Response to Referees

We thank the reviewers for their careful reading and their constructive comments on our manuscript. As detailed below, the reviewer's comments are shown as italicized font, our response to the comments are normal font. New or modified text is in blue.

Referee #1

This paper presents NO_3 and N_2O_5 observational data from a suburban site in Beijing during the summer of 2016. The authors use these data to investigate the oxidation of volatile organic compounds (VOC) by NO_3 and the effect of N_2O_5 heterogeneous uptake on reactive nitrogen loss and $ClNO_2$ production in the Beijing urban outflow. Nocturnal biogenic VOC oxidation was shown to be dominated by NO_3, and the heterogeneous uptake of N_2O_5 was found to be a significant loss mechanism for reactive nitrogen. The uptake of N_2O_5 was found to produce approximately a factor of four more inorganic nitrate than organic nitrate from the NO_3 + VOC pathway and result in significant $ClNO_2$ production. These results are compared, and broadly agree, with previously reported observations and represent a valuable contribution to the growing body of work on the importance of nocturnal chemistry on local atmospheric composition. I recommend publication of the manuscript once the following minor comments /technical corrections have been addressed.

Thanks for the referee's positive and helpful comments.

Minor comments / technical corrections.

1. Lines 60-61: Please could the author state if these are mass or molar yields.

These are the mass yields, and we added the explanation in the text.

Changed in line 60-61: "The reaction of NO_3 with isoprene has a SOA mass yield of 23.8% (Ng et al., 2008). For the reaction with monoterpene, such as limonene, the SOA mass yield can reach 174% at ambient temperatures (Boyd et al., 2017)."

2. Line 148-150 – It would be easier for the reader if the authors could be consistent with the order of N_2O_5 and $ClNO_2$ in this sentence.

Thanks for the suggestion, we now changed units of both N_2O_5 and $ClNO_2$ to "pptv".

3. Figure 3: The scale on the NO plot makes it difficult to see NO mixing ratios. Please consider either a log scale or a discontinuity to make this more visible.

We changed to log scale accordingly, and we labelled 0.06 ppbv NO in the black line in Figure 2 in the revised manuscript.

4. Lines 276-278: This sentence is confusing, please restructure.

We rewrote as: "The N_2O_5 concentration was highly correlated with NO_2 ($R^2 = 0.81$) and the NO_3 production rate ($R^2 = 0.60$), suggests the N_2O_5 concentration was solely response to the NO_2 concentration in the background air mass when enough O_3 is presented."

5. Line 289: Please re-reference the recent studies in the NCP.

We re-cited the recent studies in the NCP in Line 289 as suggested: "Tham et al., 2016; X. F. Wang et al., 2017; Z. Wang et al., 2017".

6. Figure 8 and lines 389 – 392: There is an inconsistency between the text and Fig. 8. In the text the authors state that on the three days with the largest discrepancies between the steady state calculated N_2O_5 lifetime and that calculated using the overall $k(N_2O_5)$ the steady state calculation is much higher than the overall $k(N_2O_5)$. In Fig. 8 however, the discrepancy on 30th May is in the opposite direction, with the steady state lifetime approaching a factor of 2 lower than the overall $k(N_2O_5)$. The authors should correct this statement and provide an explanation for this discrepancy. The authors should also explain why there is no steady state calculated N_2O_5 lifetime for 31st May in Fig. 8.

For the night of 29th-30th May (Referee quoted as 30th May), the calculated steady state loss rate constant of N_2O_5 is much smaller than that of the overall $k(N_2O_5)$. We agree with the reviewer that this discrepancy needs more explanations. Considering that the large uncertainties propagated from the observed parameters (e.g., NO_2, N_2O_5, S_a), the discrepancies between the calculated steady state loss rate constant of N_2O_5 and the overall $k(N_2O_5)$ is mostly within the estimated uncertainty levels. The steady state loss rate constant on the night of 30th May (mentioned 31th May in the comment) was calculated in fact, but the values are much higher than 0.02, the reason of high steady state loss rate constant on the night of 30th - 31th May was not well

understand. In the revised manuscript, we enlarged the y-axis and changed to log scale, as well as added the error bar of the estimated uncertainties in the Figure 7.

Change in the revised manuscript:

"Figure 7 shows the time series of the overall N_2O_5 loss rate constant as well as the N_2O_5 steady state loss rate constant. The overall N_2O_5 loss rate constant was calculated from the individual terms (Eq.3). The uncertainties of the N_2O_5 steady state loss rate constant and the overall $k(N_2O_5)$ are estimated to be 67% and 95%, respectively (Eq. 7 and Eq. 8). The largest error sources were from the corrected NO_2 measurements so that it is really important to have accurate NO_2 measurement instrument involved in the future campaigns.

$$\frac{\Delta Lss(N_2O_5)}{Lss(N_2O_5)} = \sqrt{(\frac{\Delta[N_2O_5]}{[N_2O_5]})^2 + (\frac{\Delta[NO_2]}{[NO_2]})^2 + (\frac{\Delta[O_3]}{[O_3]})^2 + (\frac{\Delta K_{eq}}{K_{eq}})^2} \qquad \text{(Eq. 7)}$$

$$\frac{\Delta k(N_2O_5)}{k(N_2O_5)} = \sqrt{(\frac{\Delta[N_2O_5]}{[N_2O_5]})^2 + (\frac{\Delta[S_a]}{[S_a]})^2 + (\frac{\Delta[\gamma]}{[\gamma]})^2 + (\frac{\Delta[NO_2]}{[NO_2]})^2 + (\frac{\Delta[O_3]}{[O_3]})^2 + (\frac{\Delta[VOC_s]}{[VOC_s]})^2 + (\frac{\Delta K_{eq}}{K_{eq}})^2} \qquad \text{(Eq. 8)}$$

On the night of 29 May, the steady state loss rate constant was much lower than the overall $k(N_2O_5)$; on the nights of 28, May and 3 June, the $L_{ss}(N_2O_5)$ calculated by the steady state method were much higher than the overall $k(N_2O_5)$, but these discrepancies were in the range of the uncertainties. Except the case happened on the night of 30 May, when the steady state loss rate constant was about ten times higher than the overall loss rate constant, and the reason was not well understood according to the available parameters that we have detected. In general, the overall N_2O_5 loss rate constant and the steady state N_2O_5 loss rate constant were comparable taking into considerations of the uncertainties. "
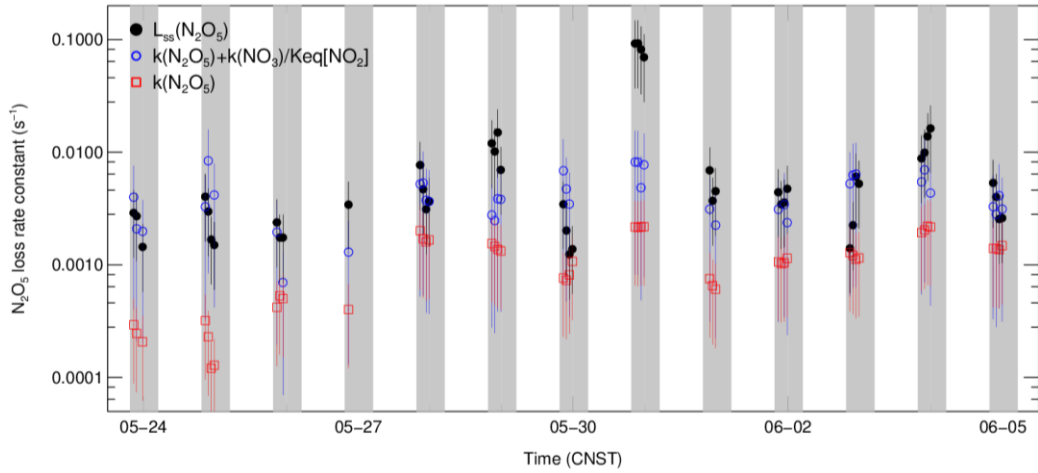

Figure 7. Time series of the individual N_2O_5 loss terms and the loss rate constant of N_2O_5 in steady state ($L_{ss}(N_2O_5)$).

7. Figure 9: Although the acronyms used in the x-axis labels are described in the text, it would help the reader if they were re-stated in the figure caption.

Added the description in the caption of Figure. 9 as following: "The nighttime VOCs reactivity of NO_3 and O_3 (defined as the pseudo first order loss rate of VOCs initialed by oxidants, include NO_3 and O_3); the VOCs are classified as isoprene (ISO), monoterpene (MNT), the terminal alkenes (OLT) and the internal alkenes (OLI). The data were selected from 20:00 to the next day 04:00."

8. Line 301 and Table 3: Please check that X. F. Wang and Z. Wang references are correct.

We corrected the reference accordingly. The study conducted in Mt. Tai, China was from Z. Wang et al., 2017 and the study conducted in Jinan, China was from Z. Wang et al., 2017