3}\ s^{-1}$, with a N_2O_5 uptake coefficient of 5×10^{-3}. N_2O_5 uptake would contribute an NO_3 loss rate of $0.4\ s^{-1}$, which is much higher than the direct NO_3 loss through the reaction of NO_3 with VOCs, even with the k_{NO3} set to a high value of $0.02\ s^{-1}$. Therefore, N_2O_5 uptake was proposed to be dominantly responsible for the NO_3 loss and the initial s(t) was set to ~~sunset). According to~~ 1. Eq. ~~1 and Eq. 2,~~3 can describe the ~~NO_2 (t=0) and O_3 (t=0)~~sum concentration ~~can derived from the duration time and the vertical measured NO_2 and O_3 at each height~~of NO_3 and N_2O_5. Assuming the equilibrium between NO_3 and N_2O_5 is maintained after a ~~time~~ period, ~~the sum concentration of NO_3 and N_2O_5 can be described by Eq. 3. Using~~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

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the ratio of N_2O_5 ~~and~~to NO_3. Combined, ~~Eq~~Eqs. 1~~–~~–4 allow for the calculation of ~~N_2O_5 concentrations, given a constant of NO_3 and N_2O_5 rate constant (k_{NO3} and k_{N2O5}). Modeled~~NO_3 and N_2O_5 concentrations considering stable NO_3 and N_2O_5 loss rate constants (k_{NO3} and k_{N2O5}, respectively). In the second step, a new s(t) was calculated using the data from the first step (Eq. 5), new initial NO_2 and O_3 concentrations were then approximated, and NO_3 and N_2O_5 values were derived using the same method as used in the first step. This process was repeated until the difference between the two s(t) values was less than 0.005. The number of adjustments to a new s(t) could not be calculated more than 10 times. Otherwise, the calculating process would become non-convergent.

The modeled N_2O_5 concentrations and given k_{N2O5} ~~are~~were then used to estimate pNO_3^- formation~~, here the~~. The HNO_3 produced in R4 ~~is~~was not ~~accounted, as a large part~~considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here~~,~~ k_{NO3} and k_{N2O5} ~~denotes~~denote the pseudo~~-~~-first~~-~~-order reaction rate ~~constant~~constants of the total NO_3 reactivity caused by ambient ~~volatile organic compounds (~~VOCs~~)~~ and N_2O_5 heterogeneous uptake, respectively. k_{N2O5} is given in Eq. ~~5~~6. S_a is the aerosol surface area, C is the mean molecular speed of N_2O_5, and γ_{N2O5} is the N_2O_5 uptake coefficient. ~~The~~Sunset and sunrise times during the measurements were 16:55 and 07:30 (Chinese National Standard Time, CNST), and the model ~~is~~was run from sunset to sunrise, ~~where~~with the ~~length of night was about~~running time set to 14.5 h.

~~(Eq. 1)~~ $$\frac{d[O_3]}{dt} = -\cancel{k_{NO2+O3}}k_{NO2+O3}[O_3][NO_2]$$

(1)

~~(Eq. 2)~~ $$\frac{d[NO_2]}{dt} \cancel{= -2 \times k_{NO2+O3}} = -(1 + s(t)) \times k_{NO2+O3}[O_3][NO_2]$$

(2)

~~(Eq. 3)~~ $$\frac{d[NO_3+N_2O_5]}{dt} = \cancel{k_{NO2+O3}}k_{NO2+O3}[O_3][NO_2] - \cancel{k_{N2O5}}k_{N2O5}[N_2O_5] - \cancel{k_{NO3}}k_{NO3}[NO_3] \qquad (3)$$

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

~~(Eq. 5) $k_{N2O5} = \frac{C\times S_a\times\gamma_{N2O5}}{4}$~~

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

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

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 ~~by~~via a growth factor (Liu et al., 2013). The uncertainty of the wet S_a was estimated to be ~30%, which was associated ~~from~~with the error from dry PNSD measurement (~20%) and the growth factor (~20%). Nighttime averaged S_a on the night of December 19 ~~is~~was about 3000 μm^2 cm^{-3}. PM measurements ~~by~~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~~ shown~~, showed small variation ~~of~~in the vertical particle number concentration, with ~~the~~a boundary layer height ~~below~~of 340 m (Zhong et al., 2017). Therefore, the S_a measured at the PKU site ~~is representative to~~ can represent the urban Beijing conditions in horizontal and ~~applied in the model is reasonable~~vertical scale (< 340 m). Although the PNSD information for particles larger than 0.7 μm was not valid during the study period, the particles smaller than 0.7 μm dominated more than 95% of the aerosol surface area in a subsequent pollution episode (01/01/2017 to 01/07/2017), and similar results also were reported in other studies (e.g., Crowley et al., 2010a; Wang et al., 2018). The possible lower bias of S_a (5%) only led to a small overestimation of N_2O_5, i.e., 3.6%–4.2%, and an underestimation of pNO_3^- of 0.2%–2.5% when γ_{N2O5} varied from 1×10^{-3} to 0.05.

The N_2O_5 uptake coefficient ~~was regard as the main uncertainty of the N_2O_5 loss, along with the~~ and $ClNO_2$ yield ~~lead to the uncertainties~~are key parameters in the estimation of ~~particulate nitrate~~ 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 ~~particular nitrate~~pNO_3^- suppression of N_2O_5 uptake aloft in the wintertime in Denver, CO, USA, ~~with~~ the uptake coefficient ~~of about~~is 0.005 when ~~particulate~~

~~nitrate fraction~~the percentage of pNO_3^- in the $PM_{2.5}$ mass concentration ~~about~~is 40%. ~~Considered~~As the ~~high~~proportion of nitrate in the particle ~~nitrate content~~ mass concentration is similarly high in North China ~~in~~during 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~~herein we ~~used a constant~~ fixed the uptake coefficient ~~of~~to 0.005 ~~as~~for the base model initial input ~~in the base case, and the uncertainty of N_2O_5 uptake coefficients will be discussed later. Since~~. Because the model input of $ClNO_2$ yield only ~~affect~~affects the value of produced ~~particulate nitrate~~pNO_3^- 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~~ The average value ~~in summertime was estimated to be 0.024~~of k_{NO3} of about 0.011 s^{-1} in ~~2006 (H.C.~~ summer Beijing was calculated in a previous work, with BVOCs contributing significantly (Wang H et al., 2017a~~). While in wintertime, the k_{NO3} should be smaller as the~~ ; Wang et al., 2018). The intensity of ~~plant~~biogenic VOCs emissions ~~reduced in~~decreased in wintertime, owing to the lower temperature and weak solar radiation~~. The~~ , thus the k_{NO3} should be smaller than it is in summer. In this work, the model input ~~$k(NO_3)$~~k_{NO3} was set to ~~an relative moderate~~a 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 ~~were~~was conducted to study the uncertainties ~~to~~of the model simulation, and the detailed test ~~set were~~sets are listed in Table 1, included the test of N_2O_5 uptake coefficient and k_{NO3}. The γ_{N2O5} sensitivity tests were set ~~to a lower limit of~~from 0.001 to ~~a upper limit of~~ 0.05, ~~as well as~~and the k_{NO3} tests were set to 0.001 s^{-1}, 0.01 s^{-1}, and 0.1 s^{-1}.

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3. Results and discussion

3.1 Ground-based observations.

A severe winter PM pollution event ~~was captured from the ground observations~~lasted from December 16 to 22, 2016, in Beijing. Figure 2a ~~shown~~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 ~~on~~from December 16~~ and reached the maximum value of~~, reaching 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~~was captured, with an overall increment of 100 µg m^{-3}~~. During the~~ on the night of December 19 (Fig. 2a). Throughout the pollution episode, the meteorological ~~condition is featured with~~conditions included high RH (50% ± 16%) and low temperature (2 ± 3 ~~°C~~°C). The slow surface wind speed (< 3 m s^{-1}), ~~indicated~~implied the atmosphere was ~~static stabilized~~stable (Fig. 2c, ~~2d~~d). The daytime O_3 concentration was low~~ due~~, 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, ~~and ~~further ~~suppressed~~suppressing N_2O_5 near the ground. Figure 2b ~~depicted large~~depicts the high amounts of NO and NO_2 that were observed ~~throughout~~at ground level during the~~ whole~~ PM pollution episode, suggesting that pNO_3^- production via N_2O_5 uptake was not important near the ground during the winter haze episode.

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3.2 Tower observations.

Six vertical measurements of the total oxidants (O_x ~~(<~~= O_3 + NO_2) below 50 m~~) was consist~~ were consistent with ~~that~~those measured at ground level and are shown in Fig. S2, ~~confirmed ~~confirming that 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 ~~concentrations of 80 ppbv and 100 ppbv, respectively. The O_3 concentrations ~~keep~~remained zero during the nighttime (Fig. 3b). The vertical profile on December 20 suggests that at least below 240 m, the N_2O_5 chemistry ~~is also~~was not important~~ like~~, which is consistent with the results at ground level as mentioned above. The case on the night of December 18 ~~is~~was similar to that on the night of December 20~~.~~

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~~The~~, whereas the vertical ~~measurement~~profile on December 19 ~~did~~was not ~~like those~~

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~~happened~~similar to that 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~~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 ~~instrument~~instrumental limit of detection ~~below 150 m~~ (Fig. 4b). Above 150 m, the O_3 concentration was 20 ± 2 ppbv, corresponding to the greatly diminished NO concentration. With respect to ~~the total oxidants (~~O_x~~$= O_3 + NO_2$),~~, the mixing ratio of O_x was 85 ± 2 ppbv at lower altitudes, ~~while~~whereas the O_x concentration at higher altitudes was 15 ppbv lower than that at lower ~~altitude~~altitudes (Fig. 4b). The ~~O_x~~O_x missing ~~at~~from the higher altitude air mass indicated an ~~additionally~~additional nocturnal removal of O_x aloft.

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Figure 5 ~~depicted~~depicts the vertical ~~measurement~~profiles of NO_x, O_3, and O_x at 09:30 on the morning of December 20~~ has~~, which have similar features ~~with~~to those observed at 21:00 on December 19~~, and the NBL~~. The vertical profiles suggested stratification still ~~not be broken.~~existed at that time. The ~~O_x~~amount of O_x missing aloft in the morning increased to 25 ppbv at 240–260 m, ~~demonstrated~~demonstrating that an additional 25 ppbv of O_x was removed or converted to other compounds at higher altitudes than at the surface layer ~~on~~during the night ~~of~~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 ~~the~~ solar radiation ~~is~~was strong enough to ~~drive~~mix the trace ~~gas mixing~~gases well in the vertical direction. NO_x and O_3 were ~~observed~~found to be well mixed indeed, with small variation from the ground level to 260 m.

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3.3 Particulate nitrate formation aloft.

N_2O_5 uptake is one of the two most important pathways of ~~the~~ ambient ~~NO_x losses,~~NO_x loss and~~ is consequently~~ an important pathway of pNO_3^- formation (Wagner et al., 2013; Stutz et al., 2010; Tsai et al., 2014). At higher altitudes (e.g~~.~~., > 150 m), NO_3 and N_2O_5 chemistry can be initiated in the co-presence of high NO_2 and significant O_3 levels.

Therefore, N_2O_5 uptake could represent a plausible explanation for the O_x observed ~~O_x~~ missing ~~in~~from 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_3 and N_2O_5 chemistry based on the observed vertical profiles of NO_2 and O_3 on the night of December 19.

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In the base case, the average initial NO_2 and O_3 levels above 150 m at sunset were about 61 ± 3 ppbv and 27 ± 6 ppbv, respectively. The measured NO_2 concentration at the PKU site at sunset (local time, 16:55) was 61 ppbv and showed good consistency with the model result. The modeled N_2O_5 concentration ~~is~~was zero below 150 m, as the high level of NO ~~consumed NO_3 formation fast. While~~made for quick consumption of the NO_3 formed. In contrast, the modeled N_2O_5 concentrations at 21:00 above 150 m were in the range of 400~~-~~–600 ~~parts per trillion volume (~~pptv~~) above 150 m~~ (Fig. ~~5a). pNO_3~~6a). Particulate NO_3^- accumulation via N_2O_5 heterogeneous ~~hydrolysis~~uptake from sunset to the measurement time, which can be calculated using Eq. 7, was significant~~, yielding~~ above 150 m, with a maximum of 24 μg m^{-3} ~~within~~ 4.5 hours after sunset (Fig. ~~5(b)).~~6b).

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

The box model enabled the analysis of the integrated pNO_3^- and $ClNO_2$ via N_2O_5 uptake ~~over~~throughout the ~~whole~~ night. As shown in Fig. ~~5c~~6c, 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 ~~O_x, shows a~~O_x, showing good agreement with the observed ~~O_x~~O_x missing aloft ~~at~~in the morning hours. During the nighttime, the pNO_3^- formed ~~pNO_3^-~~ aloft via N_2O_5 uptake ~~would lead~~led to the much higher particle nitrate concentration ~~much higher~~ 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). ~~In addition, during the morning time when NBL was broken, the~~The elevated pNO_3^- aloft ~~will vertically mixed~~ was well dispersed through vertical mixing and enhanced the surface-layer PM concentration ~~at surface layer,~~; this phenomenon was also ~~been~~ observed in previous studies (Watson et al~~.,~~.,

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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 ~~; Prabhakar et al., 2017). Zhong et al. (2017) showed that the NBL and PBL both were at 340 m from December 19 to 20, 2016 in Beijing. Daytime vertical downward transportation was helpful in mixing the air mass within the PBL. Assuming the newly formed pNO_3^- aloft from 150 m to 340 m is 50 μg m^{-3} during the nighttime ~~N_2O_5 uptake aloft would be enhanced the ground pNO_3^- mass concentration significantly with ~~and well mixed within the PBL by the next morning, the enhancement to the surface layer (ΔpNO_3^-) can be simplified to the calculation in Eq. 8 as following:

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

Here, $P(pNO_3^-)$ is the integral production of pNO_3^- and H represents height. Owing to high NO below 150 m, the pNO_3^- formation via N_2O_5 uptake was zero. The enhancement of pNO_3^- from 150 m to 340 m was calculated as 28 μg m^{-3} ~~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_2O_5 uptake aloft and downward transportation ~~are really importance in~~were critical for understanding the PM growth process.

3.4 Sensitivity studies.

Previous studies have emphasized that the N_2O_5 uptake coefficient varies greatly (0.001–0.1) in different ambient conditions (Chang et al., 2011; Brown and Stutz, 2012; ~~H.C. ~~Wang H et al., 2016), which is the main source of uncertainties in ~~the model. Sensitivity tests illustrate that~~this model. In the present research, sensitivity studies showed the modeled N_2O_5 concentration ~~varied~~dropping from 3 ppbv to 60 pptv when the N_2O_5 uptake coefficients ~~were varied~~increased from 0.001 to 0.05 (Fig. 6a), as the N_2O_5 concentration is very ~~sensitivity~~sensitive to the loss from heterogeneous

~~reaction~~reactions. Compared ~~with~~to the base case, the accumulated pNO_3^-, ~~is~~was evidently lower at $\gamma = 0.001$ with the accumulated pNO_3^- of 44 μg m^{-3}, thus the low N_2O_5 uptake coefficient condition ~~is corresponding~~corresponded to several kinds of aerosols, such as secondary organic ~~aerosol~~aerosols (Gross et al., 2009), humic ~~acid~~acids (Badger et al., 2006~~))~~), and certain solid aerosols (Gross et al., 2008). When the N_2O_5 uptake coefficient ~~enlarges~~increased from 0.005 to 0.05 (Fig. 6b, c), the increase in integral pNO_3^- ~~almost not change with~~was negligible~~ increasing, indicating~~. This indicates that the conversion capacity of N_2O_5 uptake to pNO_3^- was almost maximized at certain $ClNO_2$ yield~~, the convert capacity ~~. The conversion of NO_x to nitrate was not limited by the N_2O_5 heterogeneous reaction rate, but by the formation of NO_3 ~~by~~via the reaction of NO_2 with O_3 during the polluted night.

For describing the nocturnal NO_x ~~convert~~removal capacity ~~to particulate nitrate~~and pNO_3^- formation via NO_3 and N_2O_5 ~~uptake coefficient, here we defined~~chemistry, the ~~particle nitrate convert~~overnight NO_x loss efficiency (ε) ~~as~~was calculated using Eq. ~~6. The Δt represents the time duration from time zero at sunset till the ending time at sunrise~~9.

~~(Eq. 6) $\varepsilon = \frac{\sum_0^{\Delta t} k_{N2O5}[N_2O_5]}{\sum_0^{\Delta t} 2\times k_{NO2+O3}[O_3][NO_2]}$~~

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

The case modeled typical winter haze pollution conditions in Beijing from sunset to sunrise, with the initial model values of NO_2 and O_3 set to 60 ppbv and 30 ppbv, respectively. S_a ~~is~~was set to 3000 μm^2 cm^{-3}, the $ClNO_2$ yield ~~is zero and k_{NO3} is 0.02 s^{-1}.~~ was zero, and k_{NO3} was 0.02 s^{-1}. The reaction time was set to 14.5 h to represent an overnight period in wintertime. The consumed NO_3 by the reaction with VOCs and N_2O_5 by uptake reaction were regarded as valid NO_x loss. Figure 7 shows the dependence of the ~~particle nitrate convert efficiency varied from 10^{-5} to 0.1.~~ overnight NO_x loss efficiency on N_2O_5 uptake, as it varied from 1×10^{-5} to 0.1. This is an increase from 20% to 56%, with increasing γ_{N2O5}, and the maximum NO_x loss efficiency was very large, as was addressed by Chang et al. (2011). The ceiling of overnight NO_x loss

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via NO_3-N_2O_5 was fixed when all the NO_x loss was through N_2O_5 uptake, which is limited by the reaction time and the formation rate of NO_3 (R1). In this case, the N_2O_5 uptake was contributed about 90% of the overnight NO_x loss (50.4%) when γ_{N2O5} was equal to 0.002. When γ_{N2O5} ~~is lower~~was less than ~~0.0017, the particle nitrate formation enhanced~~2×10^{-3}, NO_x removal increased rapidly with the increasing of ~~N_2O_5 uptake coefficient, here we~~γ_{N2O5}, which was defined as the γ_{N2O5}-sensitive region. When γ_{N2O5} $\geq 2\times10^{-3}$, the contribution of N_2O_5 uptake to NO_x loss was over 90% and became insensitive, this region was defined as the γ_{N2O5} ~~sensitive region when γ_{N2O5} < 1.7×10^{-3}. While γ_{N2O5} $\geq 1.7\times10^{-3}$ is defined as γ_{N2O5} insensitive region, since the convert efficient is over 90% and not sensitive to the variation of N_2O_5 uptake coefficient.~~ -insensitive region. According to ~~Eq~~Eqs. 3 and ~~Eq.~~ 5, higher aerosol surface concentration~~, higher~~ and NO_x~~,~~ and lower k_{NO3} and temperature would further ~~enlarging~~increase the insensitivity region with lower γ_{N2O5} value~~,~~ and ~~make~~allow the N_2O_5 uptake to be more easily located in the γ_{N2O5}-insensitive region. Here, the critical value of the N_2O_5 uptake coefficient (~~1.7~~2×10^{-3}) ~~is relative~~was relatively low compared ~~with~~to that recommended by the IUPAC (International Union of Pure and Applied Chemistry) ~~recommended~~ on the surface of mineral dust (0.013, 290~~-300K~~-300 K) (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 Z et al., 2017; Brown et al., 2016; ~~H.C.~~ Wang H et al., 2017b; ~~X.F.~~ Wang X et al., 2017~~), suggesting~~). This suggests that the ~~particulate nitrate~~NO_x loss and pNO_3^- formation via N_2O_5 uptake ~~was~~were easily maximized in ~~polluted~~ the pollution episode, ~~and~~ further ~~worsen~~worsening the PM pollution.

In the base case, the modeled ~~particulate nitrate~~pNO_3^- formation via N_2O_5 uptake ~~is~~was an upper limit result, as the $ClNO_2$ yield was set to zero. ~~Since large coral~~High coal combustion emitted chloride into the atmosphere ~~in~~of Beijing during the heating period ~~in Beijing~~ (Sun et al., 2013), ~~associated with~~like the ~~emission by~~emissions from power plants in ~~North~~north China. ~~The~~This enhanced anthropogenic ~~emission of~~ chloride provides abundant chloride-containing ~~aerosol~~aerosols to form $ClNO_2$ via N_2O_5 uptake aloft, implying that significant $ClNO_2$ formed in the upper layer of the

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NBL (Tham et al., 2016; ~~Z.~~ Wang Z et al., 2017). Assuming the $ClNO_2$ yield is the average value of 0.28 determined at high altitude in ~~North~~north China (~~Z.~~ Wang Z et al., 2017), the pNO_3^- produced ~~pNO_3^-~~ throughout the ~~whole~~ night will have decreased by 7 μg m^{-3}. The $ClNO_2$ formation aloft throughout the night ~~reach up to~~reached 2.5 ppbv, which is comparable with that observed in ~~the~~ field measurement in ~~North~~north China (Tham et al., 2016;~~ Z.~~ Wang ~~et al., 2017; X.F. Wang~~ Z et al., 2017~~).~~; Wang X et al., 2017). As the error of pNO_3^- formation simulation was subject to the $ClNO_2$ yield, a higher yield would increase the model uncertainty directly, hence probing the $ClNO_2$ yield ~~are~~is warranted in future studies. As for NO_3 reactivity, ~~Figure~~Fig. 7 shows the sensitivity tests of the integral pNO_3^- formation ~~in~~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 ~~was~~ decreased when k_{NO3} ~~vary~~varied from 0.001 s^{-1} to 0.1 s^{-1}, but the variation ratio to the base case was within ±5%. The result shows the NO_3-N_2O_5 loss via NO_3 ~~react~~reaction with VOCs ~~in~~during the polluted wintertime ~~is~~was not important, which may only lead to ~~relative~~relatively small uncertainties ~~to~~in the integral pNO_3^- formation calculation. Nevertheless, if N_2O_5 uptake was extremely low (e.g~~.~~., γ_{N2O5} < 10^{-4}), the uncertainty ~~cased by~~of NO_3 oxidation ~~will be enlarged~~would increase significantly.

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4. Conclusion

During the wintertime, ambient O_3 is often fully titrated ~~to be zero~~ at the ground ~~of~~level in urban Beijing ~~due~~owing to its fast reaction with NO emissions. Consequently, the near~~–~~-surface air masses ~~were~~are chemically inert. Nevertheless, the chemical information of the air masses at higher altitudes was indicative of a reactive layer above urban Beijing, which potentially drives fast pNO_3^- production via N_2O_5 uptake~~.~~ and contributes to the surface PM mass concentration. In this study, we evidenced ~~of an~~ additional O_x missing (25 ppbv) aloft ~~with 25 ppb~~ throughout the night. Based on model simulation, we found that the particulate nitrate formed above 150 m ~~can reach up to~~ reached 50 μg m^{-3}~~,~~ and ~~enhance~~enhanced the surface level PM concentration significantly ~~with~~by 28 μg m^{-3} with downward mixing after break-up of the NBL

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~~breaking.~~in the morning. Our study also demonstrated that during the heavy PM pollution period, the particulate nitrate formation capacity via N_2O_5 uptake ~~is~~was easily maximized in the upper layer, even with N_2O_5 uptake ~~is~~ as low as ~~1.7~~2×10^{-3}~~, indicating~~. This indicates that the mixing ratio of NO_2 aloft ~~are~~was directly linked to nitrate formation, and reduction of NO_x is helpful ~~to decrease~~in decreasing nocturnal nitrate formation. Overall, this study highlights the importance of the interplay between chemical formation aloft and dynamic processes for probing the ground~~-~~-level PM pollution problem. In the future, direct observations of N_2O_5 and associated parameters should be performed to explore the physical and chemical properties of this overhead nighttime reaction layer~~,~~ and ~~reached~~to reach a better understanding of the winter haze formation.

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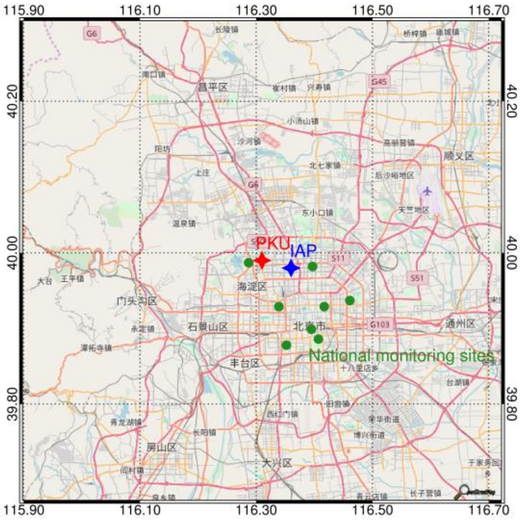

Figure 1. Location of the monitoring sites used in this study, including PKU (red diamond), IAP (blue diamond), and other National Monitoring Sites (green circles). Vertical profiles of NO_x and O_3 were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate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

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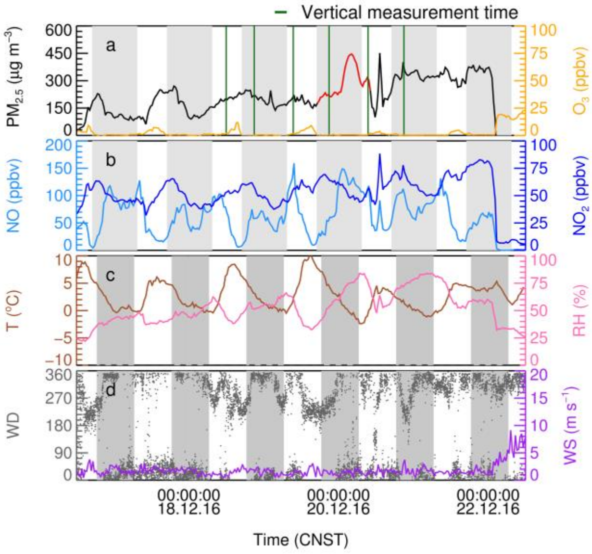

Figure 2. Time series of **(a)** PM$_{2.5}$ and O$_3$, **(b)** NO and NO$_2$, **(c)** temperature (T) and relative humidity (RH), **(d)** wind direction (WD) and wind speed (WS) from December 16 to 22, 2016 ~~(CNST, Chinese National Standard Time)~~ at PKU site in Beijing, China. The shaded region represents 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.

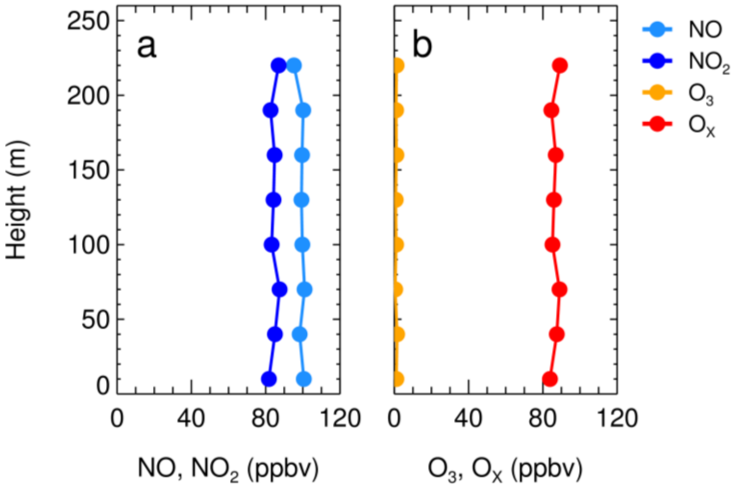

Figure 3. Vertical profiles of NO and NO_2 (**a**), O_3 and O_x (**b**) at 20:38-21:06 on the night of December 20, 2016.

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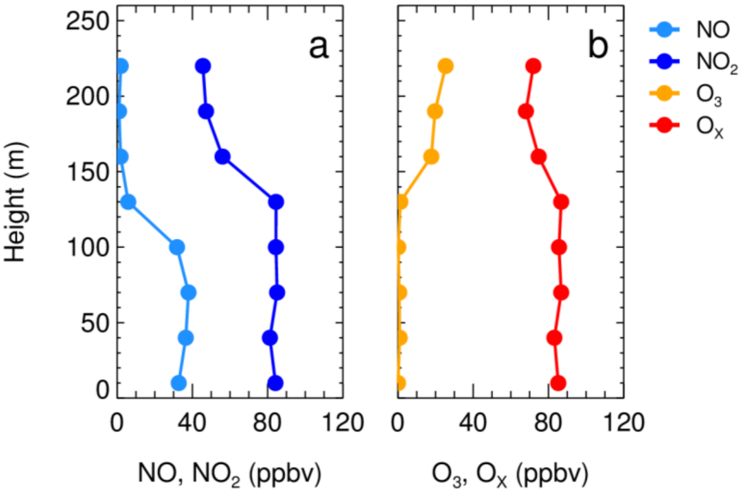

Figure 4. ~~O_x~~O_x missing case presented by the vertical profiles of (**a**) NO and NO_2, (**b**) O_3 and ~~O_x~~O_x at 20:38-21:13 on the night of December 19, 2016.

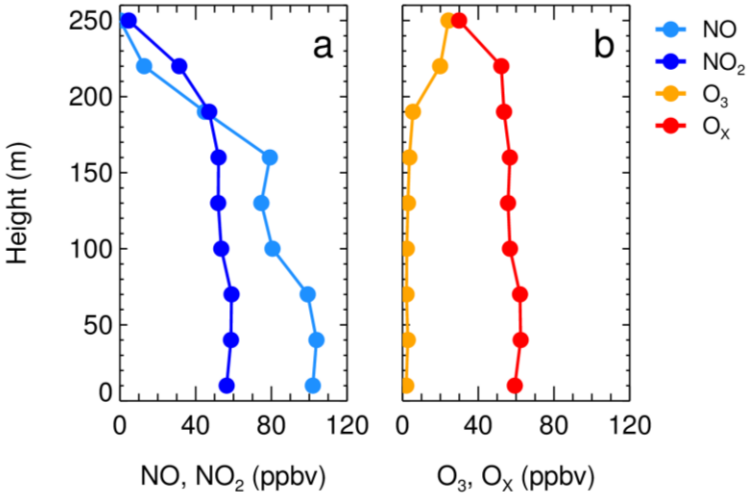

Figure 5. Vertical profiles of (**a**) NO and NO$_2$, (**b**) O$_3$ and ~~O$_x$~~O$_x$ at 09:06-09:34 in the morning of December 20, 2016.

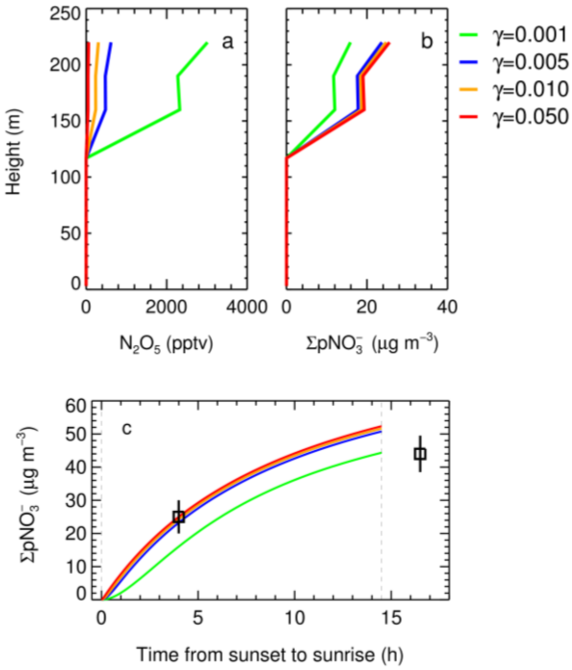

Figure 6. Base case (γ=0.005) and sensitivity tests of the vertical profile on the night of December 19 at different N_2O_5 uptake coefficients, including **(a)** the mixing ratio of N_2O_5 at 21:00, **(b)** the integral pNO_3^- production from sunset to 21:00, **(c)** the time series of the integral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

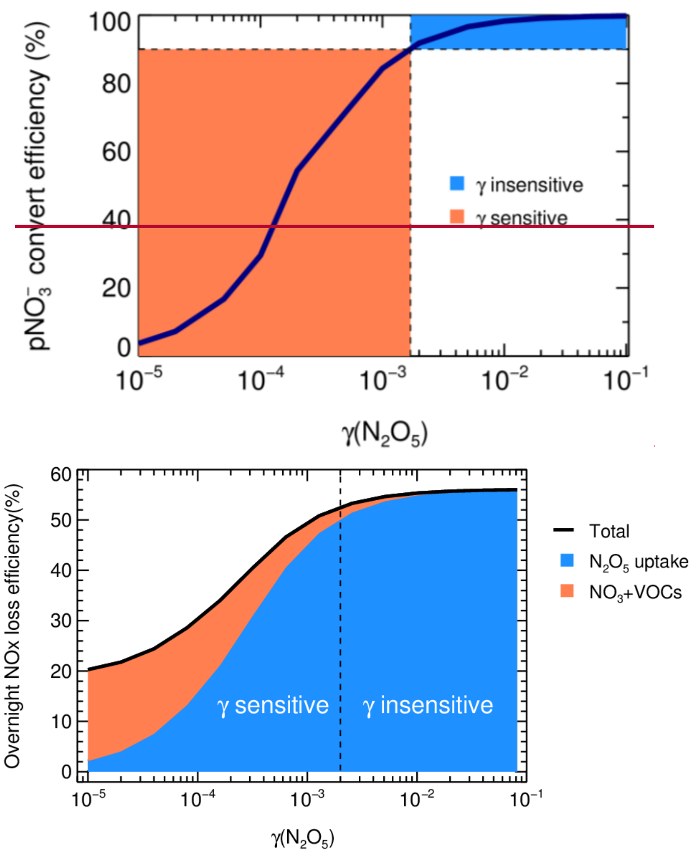

Figure 7. The dependence of ~~pNO$_3^-$ convert efficiency by~~ overnight NO$_x$ loss on N$_2$O$_5$ uptake on γ_{N2O5}~~.~~ in a typical winter pollution condition. The initial NO$_2$ and O$_3$ set to 60 ppbv and 30 ppbv, respectively, S_a set to 3000 μm^2 cm^{-3}, the ClNO$_2$ yield is zero and k_{NO3} is 0.02 s^{-1}. The reaction time set to 14.5 h. The blue and orange ~~region shows~~zone represent the ~~convert efficiency is sensitive~~ contribution by NO$_3$+VOCs and N$_2$O$_5$ uptake, the dashed line (γ = 0.002, when ~~γ < 0.0017, while the blue region shows~~N$_2$O$_5$ uptake contribute to 90% of the ~~convert efficiency is over 90%~~ maximum NO$_x$ loss) divide the loss into γ sensitive and insensitive ~~when γ ≥ 0.0017.~~region. The maximum nocturnal NO$_x$ loss by NO$_3$-N$_2$O$_5$ chemistry is 56%.

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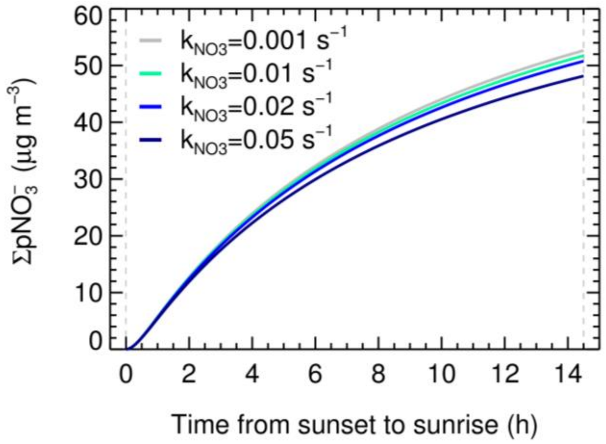

Figure 8. Base case (k_{NO3}=0.02 s^{-1}) and sensitivity tests of the integral pNO_3^- formed at 240 m via N_2O_5 uptake at different NO_3 reactivity (0.001 s^{-1}, 0.01 s^{-1}, 0.05 s^{-1}) on the whole night of December 19, 2016.

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

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

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