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-NO_2-O_3, it may subject to large uncertainties when used for estimating the loss rate of N_2O_5.

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 NO_2) offered us big advantages in avoiding uncertainties. The advantages come from two folds, on one hand, the ratio of N_2O_5 to NO_3 was normally over 100:1 in the lower temperature and high NO_2 condition and thus the production rate of NO_3 was mostly in balance with the N_2O_5 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 N_2O_5 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_{NO3} and k_{N2O5}. As for k_{NO3}, the influence was very small even set k_{NO3} up to 0.02 s^{-1}. As for k_{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 N_2O_5 uptake processes were not limited by the N_2O_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_2O_5 chemistry was efficient aloft (> 50%). The nocturnal NO_x loss was maximized once the N_2O_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_2O_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 N_2O_5 uptake was easily maximized in the high altitude above urban Beijing, even with low N_2O_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 NO_2, O_3, NO_3 and N_2O_5, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case.

With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted 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 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 NOx and about 40 ppbv O_3 (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 NO_2, O_3, NO_3 and N_2O_5, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case. With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted 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 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 NOx and about 40 ppbv O_3 (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 N_2O_5 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 N_2O_5 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 N_2O_5 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 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_2O_5 chemistry was efficient aloft (> 50%). The nocturnal NO_x loss was maximized once the N_2O_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_2O_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 N_2O_5 uptake was easily maximized in the high altitude above urban Beijing, even with low N_2O_5 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 pNO_3^- formation by N_2O_5 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 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). "

"The box model enabled the analysis of the integrated pNO_3^- and $ClNO_2$ via N_2O_5 uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO_3^- went as high as 50 μg m^{-3}. The integrated pNO_3^- at sunrise was equal to the loss of 27 ppbv O_x, showing a good agreement with the observed O_x 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 NO_x and O_3

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

Changed accordingly.

Line19: 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 N_2O_5 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 HNO_3 and particulate nitrate is an important aspect affected the contribution of N_2O_5 uptake producing particulate nitrate. We assumed that all nitrate formed from N_2O_5 uptake goes to the particle phase, the assumption would lead to the N_2O_5 uptake had an upper limit particle phase nitrate contribution.

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; 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: 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 2×10^{-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 NO_3 production which goes through N_2O_5 (either as N_2O_5 or lost through uptake) to the total NO_3 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 O_3 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 O_x and pNO_3^-. Which is the same as the reference recommend.

Added a sentence as: “The 1.5:1 relationship between O_x and pNO_3^- 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 N_2O_5 uptake was case by case, and the result represented by our specific case just address the significance of N_2O_5 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 $ClNO_2$ 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.

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Fast~~High~~ particulate nitrate formation via N_2O_5 uptake ~~in a chemically reactive layer~~ aloft ~~during wintertime~~ in winter Beijing

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Abstract.

Particulate nitrate (pNO_3^-) is an important ~~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. Here we report vertical measurement of NO_x and O_3 by in-situ instruments on a movable carriage on a tower~~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. Based on the box model simulation at different height, ~~W~~we found that pNO_3^- formation via N_2O_5 heterogeneous uptake was negligible at ground level due to N_2O_5 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 N_2O_5.~~ In contrast, the contribution from N_2O_5 uptake was large~~r~~ at high~~er~~ altitudes (e.g., > 150 m), which was supported by the low total oxidant (NO_2 + O_3) level at high~~er~~ altitudes than that at ground level. 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. Sensitivity tests suggested that the nocturnal NO_x loss by NO_3-N_2O_5 chemistry was maximized once the N_2O_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_2O_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_3-N_2O_5 chemistry was efficient aloft (> 50%). The nocturnal NO_x loss was easily maximized once the N_2O_5 uptake coefficient was over 2×10^{-3} on polluted days in wintertime. These results highlight that pNO_3^- formation via N_2O_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 G 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_2O_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_2O_5 uptake is a nighttime pathway, as NO_3 and N_2O_5 are easily photo-labile.

Particulate nitrate formation via N_2O_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_2O_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_2O_5 uptake is significant in summertime, the importance of this pathway in wintertime is not well characterized. Many differences in N_2O_5 chemistry exist between winter and summer. First, as the key precursor of NO_3 and N_2O_5, O_3 has a much lower concentration in winter than in summer, owing to the short daytime length and weak solar radiation. Second, colder temperature~~s~~ and high NO_2 level~~s~~ favor the partitioning towards N_2O_5. Third, ~~nighttime lasts much~~ longer nighttime length in winter~~,~~ ~~making~~ makes N_2O_5 heterogeneous hydrolysis potentially more important in pNO_3^- formation. Finally, the N_2O_5 uptake coefficient, as ~~the most~~an important parameter in N_2O_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_2O_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~~did not have good performance in predicting N_2O_5 uptake coefficient accurately (Chang et al., 2011; Chang et al., 2016).

In addition to the seasonal differences in pNO_3^- formation via N_2O_5 uptake, modeling and field studies showed high~~greater~~ levels of NO_3 and N_2O_5 at high~~er~~ 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_2O_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_3 ~~production~~ can't accumulate in the surface layer~~ is negligible~~ owing to high NO emissions, N_2O_5 uptake can still be active aloft without NO titration. The N_2O_5 uptake aloft leads to elevated pNO_3^- formation in the upper layer as well as effective 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). 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_2O_5 concentrations aloft. Model studies showed that pNO_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_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, ~~T~~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_3^- and the dependence of its formation on altitude in wintertime in Beijing, we conducted vertical profile measurements of NO, NO_2, and O_3 with a moving cabin at a tower platform in combination with simultaneous ground measurements of ~~these~~ more comprehensive 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.

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_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 via the observed atmospheric pressure measured by the Model 405 nm instrument. The cabin ascended and descended at a rate of 10 m min^{-1}, with a height limit of 260 m during the daytime and 240 m at night. The cabin stopped after reaching the peak, and parameters were measured continually during the last 10 min of each cycle. One vertical cycle lasted for approximately 1 h. We measured two cycles per day, one in the morning and the other in the evening. ~~, with s~~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_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) was used in a box ~~to~~ model to simulate the nighttime NO_3 and N_2O_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 $ClNO_2$ yield from N_2O_5 uptake. Homogeneous hydrolysis of N_2O_5 and NO_3 heterogeneous uptake reaction were neglected in this analysis because 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).

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

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

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

$NO_3 + VOCs \rightarrow Products$ (R4)

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

Following the work of Wagner et al. (2013), the box model can be solved using six equations (Eqs. 1–6). In the framework, O_3 is only lost via the reaction of NO_2 + O_3 and the change in the O_3 concentration can be expressed as Eq. 1. Eq. 2 can express the losses of NO_2.~~–~~ ~~Here, t~~The s(t) is between 0 and 1 and expressed as Eq. 5, the physical meaning of s(t) is the ratio of NO_3 production which goes through N_2O_5 (either as N_2O_5 or lost through uptake) to the total NO_3 production (Wagner et al., 2013). The s(t) favors 0 when direct loss of NO_3 dominates and favors 1 when N_2O_5 uptake dominates NO_3 loss. The model calculation has~~d~~ two steps. The first step is~~was~~ ~~to~~ calculate the mixing ratio of NO_2 and O_3 at time zero (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 μm^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 1×10^{-3} s^{-1}, with a N_2O_5 uptake coefficient of 5×10^{-3}. N_2O_5 uptake would contribute to the~~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 1. Eq. 3 can describe the sum concentration of NO_3 and N_2O_5. Assuming the equilibrium between NO_3 and N_2O_5 is maintained after a certain period, based on the temperature-dependent equilibrium rate constant (k_{eq}) and the modeled NO_2 at a certain time, Eq. 4 can be used to determine the ratio of N_2O_5 to NO_3. Combined, Eqs. 1–4 allow for the calculation of 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} were then used to estimate pNO_3^- formation. The HNO_3 produced in R4 was not considered because many of the products are organic nitrates (Brown and Stutz, 2012). Here, k_{NO3} and k_{N2O5} denote the pseudo-first-order reaction rate constants of the total NO_3 reactivity caused by ambient VOCs and N_2O_5 heterogeneous uptake, respectively. k_{N2O5} is given in Eq. 6. S_a is the aerosol surface area, C is the mean molecular speed of N_2O_5, and γ_{N2O5} is the N_2O_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.

$$\frac{\mathrm{d}\,[\mathrm{O_3}]}{\mathrm{d}t} = -k_{\mathrm{NO2+O3}}[\mathrm{O_3}][\mathrm{NO_2}] \qquad (1)$$

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

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

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

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

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

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 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 μm^2 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~~Overall, the S_a measured at the PKU site can represent the urban Beijing conditions in horizontal and vertical scale (< 340 m). Although the PNSD information for particles larger than 0.7 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 and $ClNO_2$ yield are key parameters in the estimation of pNO_3^- formation (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016). Wagner et al. (2013) shows the significant pNO_3^- suppression of N_2O_5 uptake aloft in the wintertime in Denver, CO, USA, the uptake coefficient is 0.005 when the percentage of pNO_3^- in the $PM_{2.5}$ mass concentration is 40%. As the proportion of nitrate in the particle mass concentration is similarly high in North China during wintertime (Sun et al., 2013, 2015a; Chen et al., 2015; Zheng et al., 2015; Wen et al., 2015), herein we fixed the uptake coefficient to 0.005 for the base model initial input. Because the model input of $ClNO_2$ yield only affects the value of produced pNO_3^- concentration and would not change the modeled N_2O_5 concentration, we set the initial f_{ClNO2} to zero. Previous work showed ~~T~~the averaged~~ value of~~ k_{NO3} ~~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 H 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_{NO3} should be smaller than it is in summer. In this work, the model input k_{NO3} was set to ~~a~~ an arbitrary and relatively high value of ~~relatively high value of~~ 0.02 s^{-1} (equivalent to 0.2 ppbv isoprene + 40 parts per trillion volume (pptv) monoterpene + 1.0 ppbv cis-2-butene), to constrain the impact of N_2O_5 uptake in the model. A series of sensitivity tests was conducted to study the uncertainties of the model simulation, and the detailed test sets are listed in Table 1, included the test of N_2O_5 uptake coefficient and k_{NO3}. The γ_{N2O5} sensitivity tests were set from 0.001 to 0.05, and the k_{NO3} tests were set to 0.001 s^{-1}, 0.01 s^{-1}, and 0.1 s^{-1}.

In the calculation of the particulate nitration formation by N_2O_5 uptake, an assumption is that all soluble nitrate formed from N_2O_5 uptake goes to the particle phase rather than the gas phase. The assumption would lead to an upper bias as the degassing of gas phase HNO_3 from particulate nitrate. While in winter Beijing, the mixing ratio of NH_3 was rich to tens of ppbv and always much higher than the nocturnal gas phase HNO_3 (e.g., Liu et al., 2017). The high NH_3 suppressed the degassing of particulate nitrate effectively. The measurement of gas phase HNO_3 and pNO_3^- in the surface layer of Beijing showed the soluble nitrate favor to particle phase in winter, especially in polluted days. For example, the nocturnal ratio of pNO_3^- to total soluble nitrate was larger than 0.95 on average (Liu et al., 2017). Due to the low temperature and high RH at high altitude, the ratio would increase and the degassing of particulate nitrate is negligible.

3. Results and discussion

3.1 Ground-based observations.

A severe winter PM pollution event lasted from December 16 to 22, 2016, in Beijing. Figure 2a shows the time series of $PM_{2.5}$ and other relevant parameters based on ground measurements at the PKU site. The mass concentration of $PM_{2.5}$ began to increase from December 16, reaching 480 μg m^{-3} on December 20. A fast PM growth event was captured, with an overall increment of 100 μg m^{-3} on the night of December 19 (Fig. 2a). Throughout the pollution episode, the meteorological conditions included high RH (50% ± 16%) and low temperature (2 ± 3 °C). The slow surface wind speed (< 3 m s^{-1}) implied the atmosphere was stable (Fig. 2c, d). The daytime O_3 concentration was low, owing to high NO emission and weak solar radiation. After sunset, O_3 at surface layer was rapidly titrated to zero by the elevated NO. The presence of high NO concentrations would have strongly suppressed the concentration of NO_3, further suppressing N_2O_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_2O_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_2O_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 t~~The vertical profile~~–~~ on December 19 was ~~not similar to~~different with that on December 20. Figure 4a shows the vertical profiles around 21:00 on December 19; NO was abundant from the ground to 100 m, then gradually decreased to zero from 100 m to 150 m, and remained at zero above 150 m. The observed NO_2 concentration was 85 ± 2 ppbv below 100 m, which gradually decreased from 100 m to 150 m, and was 50 ± 2 ppbv from 150 m to 240 m. The observed O_3 concentrations below 150 m were below the instrumental limit of detection (Fig. 4b). Above 150 m, the O_3 concentration was 20 ± 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_x concentration at higher altitudes was 15 ppbv lower than that at lower altitudes (Fig. 4b). The O_x missing from the higher altitude air mass indicated an additional nocturnal removal of O_x aloft.

Figure 5 depicts the vertical profiles of NO_x, O_3, and O_x at 09:30 on the morning of December 20, which have similar features to those observed at 21:00 on December 19. The vertical profiles suggested stratification still existed at that time. The amount of O_x missing aloft in the morning increased to 25 ppbv at 240 – 260 m, demonstrating that an additional 25 ppbv of O_x was removed or converted to other compounds at higher altitudes than at the surface layer during the night from December 19 to 20. Figure S3 shows the vertical profiles of NO, NO_2, O_3, and O_x at ~12:00 on December 18, when solar radiation was strong enough to mix the trace gases well in the vertical direction. NO_x and O_3 were found to be well mixed indeed, with small variation from the ground level to 260 m.

3.3 Particulate nitrate formation aloft.

N_2O_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 high ~~er~~ 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 missing ~~from the~~at high~~er~~ 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.

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 was zero below 150 m, as the high level of NO made for ~~quick~~ rapidly consumption of the ~~NO_3~~ formed NO_3. In contrast, the modeled N_2O_5 concentrations at 21:00 above 150 m were in the range of 400–600 pptv (Fig. 6a). The ~~Particulate NO_3^- accumulation via~~pNO_3^- formation by N_2O_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).~~

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

The box model enabled the analysis of the integrated pNO_3^- and $ClNO_2$ via N_2O_5 uptake throughout the night. As shown in Fig. 6c, the modeled integrated pNO_3^- went as high as 50 μg m^{-3}. The integrated pNO_3^- at sunrise was equal to the loss of 27 ppbv O_x, showing a good agreement with the observed O_x missing (25 ppbv) aloft in the morning hours. During the nighttime, the pNO_3^- formed aloft via N_2O_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_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_3^- aloft from 150 m to 340 m is 50 μg m^{-3} during the nighttime and well mixed within the PBL ~~by~~ in the next morning, the pNO_3^- ~~-~~enhancement ~~to~~ at 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}, which is in good agreement with the observed PM peak in the morning on December 20, with PM enhancement of ~60 μg m^{-3}. The result demonstrated that the nocturnal N_2O_5 uptake aloft and downward transportation were critical for understanding the PM growth process.

3.4 Sensitivity studies.

Previous studies have emphasized that the N_2O_5 uptake coefficient varies greatly (0.001 – 0.1) in different ambient conditions (Chang et al., 2011; Brown and Stutz, 2012; Wang H et al., 2016), which is the main source of uncertainties in this model. In the present research, sensitivity studies showed the modeled N_2O_5 concentration dropping from 3 ppbv to 60 pptv when the N_2O_5 uptake coefficients increased from 0.001 to 0.05 (Fig. 6a), as the N_2O_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 μg m^{-3}~~), thus t~~. Low N_2O_5 uptake coefficients correspond to several types of aerosols, such as~~he low N_2O_5 uptake coefficient condition corresponded to several kinds of aerosols, such as~~ secondary organic aerosols (Gross et al., 2009), humic acids (Badger et al., 2006), and certain solid aerosols (Gross et al., 2008). When the N_2O_5 uptake coefficient increased from 0.005 to 0.05 (Fig. 6b, c), the increase in integral pNO_3^- was negligible. The conversion capacity of N_2O_5 uptake to pNO_3^- is maximized for a given, fixed value of the $ClNO_2$ yield. ~~This indicates that the conversion capacity of N_2O_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 N_2O_5 heterogeneous reaction rate, but limited by the formation of NO_3 via the reaction of NO_2 with O_3 during the polluted night.

For describing the nocturnal NO_x removal capacity and pNO_3^- formation via NO_3 and N_2O_5 chemistry, the overnight NO_x loss efficiency (ε) was calculated using Eq. 9.

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

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 μm^2 cm^{-3}, the $ClNO_2$ yield was zero, and k_{NO3} was 0.02 s^{-1}. The reaction time was set to 14.5 h to represent an overnight period in wintertime. The consumed NO_3 by the reaction with VOCs and N_2O_5 by uptake reaction were regarded as NO_x removal~~valid NO_x loss~~. Figure 7 shows the dependence of the overnight NO_x loss efficiency on the N_2O_5 uptake coefficient~~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,~~which is similar to~~ as was~~ the result addressed by Chang et al. (2011). The ceiling of overnight NO_x loss via NO_3-N_2O_5 chemistry was fixed when all the NO_x loss was through N_2O_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_2O_5 uptake~~ was~~ contributed about 90% of the overnight NO_x loss (50.4%) when γ_{N2O5} was equal to 2×10^{-3}~~0.002~~. When γ_{N2O5} was less than 2×10^{-3}, NO_x removal increased rapidly with the increasing of γ_{N2O5}, which was defined as the γ_{N2O5}-sensitive region. When $\gamma_{N2O5} \geq 2\times10^{-3}$, the contribution of N_2O_5 uptake to NO_x loss was over 90% and became insensitive. T~~, t~~his region was defined as the γ_{N2O5}-insensitive region. According to Eqs. 3 and 5, high~~er~~ ~~*aerosol surface concentration*~~S_a~~ and~~ , high NO_x~~ and~~ , low~~er~~ k_{NO3} ~~and~~ or low temperature ~~would further increase the insensitivity region with lower γ_{N2O5} value and~~ 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 (2×10^{-3}) was relatively low compared with that recommended for the surface of mineral dust (0.013, 290-300K) (Crowley et al., 2010b; Tang et al., 2017)~~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_x loss and pNO_3^- formation ~~via~~ by N_2O_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_2O_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_2O_5 uptake aloft, implying that significant $ClNO_2$ formed in the upper layer of the NBL (Tham et al., 2016; Wang Z et al., 2017). Assuming the $ClNO_2$ yield is the average value of 0.28

determined at high altitude in north China (Wang Z et al., 2017), the pNO_3^- produced throughout the night ~~will have~~ decreased ~~by~~ 7 μg m^{-3}. The modeled formation of $ClNO_2$ ~~formation~~ aloft throughout the night ~~reach~~was~~ed~~ 2.5 ppbv, which is comparable with ~~that observed in field measurement in north~~the observation in North China (Tham et al., 2016; Wang Z et al., 2017; Wang X et al., 2017). Since the modeled pNO_3^- formation is sensitive to ~~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 is warranted in future studies. As for NO_3 reactivity, Fig. ~~7~~ 8 shows the sensitivity tests of the integral pNO_3^- formation for the whole night at k_{NO3} values = 0.001 s^{-1}, 0.01 s^{-1}, 0.02 s^{-1}, and 0.05 s^{-1}. The integral pNO_3^- formation decreased when k_{NO3} varied from 0.001 s^{-1} to 0.1 s^{-1}, but the variation ratio to the base case was within ~~±~~5%. The result shows the NO_3-N_2O_5 loss via NO_3 reaction with VOCs during the polluted wintertime was not important, which may only lead to relatively small uncertainties in the integral pNO_3^- formation calculation. Nevertheless, if N_2O_5 uptake was extremely low (e.g., $\gamma_{N2O5} < 10^{-4}$), the uncertainty of NO_3 oxidation would increase significantly.

The uncertainty caused by the physical changes of the air masses were analyzed from two folds, one is the dilution and the other is the mixing and exchange of the air mass. With respect to the impact of the dilution process, it would decrease the mixing ratio of NO_2, O_3, NO_3 and N_2O_5, and leads to a lower contribution to the particulate nitrate formation. An additional loss process for trace gases with a lifetime of 24 h was assumed for calculated species in the sensitivity test (Lu et al., 2012). The result shows that the integrated production of particulate nitrate decreased 28% compared with base case. With respect to the exchange and mixing of the air mass at high altitude during nighttime in polluted winter, the stable atmospheric stratification was featured with strong inversion (Zhong et al., 2017). The nocturnal atmosphere is stable and layered, the upward mixing from the surface is minimized, and air masses above the surface are less affected by nocturnal emissions (Wagner et al., 2013). Nevertheless, the injection by warm combustion sources or the clean air mass can affect the air mass in fact. If the warm combustion source emitted NO_x into the air mass after sunset, which would increase the mixing ratio of O_x, and restart the zero time of the model. Accounting for the uncertainties from the mixing, sensitivities tests of the box model to shorting the duration of 25%, the bias of the integrated pNO_3^- throughout the night was small within 12% relative to base case. If the air mass was affected by the clean air mass from the north, it would be featured with very low NO_x and about 40 ppbv O_3 (background condition), which was not consistent with our observation.

4. Conclusion

During the wintertime, ambient O_3 is often fully titrated at the ground level in urban Beijing owing to its fast reaction with NO emissions. Consequently, the near-surface air masses are chemically inert. Nevertheless, the chemical information of the air masses at higher altitudes was indicative of a reactive layer above urban Beijing, which potentially drives fast pNO_3^- production via N_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_x missing (25 ppbv) aloft throughout the night. Based on model simulation, we found that the particulate nitrate formed above 150 m reached 50 μg m^{-3} and enhanced the surface level PM concentration significantly by 28 μg m^{-3} with downward mixing after break-up of the NBL in the morning.

Our result emphasized the importance of the heterogeneous chemistry aloft the city through a case study. The model simulation also demonstrated that during the heavy PM pollution period, the particulate nitrate formation capacity via N_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 2×10^{-3}.~~ This indicates that the mixing ratio of NO_2 aloft was directly linked to nitrate formation, and reduction of NO_x is helpful in decreasing nocturnal nitrate formation. Overall, this study highlights the importance of the interplay between chemical formation aloft and dynamic processes for probing the ground-level PM pollution problem. In the future, direct observations of N_2O_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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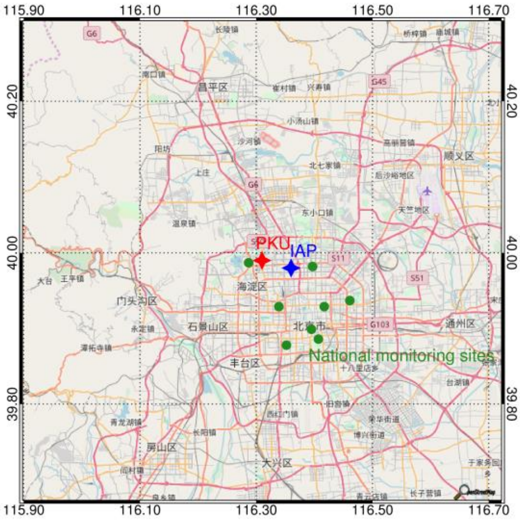

Figure 1. Location of the monitoring sites used in this study, including PKU (red diamond), IAP (blue diamond), and other National Monitoring Sites (green circles). Vertical profiles of NO_x and O_3 were collected at a tower at the IAP. Measurements of particle number and size distribution (used to calculate N_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.

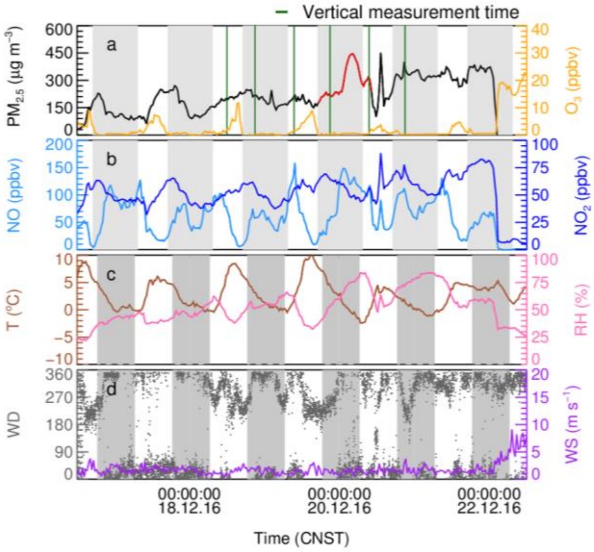

Figure 2. Time series of **(a)** PM$_{2.5}$ and O$_3$, **(b)** NO and NO$_2$, **(c)** temperature (T) and relative humidity (RH), **(d)** wind direction (WD) and wind speed (WS) from December 16 to 22, 2016 at PKU site in Beijing, China. The shaded region represents the nighttime periods. Red line in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

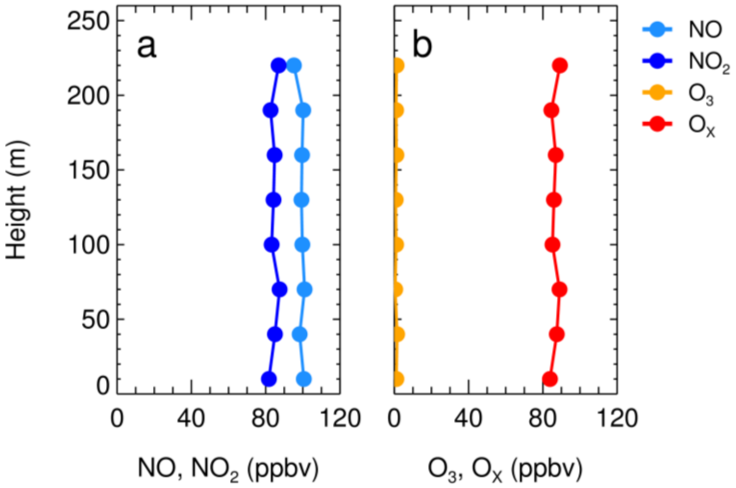

Figure 3. Vertical profiles of NO and NO_2 (**a**), O_3 and O_x (**b**) at 20:38-21:06 on the night of December 20, 2016.

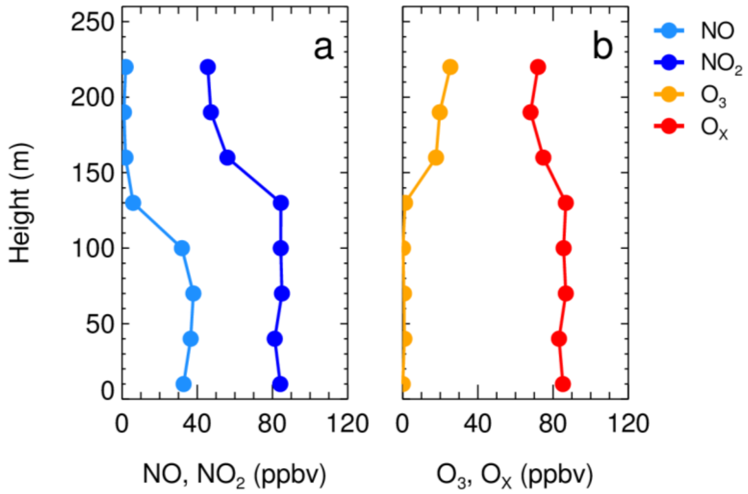

Figure 4. O_x missing case presented by the vertical profiles of (**a**) NO and NO_2, (**b**) O_3 and O_x at 20:38-21:13 on the night of December 19, 2016.

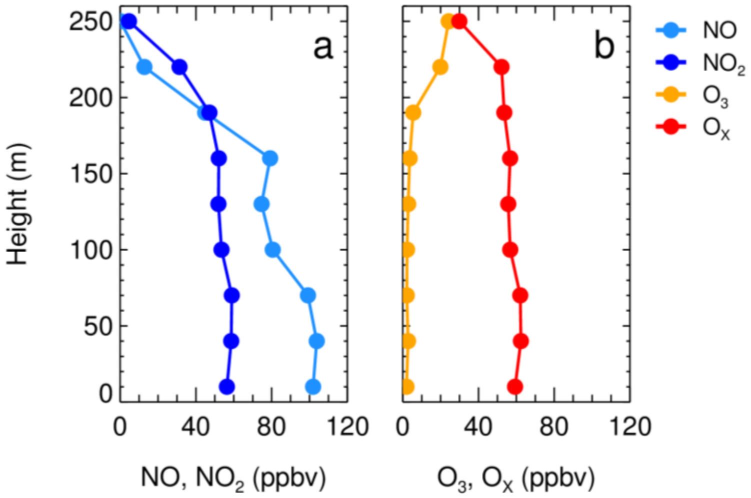

Figure 5. Vertical profiles of (**a**) NO and NO_2, (**b**) O_3 and O_x at 09:06-09:34 in the morning of December 20, 2016.

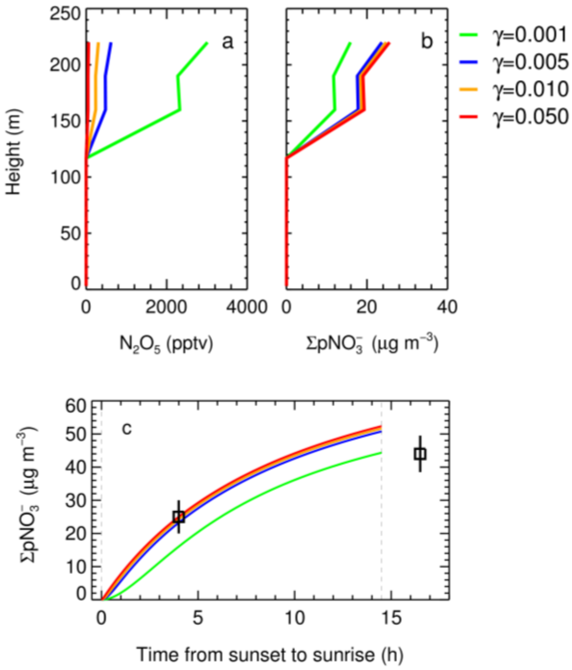

Figure 6. Base case (γ=0.005) and sensitivity tests of the vertical profile on the night of December 19 at different N_2O_5 uptake coefficients, including **(a)** the mixing ratio of N_2O_5 at 21:00, **(b)** the integral pNO_3^- production from sunset to 21:00, **(c)** the time series of the integral 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~~X~~ missing in the two vertical measurements ~21:00 and ~09:30 in the following morning.

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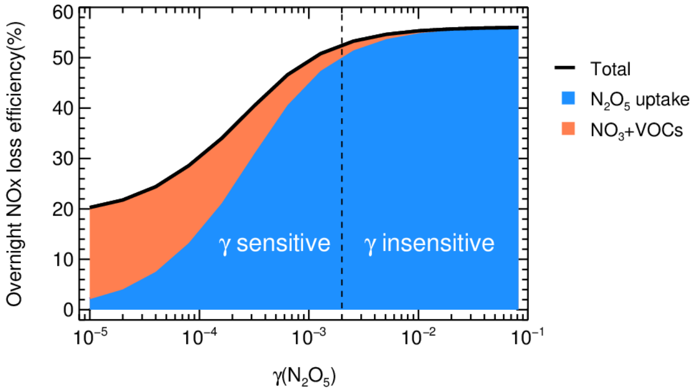

Figure 7. The dependence of overnight NO_x loss ~~on~~ via N_2O_5 uptake on γ_{N2O5} in a typical winter pollution condition. The initial NO_2 and O_3 were set to 60 ppbv and 30 ppbv, respectively, S_a was set to 3000 μm^2 cm^{-3}, the $ClNO_2$ yield ~~is~~ was zero and k_{NO3} ~~is~~ was 0.02 s^{-1}. The reaction time was set to 14.5 h. The blue and orange zone represent the contribution by NO_3+VOCs and N_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%.

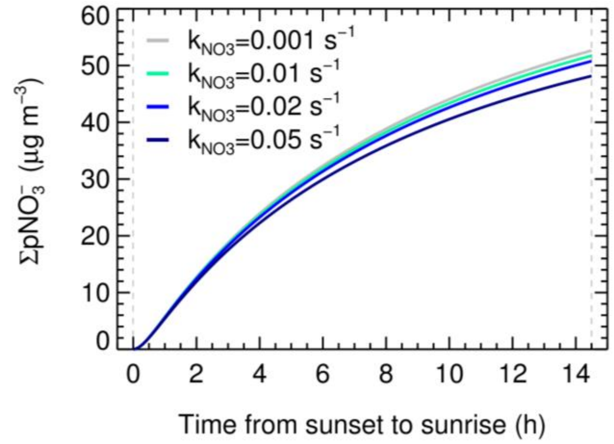

Figure 8. Base case (k_{NO3}=0.02 s^{-1}) and sensitivity tests of the integral pNO_3^- formed at 240 m via N_2O_5 uptake at different NO_3 reactivity (0.001 s^{-1}, 0.01 s^{-1}, 0.05 s^{-1}) on the whole night of December 19, 2016.

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