We thank the editor and referees for his/her careful reading and constructive comments on our manuscript. As detailed below, the referee’s comments is in black, our response to the comments is in blue. New or modified text is in red.

Referee #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 O3, NO, and NO2 which enabled calculation of NO3 production, but several key parameters, such as N2O5, VOCs and aerosol surface area density, for loss of NO3, N2O5 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.

The Referee’s concerns can be summarized in two points as follows:

Point 1, there were limited set of parameters such as NO-NO2-O3, it may subject to large uncertainties when used for estimating the loss rate of N2O5.

Point 2, the representative of the case study for the winter Beijing.

We fully understand these concerns and we agree these are fair questions which needs to be addressed better.

For the point 1 concern, there will be large uncertainties of our method if it is summer, nevertheless, the winter Beijing conditions (low temperature and high NO2) offered us big advantages in avoiding uncertainties. The advantages come from two folds, on one hand, the ratio of N2O5 to NO3 was normally over 100:1 in the lower temperature and high NO2 condition and thus the production rate of NO3 was mostly in balance with the N2O5 loss rate (as shown in Fig. 7); on the other hand, the uncertainty of the iterative box model was controllable in polluted winter time as suggested by Wagner et al., (2013) and McDuffie et al., (2018).

For the point 2 concern, here we found a special case show the importance of the N2O5 uptake to the particulate nitrate formation in the urban canopy of Beijing which fits the recent discovery on the nighttime boundary layer diagnosis (Zheng et al., 2015; Zhong et al., 2017). Nevertheless, we acknowledged that more vertical profile measurements are required to elucidate the general characteristics of the chemical development of the nighttime chemistry in winter Beijing.
In response to the point 1 concern, we checked the uncertainty by many sensitivity tests of \( k_{\text{NO3}} \) and \( k_{\text{N2O5}} \). As for \( k_{\text{NO3}} \), the influence was very small even set \( k_{\text{NO3}} \) up to 0.02 s\(^{-1}\). As for \( k_{\text{N2O5}} \), the aerosol surface area was reasonably constrained. Although the uptake coefficient fixed to 0.005 without field data constrain, the sensitivity test showed that the \( \text{N}_2\text{O}_5 \) uptake processes were not limited by the \( \text{N}_2\text{O}_5 \) uptake coefficient (see Fig. 7). Overall, we think the uncertainties of the chemistry were well characterized in the revised manuscript of our previous response.

In response to the point 2 concern, we revised our abstract and conclusion as follows,

**Abstract:** "Modeling results show the specific case that the nighttime integrated production of pNO\(_3\)- for the high-altitude air mass above urban Beijing was estimated to be 50 μg m\(^{-3}\) and enhanced the surface-layer pNO\(_3\)- the next morning by 28 μg m\(^{-3}\) through vertical mixing. The overnight NO\(_x\) loss via NO\(_3\)-N\(_2\text{O}_5\) chemistry was efficient aloft (> 50%). The nocturnal NO\(_x\) loss was maximized once the \( \text{N}_2\text{O}_5 \) uptake coefficient was over 2×10\(^{-3}\) on polluted days with \( S_a \) was 3000 μm\(^2\) cm\(^{-3}\) in wintertime. The case study provided a chance to highlight that pNO\(_3\)- formation via \( \text{N}_2\text{O}_5 \) heterogeneous hydrolysis may be an important source of the particulate nitrate in the urban airshed during wintertime."

**Conclusion:** "Our result emphasized the importance of the heterogeneous chemistry aloft the city through a case study. The model simulation also demonstrated that during the heavy PM pollution period, the particulate nitrate formation capacity via \( \text{N}_2\text{O}_5 \) uptake was easily maximized in the high altitude above urban Beijing, even with low \( \text{N}_2\text{O}_5 \) uptake coefficient."
Referee #3

General comments:
Kinetics and mechanisms of nitrate formation are of great concern in our society, and the manuscript has reported considerable Ox (O3+NO2) loss in the nocturnal residual layer in winter Beijing, immediately indicates potential nitrate formation in that nocturnal residual layer in winter Beijing, since the dominate sink of Ox is known to be nitrate formation. The authors also construct a model and run several sensitivity tests to illustrate that the N2O5 uptake is mainly responsible for the Ox loss and thus the inorganic nitrate formation stands out. Therefore, I would recommend publication of this manuscript on ACP on condition that specific weakness (see below) is resolved.

Specific comments:
1. The main premise for your analysis on the air mass evolution (or inorganic nitrate formation) overnight is that you have measured the same air mass in the evening measurement and the next morning measurement. However, dilution, exchange and mixing of the air mass cannot be ruled out considering the non-zero wind speed. How would the uncertainties originated from physical changes of the air mass affect your analysis and those many conclusions?

   The uncertainty caused by the physical changes of the air masses were analyzed from two folds, one is the dilution and the other is the mixing and exchange of the air mass.

   With respect to the impact of the dilution process, it would decrease the mixing ratio of NO2, O3, NO3 and N2O5, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case.

   With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted NOx into the air mass after sunset, which would increase the mixing ratio of Ox, and restart the zero time of the model. Accounting for the uncertainties from the mixing, sensitivities tests of the box model to shorting the duration of 25%, the bias of the integrated pNO3 throughout the night was small within 12% relative to base case. If the air mass was affected by the clean air mass from the north, it would be featured with very low NOx and about 40 ppbv O3 (background condition), which was not consistent with our observation.

   Overall, the physical changes actually affect the reaction processes in the canopy of
urban Beijing in winter time, and leads to a bias of the prediction of particulate nitrate formation. These uncertainties are further discussed in our revised manuscript.

We added a paragraph in the revise text to discuss the uncertainties originated by the physical changes of the air mass as: “The uncertainty caused by the physical changes of the air masses were analyzed from two folds, one is the dilution and the other is the mixing and exchange of the air mass. With respect to the impact of the dilution process, it would decrease the mixing ratio of NO₂, O₃, NO₃ and N₂O₅, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case. With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted NOx into the air mass after sunset, which would increase the mixing ratio of Ox, and restart the zero time of the model. Accounting for the uncertainties from the mixing, sensitivities tests of the box model to shorting the duration of 25%, the bias of the integrated pNO₃⁻ throughout the night was small within 12% relative to base case. If the air mass was affected by the clean air mass from the north, it would be featured with very low NOx and about 40 ppbv O₃ (background condition), which was not consistent with our observation.”

2. If the story of Ox loss and inorganic nitrate formation in the nocturnal residual layer in winter Beijing in one of your measurements is credible regardless of question #1, I did not see why you could safely extrapolate the story of the specific case study to (1) the winter nights since no gradient of NO, NO2 and O3 has been spotted in your measurements. (2) general situation of Beijing (3) the 50 μg m⁻³ contribution due to (1) and (2), and also that the structure of nocturnal boundary layer is not characterized anywhere in your study. Actually, it’s difficult to safely extrapolate our story to all the general situation of Beijing. Our specific study described an upper limit case about the capacity of the particulate nitrate produced by N₂O₅ uptake during nighttime and contribute to the following daytime PM mass concentration in winter Beijing.

Firstly, with respect to the case that NO concentration within 240 m was high (e.g., December 20, 2016), we did not have the vertical profile of these species above 240 m. But it is possible that we did not reach to the residual layer due to the nocturnal boundary layer was higher than 240 m under this condition.

Secondly, several studies showed that the nocturnal boundary layer was lower than 200
m in the polluted days in winter Beijing, suggested our specific case was general in Beijing (Zheng et al., 2015; Zhong et al., 2017).

Thirdly, the 50 μg m⁻³ contribution in the case study was not so general, as the mixing ratios of the precursors are different in different polluted episodes. But it highlighted that N₂O₅ heterogeneous uptake in the residual layer where far away from the NO emission would have a significant contribution to the particulate nitrate formation.

Overall, our case study just provide a chance to qualitative look insight the importance of N₂O₅ uptake to PM pollution in vertical scale, and more field studies was need to quantify the contribution. Here we modest our statement in the abstract and conclusion as following:

Abstract: “Modeling results show the specific case that the nighttime integrated production of pNO₃⁻ for the high-altitude air mass above urban Beijing was estimated to be 50 μg m⁻³ and enhanced the surface-layer pNO₃⁻ the next morning by 28 μg m⁻³ through vertical mixing. The overnight NOₓ loss via NO₃⁻N₂O₅ chemistry was efficient aloft (> 50%). The nocturnal NOₓ loss was maximized once the N₂O₅ uptake coefficient was over 2×10⁻³ on polluted days with Sₐ was 3000 μm² cm⁻³ in wintertime. The case study provided a chance to highlight that pNO₃⁻ formation via N₂O₅ heterogeneous hydrolysis may be an important source of the particulate nitrate in the urban airshed during wintertime.”

Conclusion: “Our result emphasized the importance of the heterogeneous chemistry aloft the city through a case study. The model simulation also demonstrated that during the heavy PM pollution period, the particulate nitrate formation capacity via N₂O₅ uptake was easily maximized in the high altitude above urban Beijing, even with low N₂O₅ uptake coefficient.”

3. Constraint or comparison of your model to your measurements of Ox would help.

Thanks for the suggestion, we added the description about the observed and modelled Ox loss as following:

“The pNO₃⁻ formation by N₂O₅ heterogeneous uptake from sunset to the measurement time can be calculated using Eq. 7, which was significant of 24 μg m⁻³ after sunset above 150 m. The particulate nitrate formed in 4.5 hours was equivalent to 13 ppbv Oₓ loss and consistent with the observation (15 ppbv) (Fig. 6b). Where the 1.5:1 relationship between Oₓ and pNO₃⁻ was used to calculate the Oₓ equivalence (S. S. Brown et al., 2006). ”

“The box model enabled the analysis of the integrated pNO₃⁻ and ClNO₂ via N₂O₅ uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO₃⁻ went as high as 50 μg m⁻³. The integrated pNO₃⁻ at sunrise was equal to the loss of 27 ppbv Oₓ, showing a good agreement with the observed Oₓ missing (25 ppbv) aloft in the morning hours.”

4. Need great improvement in English writing. Here only the comments on the first page (line1-line31) of the manuscript are listed.

Thanks for the detailed English gramma correction, we went through the text and improved
the language accordingly.

Line 1: consider “fast/rapid formation” or “big formation rate”
Changed to: “fast particulate nitrate formation”

Line 2: define “chemical reactive layer”
Changed the “chemical reactive layer” to “aloft”.

Change “during wintertime in Beijing” to “in winter Beijing”
Changed accordingly.

Line 13: is not “dominant”
Changed to “an important component”.

Line 16: measurement of what?
Simultaneous ground-based and tower-based measurements of NOx and O3

Line 18: change to “due to N2O5 concentration of near zero controlling by high NO emission and NO concentration”
Changed accordingly.

Line 19: No will not “limiting the production of N2O5”
Deleted the statement.

Larger or large, higher or high (if being specific on altitude like > 150 m, just delete “high”)
Changed to: “In contrast, the contribution from N2O5 uptake was larger at higher altitudes (e.g., > 150 m)”.

Line 20: Large or larger (Large is not a proper adj. for formation or missing)
Changed to “large”.

Line 21: define “production potential”
The “production potential” changed to “integrated production”.

Line 22: higher or high
Changed to “high”.

Line 23: delete “significantly”
Deleted accordingly.
Line 24-27: a conclusion drawn from nowhere, hard to follow
Deleted these words.

Line 28: higher or high
Changed to “high”.

Line 30: define “reactive air masses”
Deleted the sentence.

Line 28-31: “haze formation”, “formation and development of the reactive air masses” is not the topic of this study. Also, be specific on how are you going to improve the “chemical-transport model” based on the contribution of your study?
Deleted the sentence.

Referee #4

General comments:
As noted by the other reviewers of this manuscript, the paper presents new results on the formation of nitrate aerosol by N2O5 uptake at modest altitudes above surface level during winter in Beijing. The result is important since ozone titration by NOx at surface level makes the production rate at the surface zero. The paper quantifies the production rate in an altitude range up to 250 m above the surface and is thus a valuable contribution to the literature.

The authors quantify uncertainties in their analysis due to NO3 reactivity and ClNO2 production, both of which are unmeasured. They do not quantify the uncertainty due to partitioning between gas phase HNO3 and particulate nitrate. This aspect should be addressed, even if it is simply to state by way of assumption that all nitrate formed from N2O5 uptake goes to the particle phase rather than the gas phase. If the authors have other information to indicate that partitioning (other literature) they should state this explicitly.

The partition of gas phase HNO3 and particulate nitrate is an important aspect affected the contribution of N2O5 uptake producing particulate nitrate. We assumed that all nitrate formed from N2O5 uptake goes to the particle phase, the assumption would lead to the N2O5 uptake had an upper limit particle phase nitrate contribution.

While during the wintertime in Beijing, the mixing ratio of NH3 was rich to tens of ppbv and always much higher than the nocturnal gas phase HNO3 (e.g., Liu et al., 2017). The high NH3 suppressed the degassing of particulate nitrate effectively. The measurement of gas phase HNO3 and particulate nitrate in the surface layer of Beijing showed the soluble nitrate
favor to particle phase in winter, especially in polluted days. For example, the nocturnal ratio of particulate nitrate to total soluble nitrate was larger than 0.95 on average (Liu et al., 2017; unpublished data from the BEST-ONE campaign in Beijing (Tan et al., 2018)). Due to the low temperature and high RH in high altitude, the ratio would increase and the degassing of particulate nitrate is small. 

Therefore, the assumption that all the N_2O_5 uptake contributes to the particle phase is reasonable in the wintertime in the canopy of Beijing.

Adding a paragraph as: "In the calculation of the particulate nitration formation by N_2O_5 uptake, an assumption is that all nitrate formed from N_2O_5 uptake goes to the particle phase rather than the gas phase. The assumption would lead to an upper bias as the degassing of gas phase HNO_3 from particulate nitrate. While during the wintertime in Beijing, the mixing ratio of NH_3 was rich to tens of ppbv and always much higher than the nocturnal gas phase HNO_3 (e.g., Liu et al., 2017). The high NH_3 suppressed the degassing of particulate nitrate effectively. The measurement of gas phase HNO_3 and particulate nitrate in the surface layer of Beijing showed the soluble nitrate favor to particle phase in winter, especially in polluted days. For example, the nocturnal ratio of particulate nitrate to total soluble nitrate was larger than 0.95 on average (Liu et al., 2017). Due to the low temperature and high RH in high altitude, the ratio would increase and the degassing of particulate nitrate is negligible."

Otherwise the manuscript should be published subject to the following minor comments and grammatical corrections.

Specific comments:

Line 26: remove the word "easily"  
Removed accordingly.

Line 27: Suggest replacing "could be" with "is". At the author’s discretion.  
Changed accordingly.

The result for gamma(N2O5) is specific to the very large aerosol surface area present in Beijing during these events. The sentence in the abstract should note this so as not to imply that a gamma value of 2x10^-3 is generally the point at which other regions would become insensitive to this parameter.

Thanks for the suggestion, we added the Sa information in this sentence as following:  
"The nocturnal NO_x loss was maximized once the N_2O_5 uptake coefficient was over 2x10^-3 on polluted days with S_a was 3000 μm^2 cm^-3 in wintertime."

Line 28: Suggest replacing "could be" with "is". At the author’s discretion.

Changed accordingly.
Line 43: replace “severely limited” with “very low in concentration”
Changed accordingly.

Line 162 and equation 5: The idea behind the definition of s(t) is fairly clear, but the form of equation 5 is not. Further explanation of the form of the equation is required.
The s(t) is between 0 and 1 and expressed as Eq. 5, the physical meaning s(t) is the ratio of NO₃ production which goes through N₂O₅ (either as N₂O₅ or lost through uptake) to the total NO₃ production (Wagner et al., 2013)

Figure 2: The scale for O₃ in the upper panel goes to 100 ppbv, while the O₃ itself only goes to 25 ppbv. The scale should show the actual variability in O₃.
The scale of O₃ in Figure 2 changed to 40 ppb.

Line 235: The choice of kNO₃ is arbitrary and is intended to simply represent a high value.
The word arbitrary should appear in the sentence, i.e., “… kNO₃ was set to an arbitrary and relatively high value of …”
Changed accordingly.

Line 268: Do the authors mean to refer to December 19 rather than December 18?
Changed to: “The vertical profile on December 19 was different with that on December 20.”

Line 277: Is NO greatly diminished, or zero? Nonzero O₃ at night implies zero NO if the mixing ratio of O₃ is sustained for any length of time.
Yes, The NO is zero and changed as: “corresponding to zero NO concentration”.

Line 303: Omit the word “about”
Changed accordingly.

Line 306: “rapid” in place of “quick”
Changed accordingly.

Line 314: What relationship between Ox and pNO₃ has been used to calculate the Ox equivalence in Figure 6? Have the authors assumed a 1:1 relationship, or have they used the Ox equivalent in pNO₃, which is larger than 1? See: Brown et al., Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere. Geophys. Res. Lett., 2006. 33: p. L08801.
The 1.5:1 relationship was used to calculate the equivalence of Oₓ and pNO₃. Which is the same as the reference recommend.
Added a sentence as: “The 1.5:1 relationship between Oₓ and pNO₃ was used to calculate
the Ox equivalence (S. S. Brown et al., 2006)."

Line 332: Can the authors compare the 28 micrograms m⁻³ figure to the day over day change in nitrate mass during haze events in Beijing? In other words, what is the daily growth in nitrate mass during either this event or during typical events, and how much is explained by this 28 microgram m⁻³ per night rate?

The enhancement of particulate nitrate of 28 μg m⁻³ was a high contribution case, but the case with large enhancement of particulate nitrate of ~20 μg m⁻³ can be found at the same site on the tower in polluted winter Beijing (c.a. figure 4(a) from Sun et al., (2015)). The fast growth of particulate nitrate with 50 μg m⁻³ per day was found in BEST-ONE campaign in winter Beijing, 2016. The quantitative particulate nitrate enhancement by N₂O₅ uptake was case by case, and the result represented by our specific case just address the significance of N₂O₅ uptake in the canopy of Beijing.

Line 334: To what feature are the authors referring in stating a morning peak of 60 micrograms m⁻³ on Dec 20? This feature is not apparent in Figure 1. The feature is shown in Figure 2(a) and colored as red line.

346: Correct English grammar. Use a period and new sentence rather than a comma. The second part of the sentence should read: "Low N₂O₅ uptake coefficients correspond to several types of aerosols, such as …"

Thanks for the suggestion, we changed accordingly.

Line 352: Logic of sentence is incorrect. The ClNO₂ yield is not the variable that maximizes the conversion capacity of N₂O₅, as the sentence implies. Rephrase as: "The conversion capacity of N₂O₅ uptake to pNO₃ is maximized for a given, fixed value of the ClNO₂ yield"

Changed accordingly.

Line 363: It is not clear what is intended by the phrase “valid NOx loss.” The authors should clarify or search for other wording.

Here we use: "NOx removal".

Line 364: “the N₂O₅ uptake coefficient” rather than “N₂O₅ uptake”

Changed accordingly.

Line 369: remove the word “was”

Changed accordingly.

Line 373: “become insensitive to γ(N₂O₅).” Then start a new sentence “This region is
defined as …”
Changed accordingly.

Line 387: Sentence needs improved English grammar. The meaning of “during the heating period” is not clear. Does this refer simply to colder weather during the winter season? The heating period means very cold period in winter Beijing, and the government would supply the heating water from the thermal power plant.

Line 394: This result of 2.5 ppbv refers to a model, not a measured value. This should be made clear.
Revised as: “The modelled formation of ClNO₂ aloft throughout the night reached 2.5 ppbv,”

Line 397: “As the error of pNO₃ formation simulation was subject to” should be replace by “Since the modeled pNO₃ formation is sensitive to”
Changed accordingly.

Line 399: The reference is to Figure 8, not Figure 7.
Corrected accordingly.

Line 415: replace “evidenced” with “found evidence for”
Changed accordingly.

Line 718, figure caption 7: “via N2O5 uptake” rather than “on N2O5 uptake”, “NO2 and O3 were set to”, “Sa was set”, “reaction time was set.
Changed accordingly.

References


Fast high particulate nitrate formation via N₂O₅ uptake in a chemically reactive layer aloft during wintertime in winter Beijing

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Abstract.

Particulate nitrate (pNO₃⁻) is an important 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. Here we report vertical measurement of NOₓ and O₃ by in-situ instruments on a movable carriage on a tower. Simultaneous ground-based and tower-based measurements of NOₓ and O₃ were conducted during a winter heavy-haze episode (December 18 to 20, 2016) in urban Beijing, China. Based on the box model simulation at different height, we found that pNO₃⁻ formation via N₂O₅ heterogeneous uptake was negligible at ground level due to N₂O₅ concentration of near zero controlling by high NO emission and NO concentration, owing to the presence of high NO concentrations, which limited the production of N₂O₅. In contrast, the contribution from N₂O₅ uptake was larger at higher altitudes (e.g., > 150 m), which was supported by the low total oxidant (NO₂ + O₃) level at higher altitudes than that at ground level. Modeling results show the specific case that the nighttime integrated production of pNO₃⁻ for the high-altitude air mass above urban Beijing was estimated to be 50 μg m⁻³ and enhanced the
surface-layer pNO$_3^-$ the next morning by 28 μg m$^{-3}$ through vertical mixing. Sensitivity tests suggested that the nocturnal NO$_x$ loss by NO$_2$-N$_2$O$_5$ chemistry was maximized once the N$_2$O$_5$ uptake coefficient was over 2×10$^{-3}$ on polluted days with $S_a$ was 3000 μm$^2$ cm$^{-3}$ in wintertime. The case study provided a chance to highlight that pNO$_3^-$ formation via N$_2$O$_5$ heterogeneous hydrolysis may be an important source of the particulate nitrate in the urban airshed during wintertime. Modeling results show that the nighttime integrated production of pNO$_3^-$ for the higher altitude air mass above urban Beijing was estimated to be 50 μg m$^{-3}$ and enhanced the surface layer pNO$_3^-$ the next morning significantly by 28 μg m$^{-3}$ through vertical mixing. The overnight NO$_x$ loss via NO$_2$-N$_2$O$_5$ chemistry was efficient aloft (> 50%). The nocturnal NO$_x$ loss was easily maximized once the N$_2$O$_5$ uptake coefficient was over 2×10$^{-3}$ on polluted days in wintertime. These results highlight that pNO$_3^-$ formation via N$_2$O$_5$ heterogeneous hydrolysis in higher altitude air masses 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 matter (PM) pollution events occur frequently in China and have drawn widespread and sustained attention in recent years (Guo et al., 2014; Zhang et al., 2015; Huang et al., 2014; Wang et al., 2016). PM pollution reduces visibility (Lei and Wuebbles, 2013) and has harmful effects on public health (Cao et al., 2012). Particulate nitrate (pNO$_3^-$) is an important component of secondary inorganic aerosols and contributes 15%–40% of the PM$_{2.5}$ mass concentration in China (Sun et al., 2013, 2015a, 2015b; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015). The main atmospheric pathways of nitrate formation are (1) the reaction of OH with NO$_2$ and (2) N$_2$O$_5$ heterogeneous hydrolysis (Seinfeld and Pandis, 2006). The reaction of OH with NO$_2$ is a daytime pathway, as OH is very low in concentration severely limited at night, and N$_2$O$_5$ uptake is a nighttime pathway, as NO$_3^-$ and N$_2$O$_5$ are easily photo-labile.
Particulate nitrate formation via N$_2$O$_5$ heterogeneous hydrolysis in summer in North China was proved efficient by ground-based observation in North China (Wang H et al., 2017b; Wang Z et al., 2017), and found comparable to or even higher than the daytime formation. Several studies showed that N$_2$O$_5$ hydrolysis is responsible for nocturnal pNO$_3^-$ enhancement in summer Beijing (Pathak et al., 2009, 2011; Wang H et al., 2017a). Although pNO$_3^-$ formation via N$_2$O$_5$ uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in N$_2$O$_5$ chemistry exist between winter and summer. First, as the key precursor of NO$_3$ and N$_2$O$_5$, O$_3$ has a much lower concentration in winter than in summer, owing to the short daytime length and weak solar radiation. Second, colder temperatures and high NO$_2$ levels favor the 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, the N$_2$O$_5$ uptake coefficient, as the most important parameter in N$_2$O$_5$ heterogeneous hydrolysis, is likely very different from that in summer. This is because the properties of aerosol particles (e.g., organic compounds, particulate nitrate, liquid water contents, solubility, and viscosity) and meteorological conditions (e.g., temperature and relative humidity) differ between summer and winter (Chen et al., 2015; Zhang et al., 2007). These effects would result in large variations in the N$_2$O$_5$ uptake coefficient (Wahner et al., 1998; Mentel et al., 1999; Kane et al., 2001; Hallquist et al., 2003; Thornton et al., 2003; Bertram and Thornton, 2009; Tang et al., 2012; Wagner et al., 2013; Grzinic et al., 2015). Several parameterization methods have been unsuccessful in predicting N$_2$O$_5$ uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences in pNO$_3^-$ formation via N$_2$O$_5$ uptake, modeling and field studies showed higher levels of NO$_3$ and N$_2$O$_5$ at higher altitudes within the nocturnal boundary layer (NBL), owing to the stratification of surface NO and volatile organic compounds (VOCs) emissions, which lead to gradients in the loss rates for these compounds as a function of altitude (e.g., Brown et al., 2007; Geyer and Stutz, 2004; Stutz et al., 2004). The pNO$_3^-$ formation via N$_2$O$_5$
uptake contributes to the gradients in the compounds percentage and size distribution of the particle (Ferrero et al., 2010; 2012). On nights when NO\textsubscript{3} production can’t accumulate in the surface layer, titration is negligible owing to high NO emissions. N\textsubscript{2}O\textsubscript{5} uptake can still be active aloft without NO titration. The N\textsubscript{2}O\textsubscript{5} uptake aloft leads to elevated pNO\textsubscript{3} formation in the upper layer as well as effective NO\textsubscript{x} removal (Watson et al., 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Pusede et al., 2016; Baasandorj et al., 2017). Field observations at high altitude sites of Kleiner Feldberg, Germany (Crowley et al., 2010a); the London British Telecommunications tower, UK (Benton et al., 2010); and Boulder, CO, USA (Wagner et al., 2013) showed the elevated N\textsubscript{2}O\textsubscript{5} concentrations aloft. Model studies showed that pNO\textsubscript{3} varied at different heights and stressed the importance of the heterogeneous formation mechanism (Kim et al., 2014; Ying, 2011; Su et al., 2017). The mass fraction and concentration of pNO\textsubscript{3} in Beijing was reported higher aloft (260 m) than at the ground level in Beijing (Chan et al., 2005; Sun et al., 2015b), which was explained by favorable gas–particle partitioning aloft under lower temperature conditions. Overall, the active nighttime chemistry in the upper level plays an important role in surface PM pollution through mixing and dispersing within the planet boundary layer (PBL) (Prabhakar et al., 2017), the pollution was even worse especially in valley terrain regions coupled with adverse meteorological processes (Baasandorj et al., 2017; Green et al., 2015).

To explore the possible sources of pNO\textsubscript{3} and the dependence of its formation on altitude in wintertime in Beijing, we conducted vertical profile measurements of NO, NO\textsubscript{2}, and O\textsubscript{3} with a moving cabin at a tower platform in combination with simultaneous ground measurements of these more comprehensive parameters in urban Beijing. A box model was used to investigate the reaction rate of N\textsubscript{2}O\textsubscript{5} heterogeneous hydrolysis and its impact on pNO\textsubscript{3} formation at different altitudes during a heavy haze episode over urban Beijing. Additionally, the dependence of NO\textsubscript{x} removal and pNO\textsubscript{3} formation on the N\textsubscript{2}O\textsubscript{5} uptake coefficient was probed.
2. Methods

2.1 Field measurement

Ground measurements (15 m above the ground) were carried out on the campus of Peking University (PKU; 39°59'21"N, 116°18'25"E) in Beijing, China. The vertical measurements were conducted at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58'28"N, 116°22'16"E). The IAP site is within 4 km of the PKU site. The locations of the PKU and IAP sites are shown in Fig. 1. At the PKU site, dry-state mass concentration of PM$_{2.5}$ was measured using a TEOM 1400A analyzer. NO$_x$ was measured via a chemiluminescence analyzer (Thermo Scientific, TE-42i-TR), and O$_3$ was measured with a UV photometric O$_3$ analyzer (Thermo Scientific, TE-49i). Dry-state particle number and size distribution (PNSD) was measured from 0.01 to 0.7 µm with a Scanning Mobility Particle Sizer (SMPS; TSI Inc. 3010). The instrumental parameters are summarized in Table S1. The data were collected from December 16 to 22, 2016. Additionally, relative humidity (RH), temperature (T), and wind direction and speed data were available during the measurement period.

Vertical profile measurements were conducted from December 18 to 20, 2016, from the tower-based platform (maximum height: 325 m) on the IAP campus. The NO$_x$ and O$_3$ instruments were installed aboard a movable cabin on the tower. NO$_x$ and O$_3$ were measured with two low-power, lightweight instruments (Model 405 nm and Model 106-L, 2B Technologies, USA). The Model 405 nm instrument measures NO$_2$ directly based on the absorbance at 405 nm, and NO is measured by adding excess O$_3$ (conversion efficiency ~100%). The limit of detection of both NO and NO$_2$ is 1 part per billion volume (ppbv), with an accuracy of 2 ppbv or 2% of the reading, and the time resolution is 10 s (Birks et al., 2018). The Model 106-L instrument measures O$_3$ based on the absorbance at 254 nm, with a precision of 1 ppbv, or 2% of the reading, and a limit of detection of 3 ppbv. NO$_x$ calibration was performed in the lab using a gas calibrator (TE-146i, Thermo Electron, USA) associated with a NO standard (9.8 ppmv). The O$_3$ calibration was done with an O$_3$ calibrator (TE 49i-PS), which was
traceable to NIST (National Institute of Standards and Technology) standards annually. Before the campaign, the NO\textsubscript{3} monitor was compared with a Cavity Attenuated Phase Shift (CAPs) Particle Light Extinction Monitor, and the O\textsubscript{3} monitor was compared to a commercial O\textsubscript{3} analyzer (TE-49i, Thermo Electron, USA). Good agreement was found between the portable instruments and the conventional monitors. Height information was retrieved via the observed atmospheric pressure measured by the Model 405 nm instrument. The cabin ascended and descended at a rate of 10 m min\textsuperscript{-1}, with a height limit of 260 m during the daytime and 240 m at night. The cabin stopped after reaching the peak, and parameters were measured continually during the last 10 min of each cycle. One vertical cycle lasted for approximately 1 h. We measured two cycles per day, one in the morning and the other in the evening. Six measurement cycles were measured conducted in total during the campaign.

2.2 Box model simulation

A box model was used to model the NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} mixing ratios and the nitrate formation potential in vertical scale at the IAP site. A simple chemical mechanism (see R1–R5) was used in a box model to simulate the nighttime NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} chemistry under NO free-air-mass conditions. Physical mixing, dilution, deposition, or interruption during the transport of the air mass was not considered in the base case. The physical influence to the model result will be discussed in Sect. 3.4. Here, \(f\) represents the ClNO\textsubscript{2} yield from N\textsubscript{2}O\textsubscript{5} uptake. Homogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} and NO\textsubscript{3} heterogeneous uptake reaction were neglected in this analysis because of the low level of absolute humidity and the extremely low NO\textsubscript{3} concentration during wintertime (Brown and Stutz, 2012). The corresponding rate constants of R1–R3 are those reported by Sander et al. (2011).

\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R1)} \\
\text{NO}_2 + \text{NO}_3 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R2)} \\
\text{N}_2\text{O}_5 + \text{M} & \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \quad \text{(R3)} \\
\text{NO}_3 + \text{VOCs} & \rightarrow \text{Products} \quad \text{(R4)}
\end{align*}
\[ \text{N}_2\text{O}_5 + (\text{H}_2\text{O} \text{ or } \text{Cl}) \rightarrow (2-f) \text{NO}_3 + f\text{ClNO}_2 \quad (R5) \]

Following the work of Wagner et al. (2013), the box model can be solved using six equations (Eqs. 1–6). In the framework, O₃ is only lost via the reaction of NO₂ + O₃ and the change in the O₃ concentration can be expressed as Eq. 1. Eq. 2 can express the losses of NO₂. The s(t) is between 0 and 1 and expressed as Eq. 5, the physical meaning of s(t) is the ratio of NO₂ production which goes through N₂O₅ (either as N₂O₅ or lost through uptake) to the total NO₂ production (Wagner et al., 2013). The s(t) favors 0 when direct loss of NO₃ dominates and favors 1 when N₂O₅ uptake dominates NO₃ loss. The model calculation has two steps. The first step is to calculate the mixing ratio of NO₂ and O₃ at time zero (herein designated as sunset). According to Eqs. 1 and 2, the initial NO₂ (t=0) and O₃ (t=0) concentrations can then be integrated backward in time starting with the measured concentrations of NO₂ and O₃ at each height. During the pollution period in winter in Beijing (NO₂ = 45 ppbv, Temperature = 273 K, S₂ = 3000 μm² cm⁻³), the ratio of N₂O₅ to NO₃ is large enough, i.e., 450. The pseudo-first-order loss rate of N₂O₅ heterogeneous uptake will be 1×10⁻³ s⁻¹, with a N₂O₅ uptake coefficient of 5×10⁻³. N₂O₅ uptake would contribute to the loss rate of NO₃ with VOCs, even with the kNO₃ set to a high value of 0.02 s⁻¹. Therefore, N₂O₅ uptake was proposed to be dominantly responsible for the NO₃ loss and the initial s(t) was set to 1. Eq. 3 can describe the sum concentration of NO₃ and N₂O₅. Assuming the equilibrium between NO₃ and N₂O₅ is maintained after a certain period, based on the temperature-dependent equilibrium rate constant (kₑq) and the modeled NO₂ at a certain time, Eq. 4 can be used to determine the ratio of N₂O₅ to NO₃. Combined, Eqs. 1–4 allow for the calculation of NO₃ and N₂O₅ concentrations considering stable NO₃ and N₂O₅ loss rate constants (kNO₃ and kN2O5, respectively). In the second step, a new s(t) was calculated using the data from the first step (Eq. 5), new initial NO₂ and O₃ concentrations were then approximated, and NO₃ and N₂O₅ 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\textsubscript{2}O\textsubscript{5} concentrations and given \( k_{\text{N}_2\text{O}_5} \) were then used to estimate pNO\textsubscript{3} formation. The HNO\textsubscript{3} produced in R4 was not considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here, \( k_{\text{NO}_3} \) and \( k_{\text{N}_2\text{O}_5} \) denote the pseudo-first-order reaction rate constants of the total NO\textsubscript{3} reactivity caused by ambient VOCs and N\textsubscript{2}O\textsubscript{5} heterogeneous uptake, respectively. \( k_{\text{N}_2\text{O}_5} \) is given in Eq. 6.

\( S_a \) is the aerosol surface area, \( C \) is the mean molecular speed of N\textsubscript{2}O\textsubscript{5}, and \( \gamma_{\text{N}_2\text{O}_5} \) is the N\textsubscript{2}O\textsubscript{5} uptake coefficient. Sunset and sunrise times during the measurements were 16:55 and 07:30 (Chinese National Standard Time, CNST), and the model was run from sunset to sunrise, with the running time of the model set to 14.5 h from sunset to sunrise.

\[
\frac{d\text{[NO}_2\text{][O}_3\text{]}}{dt} = -k_{\text{N}_2\text{O}_2+\text{NO}_3}\text{[O}_3\text{][NO}_2\text{]} \tag{1}
\]

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

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

\[
\frac{[\text{N}_2\text{O}_5][\text{NO}_3]}{[\text{NO}_2]} = k_{\text{eq}}[\text{NO}_2] \tag{4}
\]

\[
s(t) = \frac{\int_k k_{\text{N}_2\text{O}_5}[\text{N}_2\text{O}_5][\text{NO}_2]dt + [\text{N}_2\text{O}_5][\text{NO}_2]}{[\text{O}_3][\text{O}_3]-[\text{O}_3][\text{O}_3]} \tag{5}
\]

\[
k_{\text{N}_2\text{O}_5} = \frac{C \times S_a \times Y_{\text{N}_2\text{O}_5}}{4} \tag{6}
\]

Dry-state \( S_a \) at the PKU site was calculated based on the PNSD measurement, which was corrected to ambient (wet) \( S_a \) for particle hygroscopicity via a growth factor (Liu et al., 2013). The uncertainty of the wet \( S_a \) was estimated to be \(~30\%\), which was associated with the error from dry PNSD measurement (~20%) and the growth factor (~20%). Nighttime averaged \( S_a \) on the night of December 19 was about 3000 \( \mu \text{m}^2 \text{ cm}^{-3} \). PM measurements at the National Monitoring Sites proved this heavy haze pollution episode was a typical regional event (Fig. S1). Furthermore, synchronous study on the night of December 19, 2016, showed small variation in the vertical particle number concentration, with a boundary layer height of 340 m (Zhong
et al., 2017). Therefore, the \( S_a \) measured at the PKU site can represent the urban Beijing conditions in horizontal and vertical scale (< 340 m). Although the PNSD information for particles larger than 0.7 \( \mu \)m was not valid during the study period, the particles smaller than 0.7 \( \mu \)m dominated more than 95% of the aerosol surface area in a subsequent pollution episode (01/01/2017 to 01/07/2017), and similar results also were reported in other studies (e.g., Crowley et al., 2010a; Wang et al., 2018). The possible lower bias of \( S_a \) (5%) only led to a small overestimation of \( \mathrm{N}_2\mathrm{O}_5 \), i.e., 3.6%–4.2%, and an underestimation of \( \mathrm{pNO}_3^- \) of 0.2%–2.5% when \( \gamma_{\mathrm{N}_2\mathrm{O}_5} \) varied from 1×10\(^{-3}\) to 0.05.

The \( \mathrm{N}_2\mathrm{O}_5 \) uptake coefficient and CINO\(_2\) yield are key parameters in the estimation of \( \mathrm{pNO}_3^- \) formation (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016). Wagner et al. (2013) shows the significant \( \mathrm{pNO}_3^- \) suppression of \( \mathrm{N}_2\mathrm{O}_5 \) uptake aloft in the wintertime in Denver, CO, USA, the uptake coefficient is 0.005 when the percentage of \( \mathrm{pNO}_3^- \) in the PM\(_{2.5}\) mass concentration is 40%. As the proportion of nitrate in the particle mass concentration is similarly high in North China during wintertime (Sun et al., 2013, 2015a; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015), herein we fixed the uptake coefficient to 0.005 for the base model initial input. Because the model input of CINO\(_2\) yield only affects the value of produced \( \mathrm{pNO}_3^- \) concentration and would not change the modeled \( \mathrm{N}_2\mathrm{O}_5 \) concentration, we set the initial \( f_{\mathrm{CINO}_2} \) to zero. Previous work showed the averaged value of \( k_{\mathrm{NO}_3} \) of about 0.011 s\(^{-1}\) in summer Beijing was calculated 0.01 - 0.02 s\(^{-1}\) in summer Beijing in a previous work, with BVOCs contributing significantly (Wang et al., 2017a; Wang et al., 2018). The intensity of biogenic BVOCs emissions decreased in wintertime, owing to the lower temperature and weak solar radiation, thus the \( k_{\mathrm{NO}_3} \) should be smaller than it is in summer. In this work, the model input \( k_{\mathrm{NO}_3} \) was set to an arbitrary and relatively high value of 0.02 s\(^{-1}\) (equivalent to 0.2 ppbv isoprene + 40 parts per trillion volume (pptv) monoterpene + 1.0 ppbv cis-2-butene), to constrain the impact of \( \mathrm{N}_2\mathrm{O}_5 \) uptake in the model. A series of sensitivity tests was conducted to study the uncertainties of the model simulation, and the detailed test sets are listed in Table 1, included the test of \( \mathrm{N}_2\mathrm{O}_5 \) uptake coefficient.
and $k_{NO3}$. The $\gamma_{N2O5}$ sensitivity tests were set from 0.001 to 0.05, and the $k_{NO3}$ tests were set to 0.001 s$^{-1}$, 0.01 s$^{-1}$, and 0.1 s$^{-1}$.

In the calculation of the particulate nitration formation by N$_2$O$_5$ uptake, an assumption is that all soluble nitrate formed from N$_2$O$_5$ uptake goes to the particle phase rather than the gas phase. The assumption would lead to an upper bias as the degassing of gas phase HNO$_3$ from particulate nitrate. While in winter Beijing, the mixing ratio of NH$_3$ was rich to tens of ppbv and always much higher than the nocturnal gas phase HNO$_3$ (e.g., Liu et al., 2017). The high NH$_3$ suppressed the degassing of particulate nitrate effectively. The measurement of gas phase HNO$_3$ and pNO$_3^-$ in the surface layer of Beijing showed the soluble nitrate favor to particle phase in winter, especially in polluted days. For example, the nocturnal ratio of pNO$_3^-$ to total soluble nitrate was larger than 0.95 on average (Liu et al., 2017). Due to the low temperature and high RH at high altitude, the ratio would increase and the degassing of particulate nitrate is negligible.

3. Results and discussion

3.1 Ground-based observations.

A severe winter PM pollution event lasted from December 16 to 22, 2016, in Beijing. Figure 2a shows the time series of PM$_{2.5}$ and other relevant parameters based on ground measurements at the PKU site. The mass concentration of PM$_{2.5}$ began to increase from December 16, reaching 480 µg m$^{-3}$ on December 20. A fast PM growth event was captured, with an overall increment of 100 µg m$^{-3}$ on the night of December 19 (Fig. 2a). Throughout the pollution episode, the meteorological conditions included high RH (50% ± 16%) and low temperature (2 ± 3°C). The slow surface wind speed (< 3 m s$^{-1}$) implied the atmosphere was stable (Fig. 2c, d). The daytime O$_3$ concentration was low, owing to high NO emission and weak solar radiation. After sunset, O$_3$ at surface layer was rapidly titrated to zero by the elevated NO. The presence of high NO concentrations would have strongly suppressed the concentration of NO$_3^-$, further suppressing N$_2$O$_5$ near the ground. Figure 2b depicts the high amounts of NO and NO$_2$ that were observed at ground level during the PM pollution episode,
suggesting that pNO$_3^-$ production via N$_2$O$_5$ uptake was not important near the ground during the winter haze episode.

### 3.2 Tower observations.

Six vertical measurements of the total oxidants (O$_x$ = O$_3$ + NO$_2$) below 50 m were consistent with those measured at ground level and are shown in Fig. S2, confirming that the two sites are comparable. On the night of December 20 (Fig. 3a), the NO$_2$ and NO from 0–240 m were abundant and conservative around 21:00, with concentrations of 80 ppbv and 100 ppbv, respectively. The O$_3$ concentrations remained zero during the nighttime (Fig. 3b). The vertical profile on December 20 suggests that at least below 240 m, the N$_2$O$_5$ chemistry was not important, which is consistent with the results at ground level as mentioned above. The case on the night of December 18 was similar to that on the night of December 20, whereas the vertical profile on December 19 was not similar to that on December 20. Figure 4a shows the vertical profiles around 21:00 on December 19; NO was abundant from the ground to 100 m, then gradually decreased to zero from 100 m to 150 m, and remained at zero above 150 m. The observed NO$_2$ concentration was 85 ± 2 ppbv below 100 m, which gradually decreased from 100 m to 150 m, and was 50 ± 2 ppbv from 150 m to 240 m. The observed O$_3$ concentrations below 150 m were below the instrumental limit of detection (Fig. 4b). Above 150 m, the O$_3$ concentration was 20 ± 2 ppbv, corresponding to the zero greatly diminished NO concentration. With respect to O$_x$, the mixing ratio of O$_x$ was 85 ± 2 ppbv at lower altitudes, whereas the O$_3$ concentration at higher altitudes was 15 ppbv lower than that at lower altitudes (Fig. 4b). The O$_3$ missing from the higher altitude air mass indicated an additional nocturnal removal of O$_3$ aloft.

Figure 5 depicts the vertical profiles of NO$_x$, O$_3$, and O$_x$ at 09:30 on the morning of December 20, which have similar features to those observed at 21:00 on December 19. The vertical profiles suggested stratification still existed at that time. The amount of O$_x$ missing aloft in the morning increased to 25 ppbv at 240–260 m, demonstrating
that an additional 25 ppbv of O$_x$ was removed or converted to other compounds at higher altitudes than at the surface layer during the night from December 19 to 20. Figure S3 shows the vertical profiles of NO, NO$_2$, O$_3$, and O$_x$ at ~12:00 on December 18, when solar radiation was strong enough to mix the trace gases well in the vertical direction. NO$_3$ and O$_3$ were found to be well mixed indeed, with small variation from the ground level to 260 m.

### 3.3 Particulate nitrate formation aloft.

N$_2$O$_5$ uptake is one of the two most important pathways of ambient NO$_x$ loss and 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$_2$O$_5$ chemistry can be initiated in the co-presence of high NO$_2$ and significant O$_3$ levels. Therefore, N$_2$O$_5$ uptake could represent a plausible explanation for the O$_x$ observed missing 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$_2$O$_5$ chemistry based on the observed vertical profiles of NO$_2$ and O$_3$ on the night of December 19.

In the base case, the average initial NO$_2$ and O$_3$ levels above 150 m at sunset were 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$_2$O$_5$ concentration was zero below 150 m, as the high level of NO made for quick consumption of the NO$_3$ formed NO$_3$. In contrast, the modeled N$_2$O$_5$ concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The particulate NO$_x$ accumulation via pNO$_3$ formation by N$_2$O$_5$ heterogeneous uptake from sunset to the measurement time, which can be calculated using Eq. 7, which was significant above 150 m, with a maximum of 24 μg m$^{-3}$ 4.5 hours after sunset above 150 m. The pNO$_3$ formed in 4.5 hours was equivalent to 13 ppbv O$_x$ loss and consistent with the observation (15 ppbv) (Fig. 6b). Where the 1.5:1 relationship between O$_x$ and pNO$_3$ was used to calculate the O$_x$ equivalence (S. S. Brown et al., 2006) (Fig. 6b).
\[
\sum \text{pNO}_3 = \int_0^1 (2 - f) \cdot k_{N\text{O}_5} \cdot [N_2\text{O}_5]dt
\]  
\tag{7}

The box model enabled the analysis of the integrated pNO\textsubscript{3} and ClNO\textsubscript{2} via N\textsubscript{2}O\textsubscript{5} uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO\textsubscript{3} went as high as 50 μg m\textsuperscript{-3}. The integrated pNO\textsubscript{3} at sunrise was equal to the loss of 27 ppbv O\textsubscript{3}, showing a good agreement with the observed O\textsubscript{3} missing (25 ppbv) aloft in the morning hours. During the nighttime, the pNO\textsubscript{3} formed aloft via N\textsubscript{2}O\textsubscript{5} uptake led to the much higher particle nitrate concentration than that in the surface layer, which has been reported in many field observations (Watson et al., 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Ferrero et al., 2012; Sun et al., 2015b). The elevated pNO\textsubscript{3} aloft was well dispersed through vertical mixing and enhanced the surface-layer PM concentration; this phenomenon was also observed in previous studies (Watson et al., 2002; S. G. Brown et al., 2006; Lurmann et al., 2006; Prabhakar et al., 2017). Zhong et al. (2017) showed that the NBL and PBL both were at 340 m from December 19 to 20, 2016 in Beijing. Daytime vertical downward transportation was helpful in mixing the air mass within the PBL. Assuming the newly formed pNO\textsubscript{3} aloft from 150 m to 340 m is 50 μg m\textsuperscript{-3} during the nighttime and well mixed within the PBL by in the next morning, the pNO\textsubscript{3} enhancement \(\Delta\text{pNO}_3\) can be simplified to the calculation in Eq. 8 as following:

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

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

3.4 Sensitivity studies.
Previous studies have emphasized that the \( \text{N}_2\text{O}_5 \) uptake coefficient varies greatly (0.001 – 0.1) in different ambient conditions (Chang et al., 2011; Brown and Stutz, 2012; Wang H et al., 2016), which is the main source of uncertainties in this model. In the present research, sensitivity studies showed the modeled \( \text{N}_2\text{O}_5 \) concentration dropping from 3 ppbv to 60 pptv when the \( \text{N}_2\text{O}_5 \) uptake coefficients increased from 0.001 to 0.05 (Fig. 6a), as the \( \text{N}_2\text{O}_5 \) concentration is very sensitive to the loss from heterogeneous reactions. Compared to the base case, the accumulated pNO\(_3^-\) was evidently lower at \( \gamma = 0.001 \) with the accumulated pNO\(_3^-\) of \((44 \mu g \text{ m}^{-3})\), thus a low \( \text{N}_2\text{O}_5 \) uptake coefficient corresponded to several types of aerosols, such as secondary organic aerosols (Gross et al., 2009), humic acids (Badger et al., 2006), and certain solid aerosols (Gross et al., 2008). When the \( \text{N}_2\text{O}_5 \) uptake coefficient increased from 0.005 to 0.05 (Fig. 6b, c), the increase in integral pNO\(_3^-\) was negligible. The conversion capacity of \( \text{N}_2\text{O}_5 \) uptake to pNO\(_3^-\) is maximized for a given, fixed value of the ClNO\(_2\) yield. This indicates that the conversion capacity of \( \text{N}_2\text{O}_5 \) uptake to pNO\(_3^-\) was almost maximized at certain ClNO\(_2\) yield. The conversion of NO\(_x\) to pNO\(_3^-\) nitrate was not limited by the \( \text{N}_2\text{O}_5 \) heterogeneous reaction rate, but limited by the formation of NO\(_3\) via the reaction of NO\(_2\) with O\(_3\) during the polluted night.

For describing the nocturnal NO\(_3\) removal capacity and pNO\(_3^-\) formation via NO\(_3\) and \( \text{N}_2\text{O}_5 \) chemistry, the overnight NO\(_3\) loss efficiency (\( \epsilon \)) was calculated using Eq. 9.

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

The case modeled typical winter haze pollution conditions in Beijing from sunset to sunrise, with the initial model values of NO\(_2\) and O\(_3\) set to 60 ppbv and 30 ppbv, respectively. \( S_a \) was set to 3000 \( \mu m^2 \text{ cm}^{-3} \), the CINO\(_2\) yield was zero, and \( k_{\text{NO}_3} \) 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 \( \text{N}_2\text{O}_5 \) by uptake reaction were regarded as NO\(_3\) removal valid NO\(_3\) loss. Figure 7 shows the dependence of the overnight NO\(_3\) loss efficiency on the \( \text{N}_2\text{O}_5 \) uptake coefficient, as it varied from \( 1\times10^{-5} \) to 0.1. This is an increase from 20% to 56% with
increasing $\gamma_{N_2O_5}$, and the maximum NO$_x$ loss efficiency was very large, which is similar to the result addressed by Chang et al. (2011). The ceiling of overnight NO$_x$ loss via NO$_3$-N$_2$O$_5$ chemistry was fixed when all the NO$_x$ loss was through N$_2$O$_5$ uptake in polluted days, which is limited by the reaction time and the formation rate of NO$_3$ (R1). In this case, the N$_2$O$_5$ uptake was contributed about 90% of the overnight NO$_x$ loss (50.4%) when $\gamma_{N_2O_5}$ was equal to $2 \times 10^{-3}$ 0.002. When $\gamma_{N_2O_5}$ was less than $2 \times 10^{-3}$, NO$_x$ removal increased rapidly with the increasing of $\gamma_{N_2O_5}$, which was defined as the $\gamma_{N_2O_5}$-sensitive region. When $\gamma_{N_2O_5}$ $\geq$ $2 \times 10^{-3}$, the contribution of N$_2$O$_5$ uptake to NO$_x$ loss was over 90% and became insensitive to this region was defined as the $\gamma_{N_2O_5}$-insensitive region. According to Eqs. 3 and 5, high aerosol surface concentration $S_a$ and high NO$_3$ and lower k$_{NO3}$ and/or low temperature would further increase the insensitivity region with lower $\gamma_{N_2O_5}$ value and allow the N$_2$O$_5$ uptake to be more easily located in the $\gamma_{N_2O_5}$-insensitive region. Here, the critical value of the N$_2$O$_5$ uptake coefficient ($2 \times 10^{-3}$) was relatively low compared with that recommended for the surface of mineral dust (0.013, 290-300K) (Crowley et al., 2010b; Tang et al., 2017) compared to that recommended by the IUPAC (International Union of Pure and Applied Chemistry) on the surface of mineral dust (0.013, 290-300 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; Wang Z et al., 2017; Brown et al., 2016; Wang H et al., 2017b; Wang X et al., 2017). This suggests that the NO$_3$ loss and pNO$_3^-$ formation via N$_2$O$_5$ uptake were easily maximized in the pollution episode, and further worsening the PM pollution.

In the base case, the modeled pNO$_3^-$ formation via N$_2$O$_5$ uptake was an upper limit result, as the ClNO$_2$ yield was set to zero. High coal combustion emitted chloride into the atmosphere of Beijing during the heating period (Sun et al., 2013), like the emissions from power plants in north China. This enhanced anthropogenic chloride provides abundant chloride-containing aerosols to form ClNO$_2$ via N$_2$O$_5$ uptake aloft, implying that significant ClNO$_2$ formed in the upper layer of the NBL (Tham et al., 2016; Wang Z et al., 2017). Assuming the ClNO$_2$ yield is the average value of 0.28
determined at high altitude in north China (Wang Z et al., 2017), the pNO₃⁻ produced
throughout the night will have decreased by 7 μg m⁻³. The modeled formation of
CINO₂⁻ formation aloft throughout the night reached 2.5 ppbv, which is
comparable with that observed in field measurement in north China (Tham et al., 2016; Wang Z et al., 2017; Wang X et al., 2017). Since the modeled pNO₃⁻ formation is sensitive to the ClNO₂ yield, a higher yield would increase the model uncertainty directly, hence probing the ClNO₂ yield is warranted in future studies. As for NO₃⁻ reactivity, Fig. 2.8 shows the sensitivity tests of the integral pNO₃⁻ formation for the whole night at kNO₃ values = 0.001 s⁻¹, 0.01 s⁻¹, 0.02 s⁻¹, and 0.05 s⁻¹. The integral pNO₃⁻ formation decreased when kNO₃ 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 NO₃⁻ nitrogen loss via NO₃⁻ reaction with VOCs during the polluted wintertime was not important, which may only lead to relatively small uncertainties in the integral pNO₃⁻ formation calculation. Nevertheless, if N₂O₅ uptake was extremely low (e.g., γN₂O₅ < 10⁻⁴), the uncertainty of NO₃ oxidation would increase significantly.

The uncertainty caused by the physical changes of the air masses were analyzed from two folds, one is the dilution and the other is the mixing and exchange of the air mass. With respect to the impact of the dilution process, it would decrease the mixing ratio of NO₂, O₃, NO₃ and N₂O₅, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case. With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted NOₓ into the air
mass after sunset, which would increase the mixing ratio of \( O_x \), and restart the zero
time of the model. Accounting for the uncertainties from the mixing, sensitivities tests
of the box model to shorting the duration of 25%, the bias of the integrated pNO\(_3\);
throughout the night was small within 12% relative to base case. If the air mass was
affected by the clean air mass from the north, it would be featured with very low NO,
and about 40 ppbv \( O_3 \) (background condition), which was not consistent with our
observation.

4. Conclusion

During the wintertime, ambient \( O_3 \) is often fully titrated at the ground level in urban
Beijing owing to its fast reaction with NO emissions. Consequently, the near-surface
air masses are chemically inert. Nevertheless, the chemical information of the air
masses at higher altitudes was indicative of a reactive layer above urban Beijing,
which potentially drives fast pNO\(_3\) production via \( N_2O_5 \) uptake and contributes to the
surface PM mass concentration. In this study, we found a case to show evidence
for evidenced additional \( O_3 \) missing (25 ppbv) aloft throughout the night. Based on
model simulation, we found that the particulate nitrate formed above 150 m reached
50 \( \mu g \) m\(^{-3}\) and enhanced the surface level PM concentration significantly by 28 \( \mu g \) m\(^{-3}\)
with downward mixing after break-up of the NBL in the morning.

Our result emphasized the importance of the heterogeneous chemistry aloft the city
through a case study. The model simulation also demonstrated that during the heavy
PM pollution period, the particulate nitrate formation capacity via \( N_2O_5 \) uptake was
easily maximized in the high altitude above urban Beijing, even with low \( N_2O_5 \) uptake
coefficient. Our study also demonstrated that during the heavy PM pollution period,
the particulate nitrate formation capacity via \( N_2O_5 \) uptake was easily maximized in the
upper layer, even with \( N_2O_5 \) uptake as low as \( 2\times10^{-3} \). This indicates that the mixing
ratio of NO\(_2\) aloft was directly linked to nitrate formation, and reduction of NO\(_2\) is
helpful in decreasing nocturnal nitrate formation. Overall, this study highlights the
importance of the interplay between chemical formation aloft and dynamic processes
for probing the ground-level PM pollution problem. In the future, direct observations of \( \text{N}_2\text{O}_5 \) and associated parameters should be performed to explore the physical and chemical properties of this overhead nighttime reaction layer and to reach a better understanding of the winter haze formation.

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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$_2$O$_5$ and particle nitrate formation) were collected from a ground site at PKU. Additional measurements on PM$_{2.5}$ concentrations were continuously measured at national monitoring sites throughout Beijing.
Figure 2. Time series of (a) PM$_{2.5}$ and O$_3$, (b) NO and NO$_2$, (c) temperature (T) and relative humidity (RH), (d) wind direction (WD) and wind speed (WS) from December 16 to 22, 2016 at PKU site in Beijing, China. The shaded region represents the nighttime periods. Red line in panel (a) shows an example of fast PM$_{2.5}$ enhancement on the night of December 19, and the green lines are the time periods when the vertical measurements conducted in IAP site.
Figure 3. Vertical profiles of NO and NO$_2$ (a), O$_3$ and O$_X$ (b) at 20:38-21:06 on the night of December 20, 2016.
Figure 4. $O_x$ missing case presented by the vertical profiles of (a) NO and NO$_2$, (b) O$_3$ and $O_x$ at 20:38-21:13 on the night of December 19, 2016.
Figure 5. Vertical profiles of (a) NO and NO$_2$, (b) O$_3$ and O$_x$ at 09:06-09:34 in the morning of December 20, 2016.
Figure 6. Base case ($\gamma=0.005$) 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 $O_3$ missing in the two vertical measurements ~21:00 and ~09:30 in the following morning.
Figure 7. The dependence of overnight NO\textsubscript{x} loss on \(\gamma\text{N}_2\text{O}_5\) uptake on \(\gamma\text{N}_2\text{O}_5\) in a typical winter pollution condition. The initial NO\textsubscript{2} and O\textsubscript{3} were set to 60 ppbv and 30 ppbv, respectively, \(S_a\) was set to 3000 \(\mu\text{m}^2\text{ cm}^{-3}\), the ClNO\textsubscript{2} yield was zero and \(k\text{NO}_3\) was 0.02 s\(^{-1}\). The reaction time was set to 14.5 h. The blue and orange zone represent the contribution by NO\textsubscript{2}+VOCs and N\textsubscript{2}O\textsubscript{5} uptake, the dashed line (\(\gamma = 0.002\), when N\textsubscript{2}O\textsubscript{5} uptake contribute to 90% of the maximum NO\textsubscript{x} loss) divide the loss into \(\gamma\) sensitive and insensitive region. The maximum nocturnal NO\textsubscript{x} loss by NO\textsubscript{2}-N\textsubscript{2}O\textsubscript{5} chemistry is 56%.
**Figure 8.** Base case ($k_{NO3}=0.02$ 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 s$^{-1}$, 0.01 s$^{-1}$, 0.05 s$^{-1}$) on the whole night of December 19, 2016.
Table 1. List of the parameter sets in base case and sensitivity tests.

<table>
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<tr>
<th>Cases</th>
<th>$k_{NO3}$ (s$^{-1}$)</th>
<th>$\gamma_{NO5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>0.02</td>
<td>0.005</td>
</tr>
<tr>
<td>$k_{NO3}$ test 1</td>
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<td>0.005</td>
</tr>
<tr>
<td>$k_{NO3}$ test 2</td>
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<td>0.005</td>
</tr>
<tr>
<td>$k_{NO3}$ test 3</td>
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<td>0.005</td>
</tr>
<tr>
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<td>0.001</td>
</tr>
<tr>
<td>$\gamma_{NO5}$ test 2</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>$\gamma_{NO5}$ test 3</td>
<td>0.02</td>
<td>0.05</td>
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