We are thankful to the two reviewers for their thoughtful comments and suggestions. We have revised the manuscript accordingly. Listed below are our point-by-point responses in blue to each reviewer's comments.

Response to Reviewer #1

Comments:

This manuscript presents measurements of ambient N_2O_5 and $ClNO_2$ in urban Beijing using chemical ionization mass spectrometry and derivertization of the uptake coefficient of N_2O_5 and the yield of $ClNO_2$. The data set are certainly of interest to the atmospheric chemistry community. On the other hand, major issues like instrument calibration, size of the data set, and presentation of the results, etc. stopped this reviewer from recommending publication of this manuscript in its present form in Atmospheric Chemistry and Physics. The authors are suggested to address the following concerns before a further consideration can be given.

Main issues:

1. The authors are suggested to be consistent in the presentation of their results. Take the abstract for example, $\tau(N_2O_5)^{-1}$ has been used whereas $\tau(N_2O_5)$ is given in Table 1; The exact values for $\tau(N_2O_5)^{-1}$ in the abstract is different from the values in the main text (Page 15 Line 15); Scientific notation has been used with $\tau(N_2O_5)^{-1}$ but not with direct N_2O_5 loss rates (0.00044-0.0034 s^{-1}); Finally, the contribution of heterogeneous uptake of N_2O_5 (7-33%) cannot be derived from the above-mentioned numbers. These certainly hurts the readability of this manuscript.

Thank the reviewer's carefulness. We checked the results in the revised manuscript. $\tau(N_2O_5)^{-1}$ represents the reactivity of N_2O_5, while $\tau(N_2O_5)$ is the steady-state lifetime. Following the reviewer's suggestions, we changed the two rows of $\tau(N_2O_5)$ and $\tau(NO_3)$ in Table 1 to $\tau(N_2O_5)^{-1}$ and $\tau(NO_3)^{-1}$ to avoid confusion and inconsistency.

$\tau(N_2O_5)^{-1}$ mentioned in the main text (Sec. 3.2), i.e., from 0.16×10^{-2} s^{-1} to 1.58×10^{-2} s^{-1} is the average value for each night, while that in the abstract (from 0.20×10^{-2} to 1.46×10^{-2} s^{-1}) refers to the instantaneous values throughout the campaign. We revise the sentence in the corresponding main text to make it clear. Now it reads:

"High N_2O_5 reactivity was observed and the average $\tau(N_2O_5)^{-1}$ was 0.16-1.58 $\times10^{-2}$ s^{-1} during these four nights corresponding to a short nighttime N_2O_5 lifetime between 1.1 and 10.7 minutes (Fig. 3), with $\tau(N_2O_5)^{-1}$ ranging from 0.20×10^{-2} to 1.46×10^{-2} s^{-1} throughout the campaign. "

The scientific notation, for example, $\tau(N_2O_5)^{-1}$ is generally used in the reference. Comparatively, the direct N_2O_5 loss cannot be ubiquitously expressed as a uniform scientific notion, for example, $k_{N_2O_5}$ or k_d. That is one of the reasons that $k_{N_2O_5}$ or k_d was not used in the abstract when no detailed information was given in the context.

The contribution of heterogeneous uptake of N_2O_5 (7-33%) was calculated according to the $\tau(N_2O_5)^{-1}$ and direct N_2O_5 loss ($k_{N_2O_5}$):

$$\tau(N_2O_5)^{-1} = \frac{p(NO_3)}{[N_2O_5]} \approx \frac{k_{NO_3}}{K_{eq}[NO_2]} + k_{N_2O_5}$$

Where $\frac{k_{NO_3}}{K_{eq}[NO_2]}$ denotes the contribution to $\tau(N_2O_5)^{-1}$ from the indirect N_2O_5 loss, while $k_{N_2O_5}$ indicates the direct loss of N_2O_5 through heterogeneous uptake. The contribution of heterogeneous uptake of N_2O_5 is the ratio of $k_{N_2O_5}$ to $\tau(N_2O_5)^{-1}$.

Without the VOCs measurements, the equation above is a robust assessment of the relative contribution between the direct and indirect loss pathway of N_2O_5. Furthermore, the uncertainty of this assessment is given in the responses below.

2. (Page 5 Line 20), I don't agree with the expression that BBCEAS was deployed for inter-comparison of N_2O_5. The IAP-CIMS was not calibrated at all. To me, BBCEAS provided a calibration reference for the IAP-CIMS. Also, as stated by the authors, BBCEAS measures the sum of N_2O_5 and NO_3. How did they determine NO_3 and subtract the values of NO_3 subsequently? Please elaborate.

Thanks for the reviewer's comments. Yes, the N_2O_5 sensitivity for IAP-CIMS was derived by comparing with the measurements from BBCEAS, instead of direct calibration. The sum of N_2O_5+NO_3 was measured by BBCEAS. We did not subtract the partial of NO_3 because the mixing ratio of N_2O_5 is much higher than NO_3 by a factor of ~11 by applying the equilibrium between N_2O_5 and NO_3. Due to the lack of equilibrium verification at the daytime, we use the sum of N_2O_5 and NO_3 for IAP-CIMS

N_2O_5 calibration in the study, which leads to an uncertainty of ~17% for N_2O_5 associated with the error of N_2O_5+NO_3 measurement (~14%). These results suggest that using the sum of N_2O_5 and NO_3 from BBCEAS for N_2O_5 calibration without subtracting NO_3 is acceptable.

Furthermore, the estimated N_2O_5 for IAP-CIMS tracked well with that measured by UoM-CIMS, and the regression slope (~1.42) was within the uncertainty of N_2O_5 measured and calibrated by UoM-CIMS (~58%). So, the inter-comparison between IAP-CIMS and UoM-CIMS further verify the reliability of N_2O_5 calibration for IAP-CIMS.

3. (Page 6 Line 1-2), the campaign is quite short, which could be still fine, but the authors are suggested to be more conservative with their findings. (Page 15 Line 13-15), expand the discussion in the time needed for the steady state assumption, and justify whether this requirement was met in the current study. (Page 17 Line 23-24), explain and justify why these three particular time periods are selected.

Thanks for the reviewer's suggestions. Although the campaign is short, our dataset is statistically reliable as suggested in Fig. R1. Therefore, the conclusions in this study are representative to some extent. We agree that the findings reported here should be careful to expand generally because the field campaign is limited to a short sampling time and influenced by different emission sources.

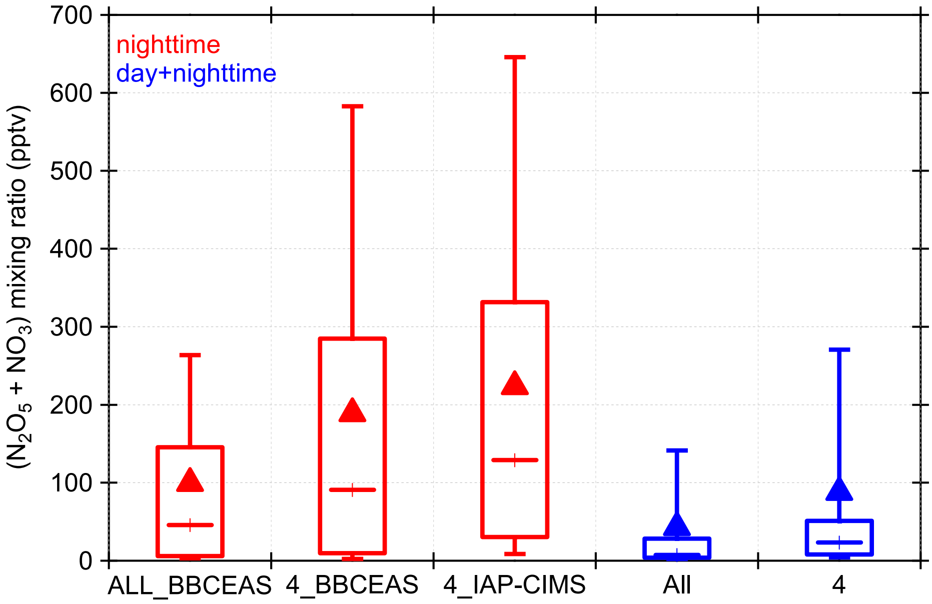

Figure R1. The box plot of mean (triangle), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) for N_2O_5 + NO_3 during the campaign. Note that "all" refers to the whole dataset measured by BBCEAS from 22 May to 26 June, while "4" refers to the four days overlapped by IAP-CIMS from 12-15 June.

Higher temperature (> 20 ^{o}C), NO_2 and O_3 concentrations (~ dozens of ppbv) suggest the more rapid steady state time than the simulation results (Brown et al., 2003). Also, the fast N_2O_5 and NO_3 lifetime in this study is similar to that in Wangdu where only data during the 0.5 h after sunset was used for calculation (Tham et al., 2016). Refer to the time required for steady-state in the literature, for example, 3 h in Hong Kong with much higher N_2O_5 lifetime (Brown et al., 2016), the first two hours after sunset were excluded in this study. Although lack of direct steady-state verification, the conclusions in this study are conservative.

The three periods used for calculation were selected for these reasons: (1) concurrent increases in $ClNO_2$ and particulate NO_3^-; (2) relatively stable air masses (stable wind direction and relative humidity); (3) no strong fresh emission (e.g., low NO).

4. (Page 6 Line 12-21), what were total ion counts of the reagent ions for the IAP-CIMS? Given the high affinity of I- with multiple species in the urban air, was reagent ion depletion observed during the campaign? Was the zero point regularly measured with the IAP-CIMS during the campaign? What were the detection limits and sensitivity of the IAP-CIMS for this particular method? While sensitivity of IAP-CIMS might be derived from comparison with other instruments, how to determine the detection limits? How would this affect the lower points in the measurements?

Thank the reviewer. The average (±σ) total counts of the reagent ions were about $4\pm0.5\times10^4$ cps (counts per second) ranging from $2.1–5.5\times10^4$ cps during the campaign. Note that the deviation of I-signals was mainly associated with the pressure fluctuation in IMR and SSQ chambers instead of depletion by target molecules, which means that I^- was sufficient during this summer measurements. However, there would be a great possibility that the reagent ion being depleted during polluted periods in the winter of urban Beijing.

We didn't do the zero point measurement but observed the background. For IAP-CIMS, the gas phase background was determined once during the five-day campaign by overflowing the inlet with dry N_2

for 35 minutes and the reported concentrations were derived by subtracting the background level in the instrument or the sampling tubes.

For IAP-CIMS, the N_2O_5 sensitivity (0.54 cps/pptv) was derived by comparing with the measurement from BBCEAS, while the $ClNO_2$ sensitivity was assumed to be similar with N_2O_5. The estimated $ClNO_2$ for IAP-CIMS agrees well with that was measured and calibrated post campaign by UoM-CIMS, suggesting that our reported $ClNO_2$ concentration for IAP-CIMS is reliable.

The detection limit was determined by the three times standard deviation of background measurement and then applied the estimated sensitivity. Although there are data points lower than the detection limit (1.66 pptv for N_2O_5 and 0.73 pptv for $ClNO_2$) in the daytime, the average concentrations of $ClNO_2$ and N_2O_5 were not much affected. Moreover, we mainly focus on the four nighttime episodes with much higher concentrations than the detection limits.

5. (Page 8-9), a lot of description was given for the calibration of UoM-CIMS but the key is that the IAP-CIMS was not. I still think that it might be OK with the current reference method. But, do consider the uncertainty caused by the assumptions during the entire process. I would like to see that the authors add a new session to evaluate the potential impact on their general conclusions (say, the relative importance of different pathways) due to this uncertainty (e.g., 10% or 20% uncertainties in the calibration factors).

Good suggestions. The quantifications of N_2O_5 and $ClNO_2$ for IAP-CIMS were determined by cross calibration with the BBCEAS and UoM-CIMS. The uncertainty of UoM-CIMS calibration is 58% determined from two $ClNO_2$ calibration methods, which can be used as the uncertainty of $ClNO_2$ measurement. Refer to the literature, the wet surface area density is estimated to be ~ 30% (Wang et al., 2017b;Wang et al., 2018). The uncertainty of $k_{\mathrm{N_2O_5}}$ is calculated to be ~35%, while the uncertainty of $\tau(N_2O_5)^{-1}$ is estimated to be ~18% associated from the error of O_3 and NO_2 (~5%), and N_2O_5 (~17%). So, the uncertainty of the direct N_2O_5 loss rates contributions estimated from Eq. (2) is ~ 40%.

$$k_{\mathrm{N_2O_5}} = \frac{1}{4} \times c \times S_{\mathrm{a}} \times \gamma_{\mathrm{N_2O_5}} \qquad (1)$$

$$\tau(\mathrm{N_2O_5})^{-1} = \frac{p(NO_3)}{[\mathrm{N_2O_5}]} \approx \frac{k_{\mathrm{NO_3}}}{K_{eq}[\mathrm{NO_2}]} + k_{\mathrm{N_2O_5}} \qquad (2)$$

I agree to add the uncertainty discussion in the corresponding main text. Now it reads:

"The direct N_2O_5 loss rates estimated from the uptake coefficient were in the range of 0.00044-0.0034 s^{-1}, which contributed 7-33% to the total N_2O_5 loss with the rest being indirect loss. The uncertainty of the direct N_2O_5 loss rates contributions is estimated to be ~40%, associated from S_a (~30%), O_3 and NO_2 (~5%), and N_2O_5 (~17%)."

6. (Page 9 Line 13), elaborate "this calibration was scaled to those in the field…"

The N_2O_5 and $ClNO_2$ measured by UoM-CIMS were calibrated post campaign, while only formic acid was calibrated throughout the campaign assuming that the ratio between formic acid and $ClNO_2$ sensitivity remains constant during this period. The $ClNO_2$ and formic acid sensitivities in the laboratory were derived by passing the inlet with known concentrations of these gas mixtures. Then, the field $ClNO_2$ sensitivity was derived by scaling to the formic acid sensitivity carried out in the field and the scaling factor is the relative ratio measured in the laboratory.

7. (Page 11 Line 7-9), do the authors mean that ambient particles were dried and then measured with the SMPS? Where did the hygroscopic growth factor come from?

Aerosol particles were dried by a diffusion silica-gel dryer before sampling into the SMPS. The dried aerosol surface area density was calculated according to the SMPS size distribution, which was then calibrated to the ambient RH condition by using the hygroscopic growth factor suggested by Liu et al. (2013) in Beijing. The RH-related parameterization is as follow:

$$f(RH) = 1+a\times(\frac{RH}{100})^{b}, \ a= 8.77, b=9.74$$

8. (Page 11 Line 16), why is $\tau(N_2O_5)^{-1}$ defined as the ration of $p(NO_3)$, instead of $p(N_2O_5)$, to the N_2O_5 mixing ratio?

The source for NO_3 is the reaction of NO_2 with O_3 (R1), and the source for N_2O_5 is the further reaction of NO_3 with NO_2. The latter reaction forms a reversible equilibrium.

$$NO_2 + O_3 \rightarrow NO_3 + O_2,\ k_1 \qquad (R1)$$

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M,\ K_{eq} \qquad (R2)$$

With the steady-state assumption for N_2O_5, the formation and destruction of N_2O_5 is equalized.

$$\frac{d[N_2O_5]}{dt} = k_1[NO_2][O_3] - [N_2O_5]\tau(N_2O_5)^{-1} = 0$$

$$\tau(N_2O_5)^{-1} = \frac{k1[NO_2][\,O_3]}{N_2O_5} = \frac{p(NO_3)}{N_2O_5}$$

where $\tau(N_2O_5)$ denotes the lifetime of N_2O_5, with respect to any sink mechanism, including loss processes for NO_3 and N_2O_5 (Platt et al., 1984;Brown et al., 2003;Brown et al., 2006).

The only source of N_2O_5 is R1, that's why $\tau(N_2O_5)^{-1}$ defined as the ration of $p(NO_3)$ rather than $p(N_2O_5)$, to the N_2O_5 mixing ratio.

9. (Page 13 Line 13-14), If this is true, why didn't we see high $ClNO_2$?

The lowest nighttime average of N_2O_5 was observed during P3. Although the $ClNO_2$ concentration was not such high in this study compared with previous studies, owing to relatively low values of $\gamma_{N2O5} \times ø$ (0.006-0.009 vs. 0.008-0.035 in reference) (Mielke et al., 2013;Wang et al., 2018), the higher $ClNO_2$ during P3 than P4 with the reversed N_2O_5 concentrations supports that fast heterogeneous hydrolysis of N_2O_5 under high RH (~ 60.5%) conditions during P3 could be a reason. Another possible explanation was the lowest precursors during P3, e.g., NO_2 and O_3, consistent with the lowest $p(NO_3)$ during P3 which indicates low production potential for N_2O_5 in terms of radical production rates. We revised the sentence:

"The lowest nighttime average of N_2O_5 (~ 38 pptv) was observed during P3 although the NO_2 showed much higher concentration than those during P2 and P4, indicating the joint influences of precursors (NO_2 and O_3). Fast heterogeneous hydrolysis of N_2O_5 under high RH (~ 60.5%) conditions during P3 could be another reason, which was supported by the higher $ClNO_2$ during P3 than P4. "

10. (Figure 2), if the steady state assumption was met, are we able to derive conc. Of NO_3 at least for two hours per day?

Yes, the NO_3 concentration can be calculated according to the NO_2 and N_2O_5 concentrations when the steady state assumption between N_2O_5 and NO_3 was met.

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M,\ \ K_{eq}$$

$$[NO_3(cal)]=\frac{[N_2O_5]}{K_{eq}[NO_2]}$$

Where K_{eq} is the equilibrium rate constant.

The time series of NO_3 was generally similar to N_2O_5. In Sec. 3.2, the NO_3 reactivity was calculated from the inferred NO_3. Note that only the periods two hours later after sunset was selected for calculation, rather than only two hours per day.

11. (Page 15 Line 7), how was Cl_2 measured? Was Cl_2 calibrated?

Cl_2 was detected as $I{\bullet}Cl_2^-$ at *m/z* 197, *m/z* 199 and *m/z* 201 by CIMS. Cl_2 was not calibrated yet, and only the raw signal of Cl_2 was used for correlation calculation with $ClNO_2$. The well done mass calibration and high resolution peak fitting allow the accurate measurement of Cl_2 raw signals despite the absence of Cl_2 calibration.

12. (Figure 4), I would like to see Figure S6 instead of Figure 4 here. The data points are quite scattered and hence the attempt to use a single linear regression for all the data points just does not make sense.

Good suggestions. Although the data points seem to be scattered, the positive linear trend is quite obvious. So, the Figure 4 is interpretable and reasonable. The single linear regression indeed failed to characterize the relationship between N_2O_5 and $ClNO_2$, and that's why we divide the nighttime into two periods i.e., before midnight and after midnight, to further explain the correlation differences in different air masses (Figure S6). Besides, considering that the time-dependent relationship between N_2O_5 and $ClNO_2$ is more visualized in Figure 4 than Figure S6, the Figure 4 is applied in Sec. 3.3 to illustrate the conclusions.

13. Check the references thoroughly. For example, Brown et al. 2003a in the main text whereas Brown, S.S., … 2013a in the reference list.

Thanks for the review's carefulness. We have checked the references in both the main text and reference list one by one.

14. (Table 1), add the range or standard deviation in addition to the average values.

Good suggestions. We add the standard deviation in Table 1 to represent more variability of the data set.

Table 1. Summary of average (±1σ) meteorological parameters (RH, *T*, WS), CIMS species (N_2O_5, $ClNO_2$, the calculated NO_3, nitrate radical production rate $p(NO_3)$, N_2O_5 reactivity ($\tau(N_2O_5)^{-1}$) and NO_3 reactivity ($\tau(NO_3)^{-1}$), trace gases (O_3, NO_2, NO), and NR-PM_1 species (NO_3^-, Cl^-) for the entire study and four nighttime periods (i.e., P1, P2, P3 and P4).

	Entire	**P1**	**P2**	**P3**	**P4**
Meteorological parameters					
RH (%)	36.8±15.9	36.3±5.5	41.3±2.5	60.5±6.5	28.0±7.0
T (^{o} C)	26.7±4.9	24.5±1.1	23.2±0.7	23.2±1.4	29.4±2.4
WS (m s^{-1})	2.9±1.4	1.9±0.9	2.3±0.7	1.9±0.6	3.7±1.7
CIMS species					
N_2O_5 (pptv)	79±157	176±137	516±206	38±29	88±68
$ClNO_2$ (pptv)	174±262	427±223	748±221	228±104	57±39
NO_3(cal) (pptv)	9±16	7±7	48±26	2±2	18±15
$P(NO_3)$ (ppbv h^{-1})	3.2±2.3	3.6±4.2	2.8±0.5	1.7±1.2	2.6±1.4
$\tau(N_2O_5)^{-1}$ (s^{-1})	0.011±0.017	0.014±0.028	0.0016±0.0008	0.014±0.0063	0.016±0.011
$\tau(NO_3)^{-1}$ (s^{-1})	0.34±0.87	0.62±1.66	0.021±0.017	0.42±0.21	0.29±0.30
Gaseous species					
O_3 (ppbv)	51.1±35.4	23.4±23.2	55.6±5.3	17.8±15.3	40.3±28.0
NO_2 (ppbv)	28.1±17.1	56.2±22.4	16.9±3.9	38.2±9.9	28.7±16.0
NO (ppbv)	8.7±16.9	15.6±14.6	0.5±0.7	2.3±3.5	7.1±13.3
NR-PM_1 species					
NO_3^-(μg m^{-3})	2.7±2.4	2.3±1.5	4.3±0.7	4.3±1.6	0.6±0.2
Cl^- (μg m^{-3})	0.10±0.16	0.13±0.14	0.09±0.02	0.08±0.09	0.04±0.07

15. (Table 2 and the corresponding main text), there are limited number of data points so that statistically we can’t draw any conclusion for sure, e.g., the effects of RH (page 18 Line 16-17).

Thank for the suggestions. There are only three episodes selected for the calculation of γ_{N2O5} and ø, which seem to confine the applicability of conclusions. For example, γ_{N2O5} appeared to increase from 0.019 to 0.090 with the RH rising from 21.1% to 63.6% from case2 to case3. The γ_{N2O5} values were comparable between case1 and case3 at low RH levels (< 40%) although RH differed by a factor of 2. The conclusion was drawn based on the results in this study and further supported by previous findings. We didn't generalize the findings to universal conclusions. Long-term measurements in future for better characterization are needed.

Minor issues:

16. (Page 2 Line 2), "on the following day"?

Thank the reviewer for pointing this out. We revised this sentence and now it reads:

"…impact on …photochemistry on the following day…"

17. (Page 4 Line 14-17), do we really want to name this methodology as I-CIMS? Personally I prefer iodine adduct CIMS. Also, the authors are suggested to put more effective numbers with m/z values since it is ToF-CIMS after all (Page 7 Line 10-15). Finally, do we really know where the electron/charge is attached? (Page 7 Line 10-15)

Thank the review's suggestions. The CIMS can use protonated water clusters, acetate, nitrate and iodide as regent ions, of which we called the CIMS using iodide as I-CIMS in this referenced methodology. I think it is interpretable.

Yes, we presented the high-resolution data set for analysis rather than the unit mass resolution since it is ToF-CIMS. The *m/z* 208 and 210 for $I{\bullet}ClNO_2^-$, and *m/z* 235 for $I{\bullet}N_2O_5^-$ are just nominated *m/z* values for these species. The effective peak fitting at *m/z* 208, 210, and 235 are shown in Fig. S1 in the supplement.

The molecules were detected as adduction products with iodide. Although we do not know the charge distribution and chemical structure, it does not have influences on the detection and quantification.

18. (Page 6 Line 13), drawn "into" the sampling room?

We have revised the sentence following the reviewer's suggestion and changed "drawn inside" to "drawn into".

19. (Page 7 Line 3), so it is CH_3I in N_2?

Yes, for the UoM-CIMS it is CH_3I (20 sccm) and N_2 (4 slm) gas mixtures produced from the custom-made manifold passing over the Tofwerk x-ray ionization source.

20. (Page 12 Line 4), do we want to add "nighttime formation"?

Thanks for the reviewer's suggestions. Yes, processes at daytime hinder the assumption that $ClNO_2$ and NO_3^- are produced only from the heterogeneous N_2O_5 uptake, including the photolysis of $ClNO_2$ and other NO_3^- formation pathways. We add this constraint in the revised manuscript to avoid the confusions. Now it reads:

"Only periods with concurrent nighttime formation of $ClNO_2$ and NO_3^- meet the requirements…"

21. (Page 12 Line 21), are those reported numbers averages of 1-min average, or 5-min average, or 30-min average?

Thanks for pointing this out. The average N_2O_5 and $ClNO_2$ mixing ratios were reported in 5-min time resolution in this manuscript if no additional explanations. We still revise this sentence and it reads:

"…with the 5-min average ($\pm 1\sigma$) mixing ratios being…"

22. (Page 13, Line 21-), units for quite many numbers are missing.

Thanks for the reviewer's carefulness. We add the units in the revised manuscript. Now it reads:

"The average nitrate radical production rate $p(NO_3^-)$ was 2.8 and 3.6 ppbv h^{-1} during P1 and P2, respectively, which are both higher than those during P3 and P4 (1.7-2.6 ppbv h^{-1})"

23. (Page 14 Line 16-18), a good correlation between NO and black carbon does not necessarily mean NO is the most scavenger for N_2O_5.

Good point. The good correlation between NO and black carbon is presented to illustrate the strong local emission of NO in Beijing. The increasing NO before sunrise concurrent with the decreasing N_2O_5 implies the significant indirect N_2O_5 loss via titration by NO, however it is not sufficient supporting that NO is the most important scavenger for N_2O_5. We revised the sentence by taking away "most" in the manuscript.

24. (Page 19 Line 2), also include indirect N_2O_5 loss via titration by NO.

Thanks for the reviewer's suggestions. Yes, the indirect N_2O_5 loss pathways also include NO_3 titration by NO except for VOCs. Indeed, the reaction of NO_3 with NO is much faster than those with VOCs, particularly the high NO_x levels in this study. Except for VOCs, we include indirect N_2O_5 loss via titration by NO.

25. (Figure 3c & 3d), repeat the figure caption "the data were binned according…" in the main text to help the readers understand how these two plots are derived.

We thank the reviewer for this suggestion. Although the box plot is a standard stuff, we still add the figure caption in the main text to help understanding the two plots.

"Figure 3c shows the N_2O_5 lifetime as a function of surface area density (S_a) with the data being binned according to the 50 μm^2 cm^{-3} S_a increment"

Response to Reviewer #2

Comments:

The authors report four nights of N_2O_5 and $ClNO_2$ observations in summer at an urban site of Beijing, China. The data were analyzed to show the concentration levels and N_2O_5 reactivity, and the N_2O_5 uptake coefficient and $ClNO_2$ product yield were estimated from the field data. This manuscript provides a new piece of measurement data as well as some insights into the nocturnal N_2O_5 chemistry in the polluted atmosphere of North China. However, the current paper lacks some important details about the measurement and calculation methods, and some interpretation of the measurement results needs to be refined. Overall, this manuscript can be considered for publication after the following specific comments being addressed.

Major Comments:

Further details are required to clarify the quality assurance and quality control of the N_2O_5 and $ClNO_2$ measurements.

-The two CIMS systems were not in-situ calibrated during the measurement campaign. The UoM-CIMS was calibrated by the synthesized N_2O_5 and $ClNO_2$ after the campaign, and the IAP-CIMS was not calibrated and only inter-compared with the BBCEAS instrument. The sensitivity of the CIMS instruments may vary with the different operation conditions. Could the authors comment on the uncertainty of the post-campaign calibration on the present N_2O_5 and $ClNO_2$ observations.

The N_2O_5 and $ClNO_2$ measured by UoM-CIMS were calibrated post campaign, while formic acid calibration was running regularly twice daily throughout the campaign. This is relying on the assumption that the ratio of sensitivity between formic acid and $ClNO_2$ remains constant throughout. The twice daily formic acid calibration ensures the stable sensitivity over time. Therefore, the post-campaign of UoM-CIMS N_2O_5 and $ClNO_2$ calibration could not introduce significant errors compared to the regularly calibration during the campaign. On the other hand, the operation conditions could be carefully controlled during post calibrations to make sure that they are under similar conditions with ambient measurements (under the same IMR and SSQ pressure, with the same TPS voltages settings, under similar $ClNO_2$ concentrations comparing to the ambient air, and the same reagent ions levels …). Our estimated $ClNO_2$ for the IAP-CIMS agrees well with that of UoM-CIMS (Slope = 0.903), which suggest the uncertainty of $ClNO_2$ for the IAP-CIMS is within 10%.

We use the sum of N_2O_5 and NO_3 measured by the BBCEAS for IAP-CIMS N_2O_5 calibration in the study. The mixing ratio of N_2O_5 is much higher than NO_3 by a factor of ~11 by applying the equilibrium between N_2O_5 and NO_3, which leads to the uncertainty of ~ 10% without subtraction of NO_3 concentration. The uncertainty of N_2O_5 of IAP-CIMS is estimated to be ~ 17% associated with the error of N_2O_5+NO_3 measurement (~ 14%). In addition, the transmission efficiency of N_2O_5 for IAP-CIMS also introduce additional uncertainty of N_2O_5. Given the regression slope of 1.42 between the IAP-CIMS and UoM-CIMS, the uncertainty of N_2O_5 could be up to ~ 42%. Considering the uncertainty between different instruments, the uncertainty of N_2O_5 is conservatively estimated to be ~ 17%. Overall, the three independent measurements correlated well with each other, which means that the uncertainty of sensitivities of iodide CIMS systems caused by post-calibration was not a concern for quantifications.

-The inlet chemistry, including the potential loss of N_2O_5 and formation of $ClNO_2$ in the sampling inlet, is an important issue in the field measurements of N_2O_5 and $ClNO_2$, especially for the highly polluted areas such as the study site in the present study. Have the authors checked the inlet issue during the present measurements.

We didn't check the potential loss of N_2O_5 and formation of $ClNO_2$ during this campaign. In fact, we removed the Teflon filter in front of the sampling line after 10 June, which had some influence of the sampled concentrations. After that, we replaced sampling lines with brand new ones, and the inlet issue should be minor considering the very fast residence time of less than 0.4 s within the sampling line, which could be further verified by the inter-comparisons results. We agree with the reviewer that the inlet issue should be evaluated in the future studies.

-The background of the CIMS instrument was determined by passing dry N_2 to the system in this study. The authors should provide a figure to show the background determination results, maybe in the supplementary materials. In addition, the authors may also need consider to check the instrument zero by adding excess NO to the ambient air, because the dry N_2 may be different from the real ambient conditions.

Thanks for the reviewer's suggestions. We provide the mass spectra and time series of raw signals of N_2O_5 and $ClNO_2$ during the background measurement in the supplement. In addition, we did not check the instrument zero during this measurement, which we should have done and will do in our following studies to make sure better data quality.

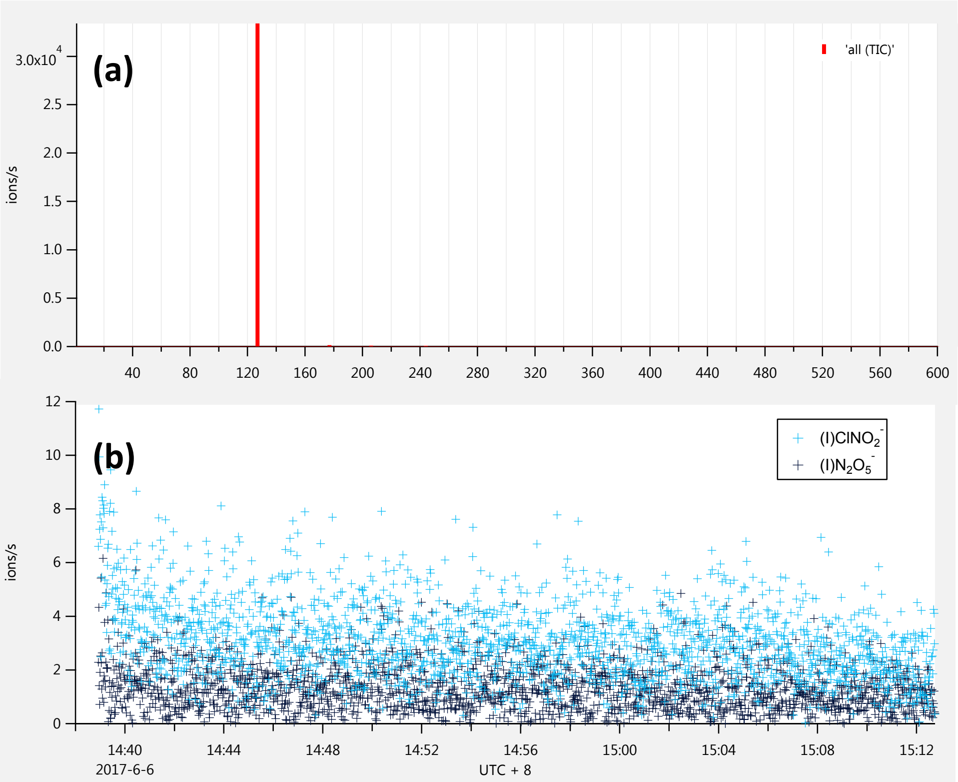

Figure R2. Mass spectra (unit mass resolution) and time series of raw signals of N_2O_5 and $ClNO_2$ during the background measurement.

-It has been proposed that the ambient RH may affect the sensitivity of the CIMS to the target compounds. This may affect the analysis results of dependence of N_2O_5 reactivity on RH. The authors are suggested to further check the potential influence of ambient RH on their CIMS measurements.

The ionization efficiency and thus sensitivity of the CIMS is dependent on the RH of the sample. The UoM-CIMS during the measurement period is independent of ambient RH changes through the tuning of the ion optics and introduction of H_2O into the ionization mix so that the threshold required for sensitivity independent of changes in water vapor (Bannan et al., 2015). The well correlations of N_2O_5

and $ClNO_2$ between the IAP-CIMS and UoM-CIMS ensure the data quality of the measurement.

Also, we plot the relationship between N_2O_5 and $ClNO_2$ and the data are color-coded by the ambient RH. Although the different slopes along with the hours after sunset can be explained by the air masses from different regions in the main text, the RH-dependent sensitively might also be a reason.

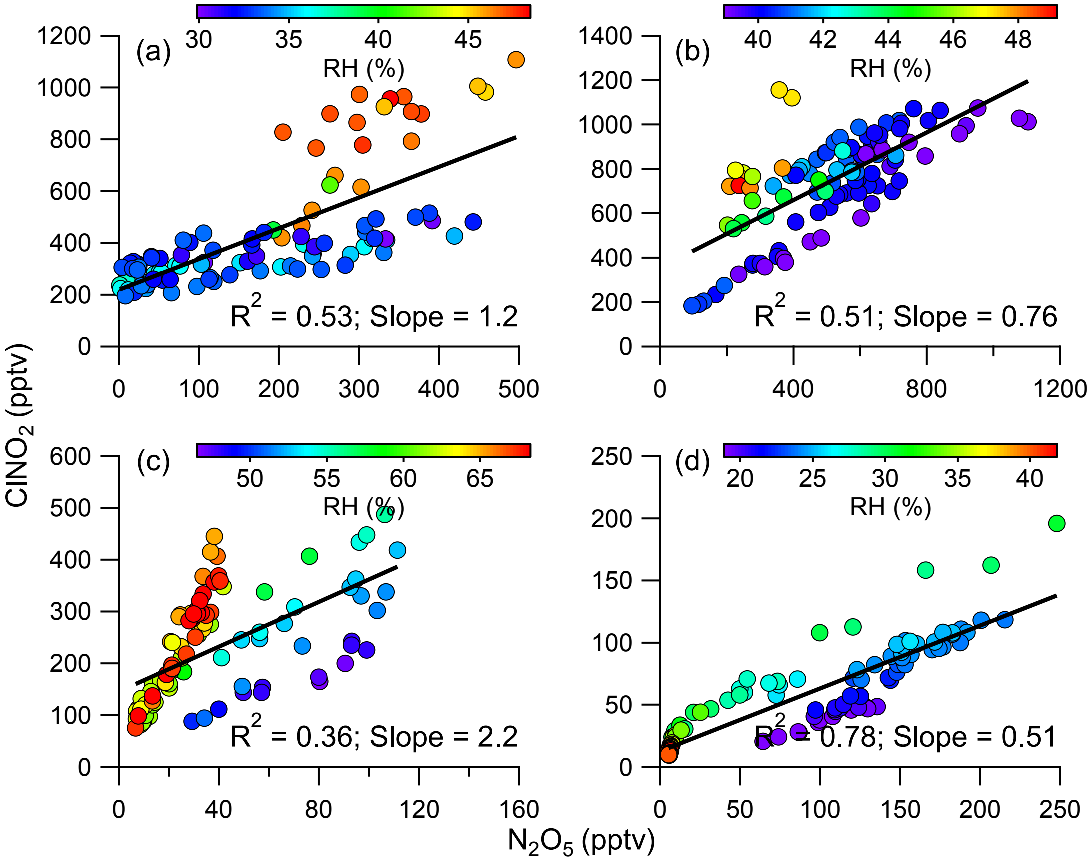

Figure R3. Correlations between $ClNO_2$ and N_2O_5 for four different nights, i.e., P1, P2, P3 and P4. The data are color-coded by the ambient relative humidity (RH). Also shown are the correlation coefficients and slopes.

-In view of the above issues, the authors should provide an overall estimation of their N_2O_5 and $ClNO_2$ measurements, at least including the detection limits and uncertainties.

Good suggestions. We provide the uncertainties and detection limits for N_2O_5 and $ClNO_2$ measurements above. Briefly, the uncertainty is 17% and 58%, detection limit is 1.7 pptv for N_2O_5 and 0.7 pptv for $ClNO_2$.

On the calculation and analysis of the N_2O_5 reactivity:

-It seems that there were no VOC measurements in this study. It is not clear how the authors calculated k(NO_3) and then N_2O_5 reactivity without the VOC data? If the VOC measurements were available, the authors should provide the concentrations and chemical compositions of major VOC species.

Thank the reviewer's comments. We do not have the VOCs measurements in this study. The N_2O_5 reactivity is defined as the inverse N_2O_5 steady state lifetime, which is the ratio of $p(NO_3)$ to the N_2O_5 mixing ratio. So, we don't need the VOCs data to calculate k(NO_3) and thus the N_2O_5 reactivity, but the data of O_3, NO_2 and N_2O_5.

$$\tau(\mathrm{N_2O_5})^{-1} = \frac{p(NO_3)}{[\mathrm{N_2O_5}]} \approx \frac{k_{\mathrm{NO_3}}}{K_{eq}[\mathrm{NO_2}]} + k_{\mathrm{N_2O_5}}$$

-NO plays a very important role in the nocturnal N_2O_5 chemistry. Only a considerable level of NO (e.g., >1 ppbv) can significantly suppress the NO_3 and then N_2O_5, as the reaction of NO_3 with NO is very fast. This is why the concentrations of N_2O_5 and $ClNO_2$ are usually low at surface sites in urban areas such as the study site in the present study. In comparison, the oxidation reactions of NO_3 and VOCs are relatively slow, and NO_3 can only oxidize a small group of specific VOCs, mainly biogenic VOCs and some oxygenated VOCs. The authors argued that the reactions of NO_3 with VOCs are important for the N_2O_5 reactivity. It is better if the authors could separately evaluate the NO_3 reactivity towards NO and VOCs.

It is really a good point to evaluate the reactions of NO_3 with NO and VOCs separately. However, lacking the VOCs data and direct NO_3 measurement limited us from further discussions about this topic so far. As the reviewer mentioned, the reaction of NO_3 with NO is much faster than that with VOCs. One previous study in urban Jinan reported that the contribution of N_2O_5 loss by VOCs could only be larger than that by NO when NO is negligible, e.g., 16.3% vs. 7.1% (Wang et al., 2017a). The N_2O_5 reactivity due to the indirect NO_3 loss pathway is mainly attributed to the reaction of NO_3 with NO rather than VOCs in the NO_x-rich air mass (for example, urban Beijing). We revise the relevant sentences on main cause of N_2O_5 reactivity in the manuscript.

-The authors assumed a steady-state for NO_3 and N_2O_5 and estimated the lifetimes for these compounds (see Table 1). It is very strange that the lifetime of N_2O_5 was much shorter than that of NO_3 radical. In general, the lifetime of NO_3 radical is quite short, but N_2O_5 may have relatively longer lifetimes during the nighttime.

Yes, we agree with the reviewer that the lifetime of NO_3 radical is generally shorter than that of N_2O_5, as Fig. 3 depicts in the manuscript. In fact, the lifetimes of NO_3 radical and N_2O_5 in Table 1 were reversed. We revised the values and also added the standard deviations in Table 1.

-Page 12, Lines 1-3: the Equation (6) was only valid if the observed nitrate increase was thoroughly contributed by the in-situ chemical production and the heterogeneous uptake of N_2O_5 contributed to 100% of the nighttime nitrate formation. The authors need consider the impacts of regional transport and other nitrate formation pathways on this calculation. As mentioned by the authors, previous studies suggested that the heterogeneous uptake of N_2O_5 only accounted for about 50-100% of nighttime nitrate formation. The authors at least should mention the assumption and limitation of this calculation method.

Thanks for the reviewer's suggestions. Previous studies suggested that the heterogeneous uptake of N_2O_5 accounted for about 50-100% of nighttime nitrate formation, which is the average results. We selected the periods when the heterogeneous uptake of N_2O_5 contributed to 100% of the nighttime nitrate formation for calculation. Also, we expanded the assumption and limitation of this calculation method in this paragraph. Now it reads:

"The production rate of particulate nitrate ($p\mathrm{NO_3^-}$) was obtained from HR-AMS measurements assuming that the measured $p\mathrm{NO_3^-}$ was totally from production of nitrate by reaction R4 (Phillips et al., 2016). Note that the formation of particulate nitrate from regional transport or via the net uptake of HNO_3 to aerosol is not taken into consideration."

Page 13, Lines 20-22: this argument is not really true. The N_2O_5 production potential in P1should be low because of its very high NO_x levels. It is also a little bit strange that the concentrations of N_2O_5 and $ClNO_2$ are moderately high given such high levels of NO_x (>15 ppbv) in P1, but it is a very interesting result. What is the possible reason for this?

The p(NO_3) during P1 was the highest among the four nighttime which might indicate the high production potential of N_2O_5. However, the N_2O_5 concentrations during P1 were lower than those during P2 due to the titration of NO. The much higher N_2O_5 concentration during P1 than those during P3 and P4 despite the high NO levels during P1 suggests that higher O_3 and NO_2 might compensate for the loss by NO.

Page 13 Line 25 to Page 14 Line 2: this interpretation is not correct. The difference in the observed N_2O_5 and $ClNO_2$ concentrations between P2 and P4 should be due to the difference in the NO levels, i.e., 0.5 versus 7.1 ppbv. Given your estimated short lifetimes of NO_3 and N_2O_5, meteorological conditions and transport should not be the major factors here.

Thanks for the reviewer's comments. Yes, the meteorological conditions and regional transport should not play a significant role in N_2O_5 and $ClNO_2$ concentrations between P2 and P4 in such a short time. We revised the sentence in the manuscript and now it reads:

"We also note that the *p*(NO_3) was comparable between P4 and P2 (2.6 pptv vs. 2.8 pptv), yet the N_2O_5 and $ClNO_2$ mixing ratios during P4 were much lower, likely due to the difference in NO levels, i.e., 0.5 vs. 7.1 ppbv. The favorable dispersing meteorological conditions with higher wind speed and lower relative humidity in P4 than those in P2 might also be an explanation (Table 1)."

Page 15, Lines 6-11: on the low particulate chloride and its weak correlation with $ClNO_2$, another possible reason is the size distribution of chloride aerosol. Only the chloride in PM_1 was measured in this study, and it may largely underestimate for the total particulate chloride. Could the authors check the size distribution of chloride from the previous measurements available in urban Beijing and discuss its impacts on the observed results in this study.

Good suggestions. We plot the average size distribution of particulate chloride during this summer campaign (from HR-ToF-AMS measurements) covering the CIMS measurement periods. As Fig. R4 depicts, the chloride peaked at accumulation-mode (~ 500 nm), while the mass-dependent size distribution above 1000 nm accounts for a small portion. Besides, the undetected fraction of chloride (including refractory and particles larger than 1000 nm) by AMS (e.g., NaCl) is mainly from dust or sea salt particles, which had minor influences on the particulate chloride concentrations in urban Beijing.

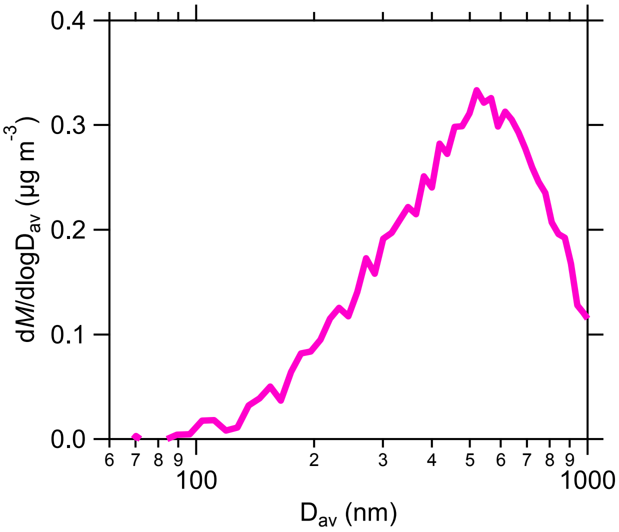

Figure R4. Average size distribution of the particulate chloride during the summer campaign from 17 May to 29 June, 2017.

Page 15, Lines 14-16 and 20-22: it was not clear how the N_2O_5 and NO_3 reactivities were calculated without the VOC data. It would be better if the authors could also calculate the reactivity from heterogeneous N_2O_5 uptake, NO_3+NO and NO_3+VOCs, and compare them among each other.

The N_2O_5 reactivity is defined as the inverse N_2O_5 steady state lifetime, which is the ratio of $p(NO_3)$ to the N_2O_5 mixing ratio. Similarly, the NO_3 reactivity is defined as the ratio of $p(NO_3)$ to the NO_3 mixing ratio. Due to the lack of VOCs data, the reactivity from heterogeneous N_2O_5 uptake, NO_3 with NO and NO_3 with VOCs could not be calculated.

$$\tau(N_2O_5)^{-1} = \frac{p(NO_3)}{[N_2O_5]} \approx \frac{k_{NO_3}}{K_{eq}[NO_2]} + k_{N_2O_5}$$

$$\tau(NO_3)^{-1} = \frac{p(NO_3)}{[NO_3]}$$

Page 15, Lines 22-24: I guess that the higher N_2O_5 reactivity in P4 than P2 should be due to the higher NO level. The authors are encouraged to examine the detailed budget of N_2O_5 reactivity for both cases and find the exact reason for this.

Thanks for the reviewer's suggestions. The higher N_2O_5 reactivity in P4 than P2 was due to the higher NO level. We revised the reason in this sentence:

"Note that P2 and P4 showed comparable $p(NO_3)$ (2.8 vs. 2.6 ppbv h^{-1}) (Table 1), yet the N_2O_5

reactivity during P4 (1.58×10^{-2} s^{-1}) was significantly higher than that during P2 (0.16×10^{-2} s^{-1}) likely due to the higher NO level, and the enhanced N_2O_5 heterogeneous loss might also be explanation."

Page 16, Lines 1-2: it is interesting that the N_2O_5 reactivity presents a non-linear dependence on aerosol surface area and RH. What are the possible reasons for this?

The N_2O_5 lifetime showed an increase as a function of RH at RH< 40%. The other factors, for example, aerosol loading and composition could also have an influence on the N_2O_5 uptake (Morgan et al., 2015), thus the N_2O_5 lifetime. The exact reason is not clear yet, which should be explored in future studies.

Page 16, Lines 6-14: it is interesting (and also strange) for the sharp decrease in the N_2O_5 reactivity with ambient RH from 40% to 50%. As mentioned above, the authors are suggested to examine the dependence of the CIMS sensitivity on the ambient RH.

Thanks for the reviewer's suggestions. The N_2O_5 lifetime $\tau(N_2O_5)$ decrease at high RH levels (RH >40%) might be caused by the increased N_2O_5 uptake rates due to the higher surface area density (S_a). In addition, the increasing aerosol liquid water content at high RH might be another reason. Also, we examine the dependence of the CIMS sensitivity on the ambient RH (see our response above).

Page 17, Lines 1-4: the authors are suggested to elaborate more about the air mass transport and its impacts on the observed N_2O_5 and $ClNO_2$. What is the difference in the air mass origins among the four cases? Which air masses contained higher N_2O_5 and $ClNO_2$?

We thank the reviewer. The 48 h back trajectories arriving at the sampling site between 19:00-05:00 were calculated every hour using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT, NOAA) model. Air masses from the southeast (e.g. P1) usually contain more gaseous pollutants, which resulted in higher concentrations of both N_2O_5 and $ClNO_2$, while air masses from the northwest were relatively clean with low levels of pollutants.

During P1 and P4, the air mass was from the similar regions before and after midnight, i.e., southeast during P1 and northeast during P4. During P2, the air mass was originated from the southeast before midnight and northwest/west after midnight. During P3, the back trajectories were different during the two periods, i.e., before and after midnight. The differences in regression coefficient among the four nights can be explained by different air masses originating from different regions.

Page 18 Line 24 to Page 19 Line 4: as mentioned above, the reactions of VOCs and NO_3 are relatively slow, and NO_3 can only react with some specific VOC compounds. In comparison, the titration of NO_3 by NO is rather fast. Given the high NO levels observed in urban Beijing in this study, the NO_3 loss should be dominated by the NO titration.

Yes, the NO_3 loss should be dominated by the NO titration, particularly with much high NO concentration in this study. But for the three cases selected for $\gamma_{N_2O_5}$and ø calculation, the NO concentrations are negligible and the indirect losses towards NO and VOCs might be different. We revise the sentences as following:

"While the uncertainties in different analysis methods, e.g., the product formation rates or steady-state assumption are one of the reasons, the high NO concentration could be the important reason for the dominant N_2O_5 loss pathway. The high VOCs emissions, particularly biogenic emissions in summer than other seasons might be another reason for the differences in dominant N_2O_5 loss pathway. Indeed, the indirect N_2O_5 loss via NO_3+VOCs was also found to dominate the total loss of N_2O_5 (67%) in summer in suburban Beijing (Wang et al., 2018)."

Minor Comments:

Page2, Line6, "79.2 and174.3pptv": pay attention to the use of significant digits. What is the detection limit of the N_2O_5 and $ClNO_2$ measurements in the present study? Could it be up to 0.1 pptv? Please check and revise the usage of significant digits throughout the manuscript.

Thanks much for the suggestions. The mixing ratio of N_2O_5 and $ClNO_2$ can be up to the level of 0.1 pptv due to the limit of detection (LOD). We carefully check and revise the usage of significant digits throughout the manuscript.

Page 2, Lines 6-8: does the N_2O_5 reactivity here include its indirect loss by NO_3? If so, the high N_2O_5 reactivity may not suggest the large nocturnal nitrate formation potential. Besides the heterogeneous reactions of N_2O_5, the nitrate formation also depends on the NO_3 reactivity and $ClNO_2$ product yield. After all, the authors also pointed out that the N_2O_5 loss was mainly attributed to the indirect loss by NO_3 (Page 2 and Lines 11-13).

Yes. The N_2O_5 reactivity here includes its indirect loss by NO_3 and the heterogeneous uptake. The following analysis indicated that the N_2O_5 loss was mainly attributed to the indirect loss by NO_3 rather than the heterogeneous uptake. Also, the $ClNO_2$ yields derived in this study were not such significant and the NO_3 reactions with VOCs and NO were fast. These results together suggest that the nocturnal nitrate formation could be small. We revised this sentence in the manuscript. Now it reads:

"High reactivity of N_2O_5, with $\tau(N_2O_5)^{-1}$ ranging from 0.20×10^{-2} to 1.46×10^{-2} s^{-1}, suggests active nocturnal chemistry."

Page 3, Line 2 "an efficient sink for the nocturnal removal of nitrogen oxides": "sink" is redundant with "removal", please rephrase this sentence.

Thanks for the reviewer's suggestions. We rephrased the sentence in the revised manuscript as follows:

"Dinitrogen pentoxide (N_2O_5) is an effective nocturnal sink for nitrogen oxides…"

Page 3, Lines 2-4: I suggest to separate this long sentence into two short ones, with one defining N_2O_5 and the other describing its thermal equilibrium with NO_3.

We agree with the reviewer to separate this into two short ones. Now it reads:

"Dinitrogen pentoxide (N_2O_5) is an efficient nocturnal sink for nitrogen oxides (NO_x) (Dentener and Crutzen, 1993; Brown et al., 2006). N_2O_5 exists in a rapid temperature-dependent thermal equilibrium with nitrate radical (NO_3) – one of the most important oxidants at night-time (Wayne et al., 1991)."

Page 3, Lines 4-5: I recall that the reactions of NO_3 with VOCs are not very fast. The N_2O_5 and NO_3 removal is mainly attributed to the rapid titration of NO_3 by NO in the high NO_x environments.

Thanks for the reviewer's ideas. The reactions of NO_3 with VOCs are slower than that with NO. We just listed the possible loss pathway of N_2O_5 and NO_3 in this sentence rather than compared the loss frequency.

Page 3, Line 9: it should be particulate NO_3^-, other than HNO_3.

The gas-particle partitioning of HNO_3 form particulate NO_3^-. To avoid the ambiguity, we change “HNO_3” to “particulate nitrate” in this the sentence.

Page 3, Line 11: delete “N_2O_5” as only $ClNO_2$ can be subject to photolysis to release NO_3 and chlorine atom.

Thanks for the reviewer carefulness. We delete “N_2O_5” in this sentence in the revised manuscript.

Page 3, Line 16: $ClNO_2$ product yield...

Thank the reviewer. We change the “$ClNO_2$ yield” in this sentence into “$ClNO_2$ product yield”.

Page 4, Lines 5-7: on the inconsistency between field-derived N_2O_5 uptake coefficient and the lab-derived parameterizations, the authors should acknowledge the work of Brown et al. 2006. Brown, S. S., et al.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-7-, 2006.

Thank the reviewer. We add the work of Brown et al. 2006 to the reference list.

Page 4, Lines 10-12: regarding this indirect measurement approach, what technique was used for the measurement of NO_3 radical?

The NO_3 radical was measured in one unheated channel. Thermal conversion of N_2O_5 to NO_3 in a second, heated channel provides simultaneous measurements of the sum of NO_3 and N_2O_5. The measurement of N_2O_5 is obtained via the difference between the two channels. Also, the collocated measurement of NO_2 and temperature can also be used for NO_3-N_2O_5 equilibrium, if without the unheated channel.

Page 4, Lines 13-15 and 17-19: please also refer to the following measurement works of N_2O_5 and $ClNO_2$ by CIMS in China.

Tham Y. J., et al.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, Chinese Sci. Bull., 59, 356-359, 2014.

Wang T., et al.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res., 121, 24572475, 2016.

Tham Y. J., et al.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

Thanks for the reviewer's suggestions. We have referred to the measurement works of N_2O_5 and $ClNO_2$ by CIMS in China in the following lines in this paragraph. But, we can also add these measurement works in the revised manuscript.

Page 4, Lines 8-19: the description of the commonly used measurement techniques for N_2O_5 and $ClNO_2$ is incomplete here. The authors need also briefly introduce the Cavity Ring-Down Spectroscopy (CRDS) and the CIMS with an unheated inlet configuration (235 m/z).

Thank the reviewer. We expanded the descriptions of the commonly used measurement techniques for N_2O_5 and $ClNO_2$. Now it reads:

"For example, N_2O_5 can be derived from the thermal equilibrium with NO_2 and NO_3 that are simultaneously measured by differential optical absorption spectroscopy (DOAS) (Platt and Stutz, 2008;Stutz et al., 2004). Another indirect measurement of N_2O_5 is subtracting ambient NO_3 from the total measured NO_3 after converting N_2O_5 to NO_3 in a heated inlet and then detected by Cavity Ring-Down Spectroscopy (CRDS), Cavity-Enhanced Absorption Spectroscopy (CEAS) or Laser-Induced Fluorescence (LIF) (O'Keefe and Deacon, 1988;Smith et al., 1995;Brown et al., 2001;Wood et al., 2003;Stutz et al., 2010). The simultaneous indirect measurements of N_2O_5 and NO_3 can be implemented using thermal dissociation – chemical ionization mass spectrometer (TD – CIMS) with high sensitivity and time resolution (Stutz et al., 2004), although the interference of m/z 62 (NO_3^-) from thermal decomposition of peroxy acetyl nitrate (PAN) and other related species need to be considered (Wang et al., 2014). Recently, the CIMS using iodide reagent ions (I-CIMS) with an unheated inlet configuration allowed the direct measurements of N_2O_5 (Kercher et al., 2009;Tham et al., 2014;Wang et al., 2016;Tham et al., 2016). "

Page 4, Line 22: change "several" to "some", as there have been about a dozen measurement studies of N_2O_5 and $ClNO_2$ in China.

We change "several" to "some" in this sentence for more rigorous wording.

Page5, 1-2: besides these measurement efforts, recently, some modeling studies have also evaluated the impacts of N_2O_5 and $ClNO_2$ chemistry on the ozone formation and regional air quality in China. The authors should consider to include these efforts to enrich the current understanding of the nocturnal nitrogen chemistry and its impacts.

Xue L. K., et al.: Development of a chlorine chemistry module for the Master Chemical Mechanism. Geosci. Model Develop. 8. 3151-3162, 2015.

Wang T., et al.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res., 121, 24572475, 2016.

Li Q. Y., et al.: Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China, Atmos. Chem. Phys., 16, 14875-14890, 2016.

Thank the reviewer for proving these modeling studies. We add the listed reference after this sentence to enrich the current understanding of the nocturnal nitrogen chemistry and its impacts. Now it reads:

"Besides these measurement efforts, recently, some modeling studies have also evaluated the impacts of N_2O_5 and $ClNO_2$ chemistry on the ozone formation and regional air quality in China (Xue et al., 2015;Wang et al., 2016;Li et al., 2016). Despite this…"

Page 5, Line 9: delete "However"

Yes, we delete "However" in the revised sentence.

Page 5, Lines 15-17: a recent modeling study has evaluated the impacts of heterogeneous $ClNO_2$ formation on the next-day ozone formation in Beijing.

Xue L. K., et al.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14, 13175- 13188, 2014.

Thank the reviewer. We add the listed reference and change the sentence in Lines 15-17. Now it reads:

"A recent modeling study has evaluated the impacts of heterogeneous $ClNO_2$ formation on the next-day ozone formation in Beijing (Xue et al., 2014). However, the role of N_2O_5 in nitrate formation and of N_2O_5 and $ClNO_2$ in night- and day-time chemistry in summer in urban Beijing during filed campaign are not characterized yet, except for one measurement…"

Page 6, Line 7: provide standard deviations for the average values of temperature and RH.

Thanks for the reviewer's suggestions. We provide the standard deviations for the average values of temperature and RH. Now it reads:

"The hourly average RH ranged from 12.9% to 82.8%, with an average value of 36.8±15.9%, and the hourly average temperature ranged from 17.9^{o}C to 38.7^{o}C, averaged at 26.7±4.9^{o}C."

Page 8, Lines 3-5: how did you estimate this uncertainty?

For the BBCEAS, a poly tetrafluoroethylene (PTFE) filter of pore size 1 μm was used to remove aerosol particles from the air stream. Because of aging effects of particles, the filter is typically change at several hours intervals. Besides, the high NO_x/NO_y ratio (~0.78) suggests that the plumes observed in the campaign were primarily from the local urban area rather than the aged air masses from regional transport. So, the less oxidized particles and regularly changed filter ensure the insignificant influence of particle aging.

Page 9, Line 20: was the slope of 1.42 derived from the least square regression method? Such slope indicates an average difference of 42% between the two CIMS instruments. Which one gave higher concentrations?

Yes, the slope of 1.42 was derived from the linear regression. The N_2O_5 of IAP-CIMS showed higher concentrations than that of UoM-CIMS.

Page 10, Lines19-20: $k(N_2O_5)$ is commonly used to refer to the heterogeneous reaction rate of N_2O_5, other than the uptake rate coefficient.

Yes, we revised this sentence as following:

"…where $k_{N_2O_5}$ is the heterogeneous reaction rate of N_2O_5, and …"

Page 13, Line 2: at Mt. Tai...

Thank the reviewer. Yes, we change the sentence in the revised manuscript by changing "in Mt. Tai…" to "at Mt. Tai…".

Page 13, Lines 6-14: please provide the observed concentrations levels of NO and NO_2, and also discuss the impact of NO_x on the observed variations of N_2O_5 and $ClNO_2$. As mentioned above, NO_x play a very important role in the variability of N_2O_5 and $ClNO_2$.

Thanks for the reviewer's suggestions. The average levels of NO and NO_2 during the four nights are shown in Table 1. We discuss the impact of NO_x on the observed variations of N_2O_5 and $ClNO_2$ in the revised manuscript. Now it reads:

"Besides, the maximal N_2O_5 occurred during P2 other than the rest nights was likely due to the insignificant titration of NO during P2, e.g., 0.5 vs. 2.3-15.6 ppbv. The lowest nighttime average of N_2O_5 (~ 38 pptv) was observed during P3 although the NO_2 showed much higher concentration than those during P2 and P4, indicating the joint influences of precursors (NO_2 and O_3). Fast heterogeneous hydrolysis of N_2O_5 under high RH (~ 60.5%) conditions during P3 could be another reason, which was supported by the higher $ClNO_2$ during P3 than P4."

Page 13, Line 10: residual boundary layer...

Thank the reviewer's carefulness. Yes, we change the sentence in the revised manuscript by changing "residential boundary layer…" to "residual boundary layer...".

Page 13, Lines 15-18: as introduced in the introduction, there have been many studies of N_2O_5 and $ClNO_2$ in both North China Plain (e.g., Mt. Tai, Beijing, Wangdu, Jinan) and Hong Kong. It would be better if the authors could compare the observed results in this study to these previous results. Is there any difference between the NCP region and Hong Kong in southern China?

Thanks for the reviewer's suggestions. $ClNO_2$ presented the highest value (1.4 ppbv, 5-minute average) on 13 June, yet it is lower than the maximum of 2.1 ppbv (1-minute average) observed at Wangdu (Tham et al., 2016), 2.9 ppbv (1-minute average) in suburban Beijing (Wang et al., 2018), and also the $ClNO_2$ peak of 2.1 ppbv (1-minute average) at Mt. Tai (Wang et al., 2017b). The ubiquitously high $ClNO_2$ in the NCP are consistent with those reported in Hong Kong, e.g., 4.7 ppbv (1-minute average maximum) (Wang et al., 2016) and 2.0 ppbv (1-minute average maximum) (Tham et al., 2014). There are insignificant differences between the NCP and Hong Kong in terms of the maximum $ClNO_2$ concentration, although the polluted air masses were originated from different sources. For example, the pollution in Hong Kong was transported from inland areas of the PRD, while it came from the power plant and industrial plumes of the NCP at Mt. Tai and outflows of urban Beijing in Wangdu.

Page 13, Lines 20-21: provide the units for 2.8 and 3.6.

We provide the units for the values in this sentence. Now it reads:

"The average nitrate radical production rate p(NO3) was 2.8 ppbv h^{-1} and 3.6 ppbv h^{-1} during P1 and P2, respectively…"

Page 14, Line 13: rephrase this sentence. Is there any relationship between the N_2O_5 formation and the decrease in $p(NO_3)$? $p(NO_3)$ is only dependent on the abundances of both O_3 and NO_2. If anything, the decrease in $p(NO_3)$ should weaken the N_2O_5 formation.

Thank the reviewer's suggestions. The variation of $p(NO_3)$ is only dependent on the abundances of both O_3 and NO_2 rather than the N_2O_5 formation. The $p(NO_3)$ can be regarded as the production potential for N_2O_5 in terms of radical production rates. So the decrease in $p(NO_3)$ weaken the N_2O_5 formation, and that's the reason we compare the average $p(NO_3)$ among the four nighttime when discussing the N_2O_5 concentrations. We revised this sentence:

"N_2O_5 was rapidly formed after sunset."

Page 15, Lines 3-4: the reference of Riedel et al. 2012 is not relevant here. It was conducted in US, not in Beijing.

We cited the reference of Riedel et al. 2012 to explain the possible chloride source contributing to the formation of $ClNO_2$ in this study, rather than explain the proven pathway observed in previous study in Beijing. But we still remove this reference in this sentence to avoid the misunderstanding.

Page 15, Line 6: high emissions from human activities...

Thanks for the carefulness. We revised the sentence in the revised manuscript as following:

"… gas-phase HCl due to the high emissions from human activities."

Page 15, Lines 13-14: it is not clear why only the two-hour data after sunset was used here. Please clarify.

The NO_3 concentration can be calculated according to NO_2 and N_2O_5 when the steady state assumption between N_2O_5 and NO_3 was met. Only the periods two hours later after sunset was selected for calculation to consider for the maximum steady state time, rather than only two hours per day.

Page 15, Lines 18-19: provide the numbers for the N_2O_5 loss in southern China and USA for easy comparison.

Yes, we add the numbers for the N_2O_5 loss in southern China and USA for easy comparison. Now it reads:

"In comparison, the N_2O_5 loss is much more rapid than that previously reported in southern China (1-5 h) (Brown et al., 2016) and the USA (a few hours) (Wagner et al., 2013)."

Table 1: provide the standard deviations and units for the aerosol species.

Thank the reviewer's suggestions. We provide the standard deviations for the average values in Table 1.

Figure 1: provide the time series of the aerosol surface area concentrations.

Thanks for the reviewer's suggestions. We add the time series of aerosol surface area concentrations in Figure 1 in the revised manuscript.

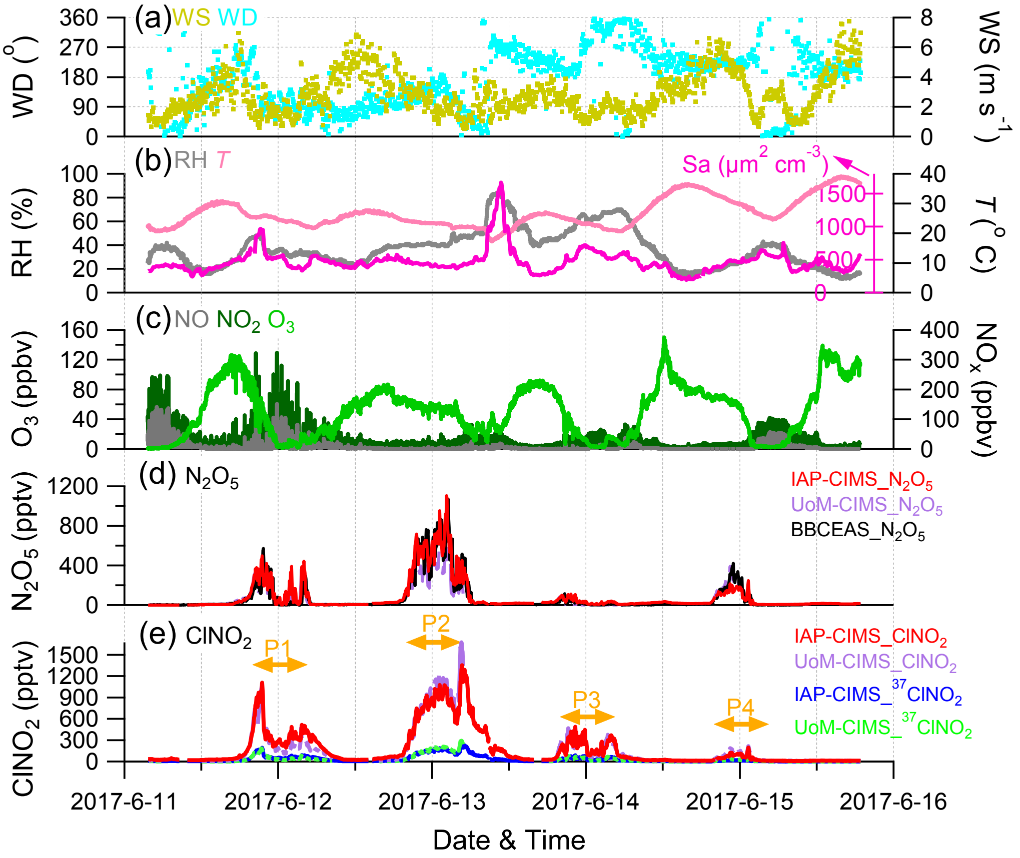

Figure 1. Time series of (a-b) meteorological parameters (RH, T, WS, WD) and surface area density (Sa), (c) trace gases (O_3, NO, NO_2), (d-e) IAP-CIMS species (N_2O_5, $ClNO_2$). The UoM-CIMS and BBCEAS measurements are also shown for inter-comparisons. The four nights (i.e., P1, P2, P3 and P4) are marked for further discussions.

Figure 2: provide the units for N_2O_5 and $ClNO_2$.

Thanks for the suggestions. We have already provided the units of gaseous species on the left axis. But, we also add the units for each species in Fig.2 for more clear understanding.

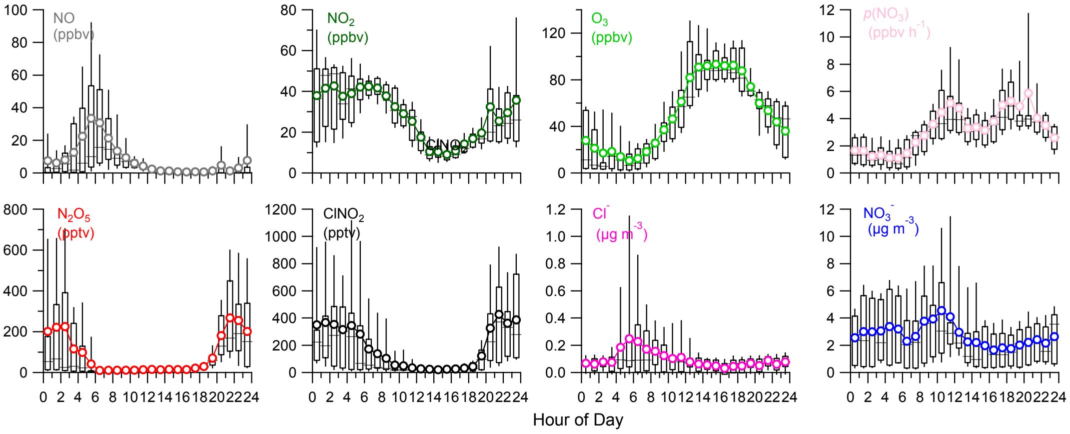

Figure 2. Diurnal variations of trace gases (NO, NO_2, O_3), IAP-CIMS species (N_2O_5, $ClNO_2$), nitrate radical production rate $p(NO_3)$, and NR-PM1 species (Cl^-, NO_3^-).

Figure 4: provide the slopes for the regression analysis.

Yes, we add the slopes for the regression analysis in Fig. 4.

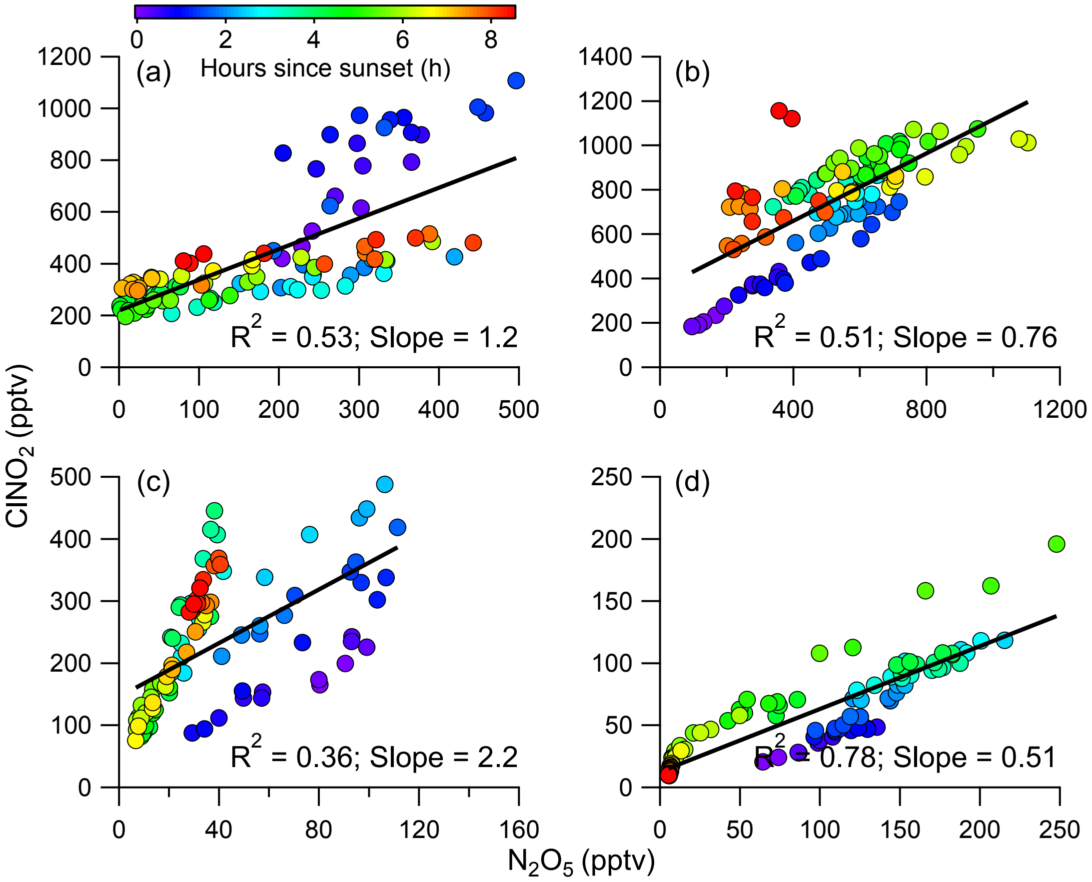

Figure 4. Correlations between $ClNO_2$ and N_2O_5 for four different nights, i.e., P1, P2, P3 and P4. The data are color-coded by the hours since sunset. Also shown are the correlation coefficients and slopes.

Figure 6: plot the wind sectors to show if the metrological conditions were stable.

Thanks for the ideas. We add the plot of time series of wind direction in the supplement to prove that the meteorological conditions during the selected periods were relatively stable.

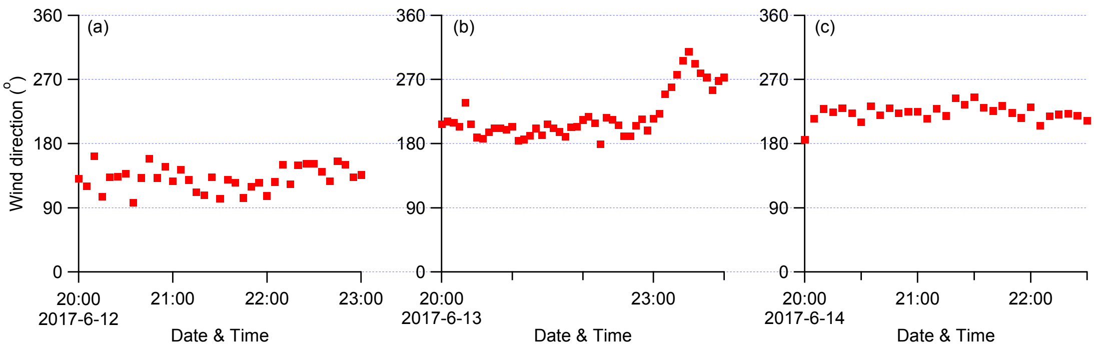

Figure R5. The time series of wind direction for the selected periods at three nights.

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Production of N_2O_5 and $ClNO_2$ in summer in urban Beijing, China

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Abstract. The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) has a significant impact on both nocturnal particulate nitrate formation and photochemistry on the following day through photolysis of nitryl chloride ($ClNO_2$), yet these processes in highly polluted urban areas remain poorly understood. Here we present measurements of gas-phase N_2O_5 and $ClNO_2$ by high-resolution time-of-flight chemical ionization mass spectrometers (ToF-CIMS) during summer in urban Beijing, China as part of the Air Pollution and Human Health (APHH) campaign. N_2O_5 and $ClNO_2$ show large day-to-day variations with average (±1σ) mixing ratios of 79.2 ± 157.1 and 174.3 ± 262.0 pptv, respectively. High reactivity of N_2O_5, with $\tau(N_2O_5$~~)~~$)^{-1}$ ranging from 0.20×10^{-2} to 1.46×10^{-2} s^{-1}, suggests active nocturnal chemistry and a large nocturnal nitrate formation potential via N_2O_5 heterogeneous uptake. The life time of N_2O_5, $\tau(N_2O_5)$, decreases rapidly as the increase of aerosol surface area, yet it varies differently as a function of relative humidity with the highest value peaking at ~40%. The N_2O_5 uptake coefficients estimated from the product formation rates of $ClNO_2$ and particulate nitrate are in the range of 0.017-0.19, corresponding to direct N_2O_5 loss rates of 0.00044-0.0034 s^{-1}. Further analysis indicates that the fast N_2O_5 loss in the nocturnal boundary layer in urban Beijing is mainly attributed to its indirect loss via NO_3, for example through the reactions with volatile organic compounds and NO, while the contribution of heterogeneous uptake of N_2O_5 is comparably small (7-33%). High $ClNO_2$ yields ranging from 0.10 to 0.35 were also observed which might have important implications for air quality by affecting nitrate and ozone formation.

1 Introduction

Dinitrogen pentoxide (N_2O_5) is an efficient ~~sink for the~~ nocturnal ~~removal of~~sink for nitrogen oxides (NO_x) (Dentener and Crutzen, 1993;Brown et al., 2006)~~, and~~. N_2O_5 exists in a rapid temperature-dependent thermal equilibrium with nitrate radical (NO_3) – one of the most important oxidants at night-time (Wayne et al., 1991). Although NO_3 and N_2O_5 levels can be suppressed by rapid titration of NO_3 against NO and volatile organic compounds (VOCs) in urban areas (Brown et al., 2003b), heterogeneous uptake by aerosol particles, fog and cloud droplets is often found to be the major pathway for direct N_2O_5 removal (~~Thornton et al., 2003; Brown et al., 2006;~~ Bertram and Thornton, 2009;~~ Chang et al., 2011;~~ Wagner et al., 2013;Brown et al., 2006;Chang et al., 2011;Thornton et al., 2003). N_2O_5 can produce nitryl chloride ($ClNO_2$) on chloride–containing aerosols which serves as an important reservoir of NO_x (Finlayson-Pitts et al., 1989;Thornton et al., 2010;Phillips et al., 2012). It has been found that levels of ~~HNO_3~~particulate nitrate formed through hydrolysis of N_2O_5 at night-time were comparable to ~~the levels~~those produced from the reaction of NO_2 with OH radical during daytime (Geyer et al., 2001). Furthermore~~ N_2O_5 and~~ $ClNO_2$ can be photolyzed into NO_2 and atomic chlorine (Cl) after sunrise, resulting in significant impacts on daytime photochemistry, for example trace gas degradation and ozone formation (Osthoff et al., 2008; Sarwar et al., 2014;Riedel et al., 2012;Mielke et al., 2013~~; Sarwar et al., 2014~~). Thus, it is of great importance to understand N_2O_5 and $ClNO_2$ chemistry in the nocturnal boundary layer of various environments.

The heterogeneous reaction of N_2O_5 and activation of $ClNO_2$ are parameterized by the N_2O_5 uptake coefficient ($\gamma_{N_2O_5}$) and $ClNO_2$ product yield (ø), which are defined as the reaction probability of N_2O_5 upon its collision on an aerosol surface and the number of $ClNO_2$ molecules formed per lost N_2O_5 molecule upon uptake, respectively (Wagner et al., 2013;Brown~~ et al.,~~, 2006;Roberts et al., 2009~~; Wagner et al., 2013~~). Previous laboratory studies have shown a large variability of $\gamma_{N_2O_5}$(0.0002~~-~~ – 0.3) depending on the physical characteristics of the substrates (e.g., aerosol surfaces, water droplets, and ice/crystal surfaces), environmental conditions (e.g., acidity, relative humidity and temperature), and chemical composition of aerosol particles (e.g., nitrate, sulfate, black carbon and organic coating) (Sander et al., 2006;Chang et al., 2011;Anttila et al., 2006;Cosman et al., 2008;Thornton and Abbatt, 2005;~~ Anttila et al., 2006;~~ McNeill et al., ~~2006; Sander et al.,~~ 2006~~; Cosman et al., 2008; Chang et al., 2011~~). To reveal the effects of each factor on N_2O_5/$ClNO_2$ chemistry, several parameterizations of $\gamma_{\mathrm{N_2O_5}}$ and ø have been proposed during the last decade (Riemer et al., 2003;Evans and Jacob, 2005; Anttila et al., 2006;Davis et al., 2008;~~ Griffiths et al., 2009; ~~Riemer et al., 2009;Griffiths et al., 2009). For example, Bertram and Thornton (2009) constructed a parameterization of $\gamma_{\mathrm{N_2O_5}}$ as a function of aerosol liquid water, nitrate, and chloride content based on the measurements of laboratory-generated internally mixed chloride-nitrate particles. Similarly, ø was parameterized as a function of aerosol liquid water content and aerosol chloride (Roberts et al., 2009). These results have great implications for regional/global chemical transport models which aim to improve the simulations of nitrate and ozone (Evans and Jacob, 2005;Sarwar et al., 2014). However, the field-derived values of $\gamma_{\mathrm{N_2O_5}}$ and ø often exhibit large inconsistencies with laboratory results, suggesting a more complex nature of heterogeneous N_2O_5 uptake in the ambient atmosphere ~~(Chang et al., 2011)~~(Brown et al., 2006;Chang et al., 2011).

N_2O_5 and NO_3 can be measured by various different techniques which have been summarized in Chang et al. (2011). For example, N_2O_5 can be derived from the thermal equilibrium with NO_2 and NO_3 that are simultaneously measured by differential optical absorption spectroscopy (DOAS) (Platt and Stutz, 2008;Stutz et al., 2004). Another indirect measurement of N_2O_5 is subtracting ambient NO_3 from the total measured NO_3 after converting N_2O_5 to NO_3 in a heated inlet and then detected by Cavity Ring-Down Spectroscopy (CRDS), Cavity-Enhanced Absorption Spectroscopy (CEAS) or Laser-Induced Fluorescence (LIF) (O'Keefe and Deacon, 1988;~~ Smith et al., 1995; ~~Brown et al., 2001;Smith et al., 1995;Wood et al., 2003; Stutz et al., 2010). ~~It should be noted that N_2O_5 measured with these two approaches may introduce additional uncertainties because it is not directly measured. N_2O_5 ~~The simultaneous indirect measurements of N_2O_5 and NO_3 can be ~~directly measured by ~~implemented using thermal dissociation – chemical ionization mass spectrometer (~~CIMS) using iodide (I^-) as the reagent ion (I~~TD – CIMS) with high sensitivity and time resolution ~~(Slusher et al., 2004; Zheng et al., 2008; Kercher et al., 2009). However, simultaneous measurements of N_2O_5 and NO_3 using thermal dissociation (TD) CIMS need to consider~~(Stutz et al., 2004), although the interference of m/z 62 (NO_3^-) from thermal decomposition of peroxy acetyl nitrate (PAN) and other related species need to be considered (Wang et al., 2014)~~.~~. Recently, the CIMS using iodide reagent ions (I-CIMS) with an unheated inlet configuration allowed the direct measurements of N_2O_5 (Kercher et al., 2009;Tham et al., 2014;Tham et al., 2016;Wang et al., 2016). The I-CIMS is also widely used to measure $ClNO_2$ in both laboratory and field studies ~~(Thornton and Abbatt, 2005; McNeill et al., 2006; Osthoff et al., 2008).~~(Thornton and Abbatt, 2005;McNeill et al., 2006;Osthoff et al., 2008;Tham et al., 2014;Tham et al., 2016;Wang et al., 2016). A large amount of $ClNO_2$ was first observed in polluted coastal regions owing to the abundant chloride from sea salt aerosol, for example, the Gulf of Mexico and the Los Angeles basin (Osthoff et al., 2008;Riedel et al., 2012;Kercher et al., 2009~~; Riedel et al., 2012~~). High levels of $ClNO_2$ from anthropogenic chloride sources were also reported in some inland areas (Thornton et al., 2010;Mielke et al., 2011;Phillips et al., 2012;~~ Bannan et al., 2015; ~~Phillips et al., 2016;Bannan et al., 2015). More recently, ~~several~~some studies in Hong Kong (Tham et al., 2014;Brown et al., ~~2016b; ~~2016a;Wang et al., ~~2016a~~2016) and in the North China Plain (NCP) (Tham et al., 2016;Wang et al., 2017b;Wang et al., 2017c;Wang et al., 2018) observed consistently high mixing ratios of N_2O_5 and $ClNO_2$. In particular, $ClNO_2$ can be rapidly formed in the plumes of coal-fired power plants in the NCP, which serves as an important source of chloride in non-ocean regions. Besides these measurement efforts, recently, some modeling studies have also evaluated the impacts of N_2O_5 and $ClNO_2$ chemistry on the ozone formation and regional air quality in China (Xue et al., 2015;Wang et al., 2016;Li et al., 2016). Despite this, our understanding of N_2O_5 and $ClNO_2$ chemistry in highly polluted urban regions with high levels of NO_x and O_3, and high particulate matter is far from complete.

Beijing has been suffering from severe haze pollution during the last two decades (Chan and Yao, 2008). As a result, extensive studies have been conducted to characterize the sources and formation mechanisms of haze episodes (Huang et al., 2014;Guo et al., 2014;~~ Huang et al., 2014; ~~Li et al., 2017). The results show that nitrate and its precursors have been playing increasingly important roles in pollution events since 2006 mainly due to the continuous decrease in SO_2 (van der A et al., 2017). While the formation mechanisms of nitrate are relatively well known, the relative contributions of different mechanisms can have large variability and uncertainties. Pathak et al. (2009) found that heterogeneous hydrolysis of N_2O_5 contributed 50-100% of the nighttime enhancement of nitrate concentration in Beijing. ~~However, ~~WRF-Chem model simulations showed only 21% enhancement of nitrate during highly polluted days (Su et al., 2016). A recent study also observed a large nocturnal nitrate formation potential from N_2O_5 heterogeneous uptake, which is comparable to and even higher than that from the partitioning of HNO_3 in rural Beijing in autumn (Wang et al., 2017a). ~~A large contribution of heterogeneous hydrolysis of N_2O_5 to the high $PM_{2.5}$ nitrate even in the daytime, due to persistently high NO_2, was also reported in Hong Kong (Xue et al., 2014).~~A large contribution of heterogeneous hydrolysis of N_2O_5 to the high $PM_{2.5}$ nitrate even in the daytime, due to persistently high NO_2, was also reported in Hong Kong (Xue et al., 2014a). All these results highlight that N_2O_5 heterogeneous uptake might be an important pathway of nitrate formation in Beijing. ~~However, the roles of N_2O_5 in nitrate formation, and of N_2O_5 and $ClNO_2$ in night- and day-time chemistry in summer in urban Beijing~~A recent modeling study has evaluated the impacts of heterogeneous $ClNO_2$ formation on the next-day ozone formation in Beijing (Xue et al., 2014b). However, the roles of N_2O_5 in nitrate formation, and of N_2O_5 and $ClNO_2$ in night- and day-time chemistry in summer in urban Beijing during field campaign are not characterized yet, except for one measurement in suburban Beijing in the summer of 2016 (Wang et al., 2018).

In this work, two high-resolution time-of-flight CIMSs using the same iodide ionization system operated by the Institute of Atmospheric Physics (IAP-CIMS) and University of Manchester (UoM-CIMS), respectively, were deployed in urban Beijing for real-time measurements of gas phase N_2O_5 and $ClNO_2$. A broadband cavity enhanced absorption spectrometer (BBCEAS) operated by the University of Cambridge was also deployed synchronously for the inter-comparison of N_2O_5. The temporal variations of N_2O_5 and $ClNO_2$ in summer and their relationships are characterized. The heterogeneous N_2O_5 uptake coefficients and $ClNO_2$ production yields are estimated, and their implications in nitrate formation are elucidated.

2 Experimental methods

2.1 Field campaign site and meteorology

The measurements were conducted during the Air Pollution and Human Health (APHH) summer campaign from 11 to 16 June, 2017 at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences (39°58′28″N, 116°22′16″E, ASL: 49 m), which is an urban site located between the north 3rd and 4th ring roads in Beijing. The meteorological variables including wind direction (WD), wind speed (WS), relative humidity (RH), and temperature (*T*) at 15 m and 100 m were obtained from the Beijing 325 m Meteorological Tower (BMT) at the sampling site. The hourly average RH ranged from 12.9% to 82.8%, with an average value of 36.~~7~~8 ± 15.9%, and the hourly average temperature ranged from 17.9°C to 38.7°C, averaged at 26.~~7°C~~7 ± 4.9°C. All IAP instruments were deployed on the roof of a two-storey building (~10 m) while those of UoM-CIMS and BBCEAS were housed in two containers at ground level (~4 m) which are approximately 20 m away. More details about the sampling site can be found in previous studies (Sun et al., 2012).

2.2 Instruments

2.2.1 IAP-CIMS

Ambient air was drawn ~~inside~~into the sampling room through a ~2 m Teflon perfluoroalkoxy tubing (PFA, ¼ inch inner diameters) at a flow rate of 10 standard liters per minute (slm), from which ~2 slm was sub-sampled into the CIMS. Methyl iodide gas (CH_3I) from a heated CH_3I permeation tube cylinder (VICI, 170-015-4600-U50) was ionized by flowing through a soft X-ray ionization source (Tofwerk AG, type P) under an ultra-high purity nitrogen (N_2, 99.999%) flow (2.5 slm). This flow enters an ion molecule reaction (IMR) chamber which was maintained at a pressure of 200 mbar using an SH-112 pump fitted with a Tofwerk blue pressure control box to account for changes in ambient pressure. A short segmented quadrupole (SSQ) positioned behind the IMR was held at a pressure of 2 mbar using a Tri scroll 600 pump. Note that the voltage settings used for the guidance of ions were carefully tuned to avoid declustering as much as possible (Lopez-Hilfiker et al., 2016). The gas phase background was determined once during the campaign by passing dry N_2 into inlet for 5 minutes.

2.2.2 UoM-CIMS

The UoM-CIMS setup has been described elsewhere (Priestley et al., 2018) except a Filter Inlet for Gases and AEROsols (FIGAERO) (Lopez-Hilfiker et al., 2014) was used in this study. The gas phase inlet of UoM-CIMS consisted of 5 m ¼" I.D. PFA tubing connected to a fast inlet pump with a total flow rate of 13 slm from which the ToF-CIMS sub-sampled 2 slm. CH_3I gas mixtures in N_2 were made in the field using a custom-made manifold (Bannan et al., 2014). 20 standard cubic centimetres per minute (sccm) of the CH_3I mixture was diluted in 4 slm N_2 and ionized by flowing through a Tofwerk x-ray ionization source. This flow enters into the IMR which was maintained at a pressure of 400 mbar using an SSH-112 pump also fitted with a Tofwerk blue pressure control box, while the subsequent SSQ was held at a pressure of 2 mbar using a Tri scroll 600 pump. During the campaign, gas phase backgrounds were established through regularly overflowing the inlet with dry N_2 for 5 continuous minutes every 45 minutes as has been performed previously.

The ambient target molecules were first ionized by reagent ions in the IMR, and then detected as adduction products with iodide, for instance, $ClNO_2$ as $I{\bullet}ClNO_2^-$ at *m/z* 208 and *m/z* 210 ($I{\bullet}{}^{37}ClNO_2^-$), and N_2O_5 as $I{\bullet}N_2O_5^-$ at *m/z* 235 (Slusher et al., 2004;~~-~~Kercher et al., 2009) at a time resolution of 1 s. Data analysis is performed using the "Tofware" package (version 2.5.11) running in Igor Pro (WaveMetrics, OR, USA) environment. The mass axis of UoM-CIMS was calibrated using I^-, I_2^- and I_3^-, while that of IAP-CIMS was calibrated using NO_3^-, I^-, $I \bullet H_2O^-$, $I \bullet CH_2O_2^-$, $I \bullet HNO_3^-$, and I_3^-, covering a wide range from *m/z* 62 to 381. Examples of high resolution peak fittings of *m/z* 208, 210 and 235 for IAP-CIMS are presented in Fig. S1.

2.2.3 Broadband cavity enhanced absorption spectrometer (BBCEAS)

A detailed description of BBCEAS has been given in Kennedy et al. (2011). Briefly, ambient air is first heated to 140 °C to thermally dissociate N_2O_5 into NO_3 and then enters the observational cavity that consists of two high-reflectivity mirrors. The sum of N_2O_5 and NO_3 is determined using the measured optical absorption of NO_3 in the wavelength of 640-680 nm. The temperature of the cavity is kept at 85~~±~~ ± 1 °C to prohibit the recombination of NO_3 and NO_2 and to maintain the stability of the optical transmission signal. A very fast flow rate of 20 lpm is adopted to minimize the residence time of gases through PFA tubes. The loss of NO_3 through the system was estimated to be approximately 10%.

Considering that the relatively high aerosol loadings in Beijing can attenuate the intracavity light intensity and thus deteriorate instrument sensitivity, a poly tetrafluoroethylene (PTFE) filter of pore size 1 μm was used to remove aerosol particles from the air stream. This filter acts also a point loss (~10%) for NO_3 but has a negligible impact on N_2O_5 (Dube et al., 2006). Because the mixing ratio of N_2O_5 is higher than NO_3 by a factor of >10 during APHH summer campaign, the influence of filter loss on the measurements of $N_2O_5+NO_3$ is expected to be small. Aging of aerosol particles on the filter may potentially introduce uncertainties for the transmission efficiencies of NO_3 and N_2O_5, but was found to be insignificant in this study.

2.3 Calibrations and inter-comparisons

During the campaign, field calibrations for UoM-CIMS were regularly carried out using known concentration formic acid gas mixtures made in the custom-made manifold. A range of other species were calibrated after the campaign, and relative calibration factors were derived using the measured formic acid sensitivity during these calibrations as has been performed previously (Le Breton et al., 2014, 2017; Bannan et al., 2014, 2015).

The UoM-CIMS was calibrated post campaign for both N_2O_5 and $ClNO_2$, relative to formic acid that was calibrated and measured throughout the campaign. This is completed assuming that the ratio between formic acid and $ClNO_2$ sensitivity remains constant. $ClNO_2$ was calibrated using the method described in Kercher et al. (2009). Briefly, a stable source of N_2O_5 is generated and passed over a salt slurry where excess chloride reacts to produce gaseous $ClNO_2$. The N_2O_5 for this process was synthesised based on the methodology described by Le Breton et al. (2014). Excess O_3 is generated through flowing 200 sccm O_2 (BOC) through an ozone generator (BMT, 802N) into a 5 litre glass volume containing NO_2 (Sigma, >99.5%). The outflow from this reaction vessel is cooled in a cold trap held at -78°C (195K) by a dry ice/glycerol mixture where N_2O_5 is condensed and frozen. The trap is allowed to reach room temperature and the flow is reversed where it is then condensed in a second trap held at 220 K. This process is repeated several times to purify the mixture. The system is first purged by flowing O_3 for ten minutes before usage. To ascertain the N_2O_5 concentration in the line, the flow is diverted through heated line to decompose the N_2O_5 and into to a Thermo Scientific 42i NO_x analyser where it is detected as NO_2. According to the inter-comparisons with the BBCEAS, including this study and others (e.g., Le Breton et al. (2014); Bannan et al. (2017)), the possible interference of NO_y on the NO_x analyser is not deemed important in terms of our reported N_2O_5 concentrations.

$ClNO_2$ was produced by flowing a known concentration of N_2O_5 in dry N_2 through a wetted NaCl scrubber. Conversion of N_2O_5 to $ClNO_2$ can be as efficient as 100% on sea salt, but it can also be lower, for example if $ClNO_2$ is converted to Cl_2 (Roberts et al., 2008). In this calibration we have followed the accepted methods of Osthoff et al. (2008) and Kercher et al. (2009) that show a conversion yield of 100% and have assumed this yield in the calibrations of this study.

The second method used to verify our $ClNO_2$ calibration is by cross calibration with a turbulent flow tube chemical ionisation mass spectrometer (TF-CIMS) (Leather et al., 2012). A known concentration of 0-20 sccm Cl_2 (99.5% purity Cl_2 cylinder, Aldrich) from a diluted (in N_2) gas mix is flowed into an excess constant flow of 20 sccm NO_2 (99.5% purity NO_2 cylinder, Aldrich) from a diluted (in N_2) gas mix, to which the TF-CIMS has been calibrated. This flow is carried in 52 slm N_2 that is purified by flowing through two heated molecular sieve traps. This flow is sub-sampled by the ToF-CIMS where the $I{\bullet}ClNO_2^-$ adduct is observed. The TF-CIMS is able to quantify the concentration of $ClNO_2$ generated in the flow tube as the equivalent drop in NO_2^- signal. This indirect measurement of $ClNO_2$ is similar in its methodology to $ClNO_2$ calibration by quantifying the loss of N_2O_5 reacted with Cl^- (e.g., Kercher et al. (2009)). The TF-CIMS method gives a calibration factor 58% greater than that of the N_2O_5 synthesis method therefore this is taken as our measurement uncertainty. This calibration was scaled to those in the field using formic acid calibrations carried out in the laboratory by overflowing the inlet with various known concentrations of gas mixtures (Bannan et al., 2014).

The IAP-CIMS calibration for N_2O_5 was performed by comparing with the measurements from the BBCEAS. As shown in Fig. S2, the raw signals of N_2O_5 from the IAP-CIMS measurements were highly correlated with those from BBCEAS (R^2 = 0.84). Given that the inter-comparison between the two instruments was relatively constant throughout the study, the average regression slope of 0.54 was then applied to determine the mixing ratio of N_2O_5 for the IAP-CIMS. The estimated N_2O_5 mixing ratios were then compared with those measured by UoM-CIMS. As shown in Fig. 1, the two N_2O_5 measurements tracked well with each other (R^2 = 0.84, slope =1.42) although some differences at the midnight of 13 June were observed. The raw signals of $ClNO_2$ given by the IAP-CIMS were first converted to mixing ratios by assuming the same sensitivity between $ClNO_2$ and N_2O_5 (i.e., 0.54 cps pptv^{-1}). The results show that the estimated $ClNO_2$ for the IAP-CIMS agrees well with that was measured by UoM-CIMS and calibrated post campaign (R^2 = 0.93, slope = 0.905, Fig. 1). Overall, the uncertainty is 17% and 58%, detection limit is 1.7 pptv and 0.7 pptv for N_2O_5 and $ClNO_2$ of IAP-CIMS, respectively. All the discussions below are based on IAP-CIMS measurements unless otherwise stated.

2.3 Collocated measurements

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS hereafter) and an Aethalometer (AE33, Magee Scientific Corp.) were deployed on the roof of the two-storey building to measure the size-resolved non-refractory submicron aerosol (NR-PM_1) species with a time resolution of 5 min, including organics (Org), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-) (DeCarlo et al., 2006; Canagaratna et al., 2007), and black carbon (BC), respectively. A more detailed description of the operations and calibrations of this HR-AMS can be found in Xu et al. (2015~~)~~ ~~and~~);Sun et al. (2016). Other collocated measurements in two containers at ground level included gaseous species of O_3 (TEI 49C UV absorption analyzer), NO (TEI 42i TL NO analyzer), and NO_2 (CAPS NO_2 monitor, Aerodyne Research Inc.), and size-resolved particle number concentrations (11-550 nm) by a scanning mobility particle sizer (SMPS) equipped with a long Differential Mobility Analyzer (DMA, TSI, 3081A) and a Condensation Particle Counter (CPC, TSI, 3772).

2.4 Data analysis

2.4.1 Estimation of $\gamma_{N_2O_5}$ and ø

NO_3 is formed from the reaction of NO_2 with O_3 (R1) with a temperature-dependent reaction rate constant k_1. NO_3 rapidly photolyzes during daytime, but at night it reacts with NO_2 to produce N_2O_5 (R2). N_2O_5 can thermally decompose back to NO_3 and NO_2, and the equilibrium rate coefficient K_{eq} is a function of ambient temperature. In this study, values of k_1 and K_{eq} recommended by Atkinson et al. (2004) and Brown and Stutz (2012) were used. The indirect loss of N_2O_5 is mainly through the reactions of NO_3 with either NO or VOCs (R3), while the direct N_2O_5 loss is predominantly from the heterogeneous hydrolysis on the surface of aerosol particles that contain water (R4) or chloride (R5). Note that het is an abbreviation of heterogeneous in the equations. The net reaction of R4 and R5 can be described as R6 where $k_{N_2O_5}$ is the heterogeneous uptake rate ~~coefficient for~~of N_2O_5, and ø is the $ClNO_2$ yield.

$$NO_2 + O_3 \rightarrow NO_3 + O_2,\ k_1 \quad \text{(R1)}$$

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M,\ K_{eq} \quad \text{(R2)}$$

$$NO_3 + (NO\ \text{or}\ VOCs) \rightarrow \text{products},\ k_{NO_3} \quad \text{(R3)}$$

$$N_2O_5 + H_2O(\text{het}) \rightarrow 2HNO_3(\text{aq}) \quad \text{(R4)}$$

$$N_2O_5 + Cl^-(\text{het}) \rightarrow NO_3^-(\text{aq}) + ClNO_2 \quad \text{(R5)}$$

$$N_2O_5 + (H_2O\ \text{or}\ Cl^-)(\text{het}) \rightarrow (2\text{-ø})NO_3^-(\text{aq}) + \text{ø}\ ClNO_2,\ k_{N_2O_5} \quad \text{(R6)}$$

When the uptake reaction was not limited by gas-phase diffusion, $k_{N_2O_5}$ can be simplified as Eq. (1) (Riemer et al., 2003;Dentener and Crutzen, 1993~~; Riemer et al., 2003~~):

$$k_{N_2O_5} = \frac{1}{4} \times c \times S_a \times \gamma_{N_2O_5} \quad (1)$$

Where c is the mean molecular speed of N_2O_5 (unit, m s^{-1}), and S_a is the aerosol surface area density calculated from the size-resolved particle number concentrations assuming spherical particles (unit, µm cm^{-3}). Note that S_a determined under dry conditions was converted to that under ambient RH levels by using the hygroscopic growth factor in Liu et al. (2013).

The nocturnal mixing ratio of NO_3 can be derived from the simultaneous measurements of NO_2 and N_2O_5 (R2) assuming that the equilibrium between NO_3 and N_2O_5 is rapidly established after sunset (Brown et al., 2003a).

$$[\mathrm{NO_3(cal)}]=\frac{[\mathrm{N_2O_5}]}{K_{eq}[\mathrm{NO_2}]} \tag{2}$$

The nitrate radical production rate $p(\mathrm{NO_3})$ can be calculated from reaction R1 assuming that the nitrate radical is solely from reaction R1.

$$p(\mathrm{NO_3})= k_1[\mathrm{NO_2}][\mathrm{O_3}] \tag{3}$$

With a steady-state assumption for NO_3 and N_2O_5, the inverse N_2O_5 steady state lifetime, $\tau(N_2O_5$~~$)^{-}$~~$)^{-1}$, which is defined as the ratio of $p(NO_3)$ to the N_2O_5 mixing ratios, can be expanded to Eq. (4) after the substitution of Eqs. (2) and (3) into the approximate time change rate for N_2O_5 (Brown et al., 2003a).

$$\tau(\mathrm{N_2O_5}\cancel{)^{-}})^{-1} = \frac{p(NO_3)}{[\mathrm{N_2O_5}]} \approx \frac{k_{\mathrm{NO_3}}}{K_{eq}[\mathrm{NO_2}]} + k_{\mathrm{N_2O_5}} \tag{4}$$

$\frac{k_{\mathrm{NO_3}}}{K_{eq}[\mathrm{NO_2}]}$ represents the contribution to $\tau(N_2O_5$~~$)^{-}$~~$)^{-1}$ from the indirect N_2O_5 loss pathway, i.e. through the NO_3 reactions with VOCs and~~/or~~ NO, while $k_{\mathrm{N_2O_5}}$ indicates the direct loss of N_2O_5 through heterogeneous uptake.

Considering that the production of $ClNO_2$ is predominantly from the heterogeneous N_2O_5 uptake within stable air masses and precursors, the production rate of $ClNO_2$ ($p\mathrm{ClNO_2}$) can be related to the heterogeneous loss rate of N_2O_5 by:

$$p\mathrm{ClNO_2} = \frac{\mathrm{dClNO_2}}{\mathrm{dt}} = ø \times (\frac{1}{4} \times c \times S_a \times \gamma_{\mathrm{N_2O_5}}) \tag{5}$$

~~The production rate of particulate nitrate ($p\mathrm{NO_3^-}$) was obtained from HR-AMS measurements assuming that the measured $p\mathrm{NO_3^-}$ can account for the total production of nitrate by reaction R4 (Phillips et al., 2016).~~

The production rate of particulate nitrate ($p\mathrm{NO_3^-}$) was obtained from HR-AMS measurements assuming that the measured $p\mathrm{NO_3^-}$ was totally from production of nitrate by reaction R4 (Phillips et al., 2016). Note that the formation of particulate nitrate from regional transport or via the net uptake of HNO_3 to aerosol is not taken into consideration.

$$p\mathrm{NO_3^-} = \frac{\mathrm{dNO_3^-}}{\mathrm{dt}} = (2 - ø) \times (\frac{1}{4} \times c \times S_a \times \gamma_{\mathrm{N_2O_5}}) \tag{6}$$

Only periods with concurrent nighttime formation of $ClNO_2$ and NO_3^- meet the requirements that both of them are produced only from the heterogeneous N_2O_5 uptake. By combining Eq. (5) with Eq. (6), $\gamma_{\mathrm{N_2O_5}}$ and $ø$ can be represented as:

$$\gamma_{\mathrm{N_2O_5}} = \frac{2(p\mathrm{ClNO_2} + p\mathrm{NO_3^-})}{c \times S_a \times [\mathrm{N_2O_5}]} \tag{7}$$

$$\text{ø} = 2\left(\frac{pNO_3^-}{pClNO_2} + 1\cancel{)}\right)^{-1} \tag{8}$$

2.4.2 Parameterization of $\gamma_{N_2O_5}$ and ø

Aerosol liquid water content associated with inorganic species was estimated using the ISORROPIA-II thermodynamic equilibrium model (Nenes et al., 1998; Fountoukis and Nenes, 2007), with input data of ambient NR-PM$_1$ species, and RH and T at 15 m. The N_2O_5 uptake coefficient and $ClNO_2$ yield can also be calculated by the parameterization proposed by Bertram and Thornton (2009).

$$\gamma_{N_2O_5} = Ak\left(1 - \frac{1}{1 + \frac{29[Cl^-]}{[NO_3^-]} + \frac{0.06[H_2O]}{[NO_3^-]}}\right) \tag{9}$$

$$\text{ø} = \left(1 + \frac{[H_2O]}{483[Cl^-]}\cancel{)}\right)^{-1} \tag{10}$$

Where $[H_2O]$, $[NO_3^-]$ and $[Cl^-]$ are molar concentrations of liquid water, particle nitrate and chloride, respectively, and the empirical parameters A= 3.2×10^{-8}, and $k = 1.15\times10^6\times(1 - e^{-0.13[H_2O]})$ are used.

3 Results and discussion

3.1 Overview of N_2O_5 and $ClNO_2$ measurements

Figure 1 shows the time series of N_2O_5~~, $ClNO_2$ and $p(NO_3)$, submicron aerosol species of NO_3^- and non-refractory Cl^-,~~ and $ClNO_2$, gaseous species of NO, NO_2 and O_3, and meteorological parameters during the field campaign. Both N_2O_5 and $ClNO_2$ exhibited large day-to-day variability with the 5-min average (±1σ) mixing ratios being 79.2 ± 157.1 pptv and 174.3 ± 262.0 pptv, respectively. Such dramatic variations of N_2O_5 and $ClNO_2$ are consistent with previous observations in various environments, for example, ground sites in Colorado and London (Bannan et al., 2015;Thornton et al., 2010~~; Bannan et al., 2015~~)~~ and the residual layer in Mt. Tai (Wang et al., 2017c)~~ and the residual layer at Mt. Tai (Wang et al., 2017c). Four nights (i.e., P1, P2, P3 and P4 from 20:00 to 04:30) were selected to investigate nocturnal chemistry of N_2O_5 and $ClNO_2$ in this study. The first two nights (P1 and P2) showed much higher mixing ratios of N_2O_5 and $ClNO_2$ than those during P3 and P4, although the NO_x and O_3 levels during P4 were comparable to those during P2 (Table 1).

The highest N_2O_5 mixing ratio (1.10 ppbv, ~~1~~5-minute average) was observed at 2:15 on 13 June (P2), which is comparable to the previous observation in urban Beijing (1.3 ppbv) (Wang et al., 2017a), but much lower than that in the aged air masses in Hong Kong ~7.8 ppbv (Brown et al., ~~2016a~~2016b). A recent measurement at a suburban site in Beijing impacted by the outflow of urban Beijing air masses also reported consistently high N_2O_5 (1-minute maxima 937 pptv) (Wang et al., 2018). The mixing ratio of N_2O_5 was also much higher than that in the nocturnal ~~residential boundary layer in Mt. Tai (167 pptv) (Wang et al., 2017c)~~residual boundary layer at Mt. Tai (167 pptv) (Wang et al., 2017c), indicating potentially significant nighttime N_2O_5 chemistry in highly polluted urban areas. One of the reasons for this could be due to the high mixing ratios of precursors, for instance, the average O_3 mixing ratios at night-time were as high as 18-56 ppbv. Besides, the maximal N_2O_5 occurred during P2 other than the rest nights was likely due to the insignificant titration of NO during P2, e.g., 0.5 vs. 2.3-15.6 ppbv. The lowest nighttime average of N_2O_5 (~ 37.8 pptv) was observed during P3 ~~mainly attributed to the fast~~although the NO_2 showed much higher concentration than those during P2 and P4, indicating the joint influences of precursors (NO_2 and O_3). Fast heterogeneous hydrolysis of N_2O_5 under high RH (~ 60.5%) conditions~~.~~ during P3 could be another reason, which was supported by the higher $ClNO_2$ during P3 than P4.

Similar to N_2O_5, $ClNO_2$ presented the highest value (1.44 ppbv, ~~1~~5-minute average) before sunrise on 13 June (P2), yet it is lower than the maximum of 2.1 ppbv (1-minute average) observed at a rural site located to the southwest of Beijing (Tham et al., 2016), and also the $ClNO_2$ peak of 2.9 ppbv (1-minute average) in suburban Beijing ~~(Wang et al., 2018)~~(Wang et al., 2018). These results indicated ubiquitously observed $ClNO_2$ in the NCP, although high $ClNO_2$ mixing ratios have been also observed previously in both marine and continental environments in North America, Europe and Asia (Osthoff et al., 2008;Mielke et al., 2011;Thornton et al., 2010;~~Mielke et al., 2011;~~ Phillips et al., 2012;Tham et al., 2014). The average nitrate radical production rate $p(NO_3)$ was 2.8 ~~and~~ppbv $h^{-1}$and 3.6 ppbv h^{-1} during P1 and P2, respectively, which are both higher than those during P3 and P4 (1.7-2.6) (Table 1). This result supports a higher production potential for N_2O_5 during P1 and P2. On average, $p(NO_3)$ was 2.6 ± 2.4 ppbv h^{-1} at night-time, indicating more active nocturnal chemistry than previous studies in NCP in terms of radical production rates, for example, 1.2 ± 0.9 ppbv h^{-1} in suburban Beijing, 1.7 ± 0.6 ppbv h^{-1} in Wangdu, and 0.45 ± 0.40 ppb h^{-1} ~~in~~at Mt. Tai (Tham et al., 2016;Wang et al., 2017c;Wang et al., 2018). We also note that the $p(NO_3)$ was comparable between P4 and P2 (2.6 pptv vs. 2.8 pptv), yet the N_2O_5 and $ClNO_2$ mixing ratios during P4 were much lower, likely due to the difference in NO levels, i.e., 0.5 vs. 7.1 ppbv. The favorable dispersing meteorological conditions with higher wind speed and lower relative humidity in P4 than those in P2 might also be an explanation (Table 1). Our results illustrate that precursors levels, reaction rates, and meteorological conditions can all affect the variability of N_2O_5 and $ClNO_2$.

The average diurnal variations of trace gases, N_2O_5, $ClNO_2$ and submicron nitrate and chloride are depicted in Fig. 2. O_3 showed a pronounced peak of 93.3 ppbv between 14:00 and 16:00 corresponding to a minimum mixing ratio of NO_2 (9.1 ppbv). As a consequence, $p(NO_3)$ showed relatively high values around noon with a decrease in the middle of the afternoon owing to the depletion of NO_2 and then reached a maximum of 5.9 ppbv h^{-1} before sunset. A similar diurnal pattern of $p(NO_3)$ was also observed at a rural site in the autumn of Beijing (Wang et al., 2017a). Both NO and NO_2 showed pronounced diurnal cycles with lowest concentrations in the afternoon. In addition to the rising boundary layer, the formation of NO_z is another important reason for the low levels of NO_x during this time period in urban Beijing (Sun et al., 2011). Nitrate and chloride also showed lowest concentrations in the late afternoon, mainly due to the evaporative loss under high temperature conditions (Sun et al., 2012).

~~After sunset,~~ N_2O_5 was rapidly formed ~~associated with a corresponding decrease in $p(NO_3)$.~~after sunset. The mixing ratio of N_2O_5 peaked approximately at 22:00 and then remained at a consistently high level (~200-300 pptv) until 3:00. After that, N_2O_5 showed a rapid decrease due to the significant titration by NO. Similar loss of N_2O_5 due to the injection of NO-containing air was also reported at sites near urban areas (Brown et al., 2003b). Because NO is predominantly from local emissions as supported by the tight correlation (R^2 = 0.64-0.73, Fig. S3) with black carbon, a tracer for combustion emissions, our results demonstrated that the local NO emissions serve as ~~the most~~ important scavenger of N_2O_5 before sunrise in urban Beijing. In comparison, the decrease in N_2O_5 due to the NO titration only occurred during the second half of the night with low O_3 in suburban Beijing (Wang et al., 2018). This study also found high N_2O_5 after midnight due to the incomplete titration of O_3, for instance, ~52.9 ppbv after midnight on 13 June, which is different from previous findings that high N_2O_5 mixing ratios were typically observed before midnight due to the rapid depletion of O_3 (Wang et al., 2017a;~~-~~Wang et al., 2017c). The high nocturnal mixing ratios of O_3 and NO_2 (Fig. 2) highlight much higher oxidative capacity at night in summer in urban Beijing compared to the other seasons and/or rural locations.

$ClNO_2$ showed clear nocturnal formation from heterogeneous processing and decreased rapidly after sunrise mainly due to photolysis (Fig. 2). Note that $ClNO_2$ peaked at a similar time (21:00-22:00) as that of N_2O_5 without showing a time lag of 1-3 h as previously observed in Jinan ~~(Wang et al., 2017b)~~(Wang et al., 2017b), indicating that either particulate Cl^- was sufficient for the heterogeneous reactions or other chlorine sources (e.g., HCl) contributed to the formation of $ClNO_2$ in urban Beijing~~.~~. According to previous studies, the partitioning of HCl to particulate Cl^- could contribute to $ClNO_2$ formation substantially at urban sites (Thornton et al., 2010(Riedel et al., 2012)~~. According to previous studies, the partitioning of HCl to particulate Cl^- could contribute to $ClNO_2$ formation substantially at urban sites (Thornton et al., 2010).~~. In addition, Wang et al. (2018) also speculated that large particle chloride during the campaign was possibly replenished by gas-phase HCl due to the high emissions ~~of~~ from human activities. We also found that $ClNO_2$ was well correlated with chlorine (Cl_2) derived from IAP-CIMS (R^2 = 0.90-0.99) rather than particulate chloride (Cl^-~~)~~) (R^2 = 0.01-0.44) at the night-time, indicating that $ClNO_2$ might act as an intermediate during the formation of Cl_2 under sufficient chloride conditions (Roberts et al., 2008). Indeed, the much lower particulate Cl^- than $ClNO_2$ also indicated other chlorine sources. Therefore, we need simultaneous measurements for further supporting this conclusion in this study, e.g., HCl.

3.2 Reactivity of N_2O_5 and NO_3

Considering the time needed for meeting the steady-state assumption, only the data two~~-~~ hour ~~data~~later after sunset were used to calculate N_2O_5 steady-state lifetime via Eq. (4) (Wagner et al., 2013). High N_2O_5 reactivity was observed and the average $\tau(N_2O_5)^{-1}$ was 0.16-1.58 ×10^{-2} s^{-1} during these four nights ~~with average $\tau(N_2O_5)^{-1}$ ranging from 0.16×10^{-2} to 1.58×10^{-2} s^{-1}, which corresponds~~corresponding to a short nighttime N_2O_5 lifetime between 1.1 and 10.7 ~~min~~minutes (Fig. 3~~).~~), with $\tau(N_2O_5)^{-1}$ ranging from 0.20×10^{-2} to 1.46×10^{-2} s^{-1} throughout the campaign. Such values are overall consistent with those measured at surface sites and in the nocturnal residual layer in NCP, for example, 1.30×10^{-2} s^{-1} in Wangdu (Tham et al., 2016) and 1.30-1.40×10~~$^{-2}$ s^{-1} in Mt. Tai (Wang et al., 2017c). In comparison, the N_2O_5 loss is much more rapid than that previously reported in southern China~~$^{-2}$ s^{-1} at Mt. Tai (Wang et al., 2017c) . In comparison, the N_2O_5 loss is much more rapid than that previously reported in southern China (1-5 h) (Brown et al., ~~2016a~~2016b)~~ and the USA (Brown et al., 2009; Wagner et al., 2013)~~ and the USA (a few hours) (Wagner et al., 2013), mainly due to the high aerosol loading in NCP leading to an enhanced N_2O_5 sink through both indirect and direct pathways. Correspondingly, the average $\tau(NO_3$~~)~~$)^{-1}$ calculated from the inferred NO_3 were 0.02-0.62 s^{-1} during the four nights, indicating active NO_3 nighttime chemistry through reactions with NO and VOCs in the polluted nocturnal boundary. Note that P2 and P4 showed comparable $p(NO_3)$ (2.8 vs. 2.6 ppbv h^{-1}) (Table 1), yet the N_2O_5 reactivity during P4 (1.58×10^{-2} s^{-1}) was significantly higher than that during P2 (0.16×10^{-2} s^{-1}) likely due to the higher NO level, and the enhanced N_2O_5 heterogeneous loss ~~(discussed in Sec.3.4).~~might also be explanation. Consistently, τ(NO_3~~)~~)$^{-1}$ showed similar patterns to those of τ(N_2O_5~~)~~)$^{-1}$. Indeed, the N_2O_5 reactivity presented a nonlinear dependence on aerosol surface area (S_a) and relative humidity (Figs. 3c and 3d). Although P3 showed much higher RH than P4 (60.5% vs. 28.0%), the N_2O_5 reactivity was comparable between P3 and P4 (0.014 vs. 0.016 s^{-1}), illustrating the complex heterogeneous process of N_2O_5.

Figure 3c shows the N_2O_5 lifetime as a function of surface area density~~.~~ (S_a) with the data being binned according to the 50 μm^2 cm^{-3} S_a increment. τ(N_2O_5) decreased rapidly from 11.8 minutes to 2.2 minutes as S_a increased up to 500 μm^2 cm^{-3} , and then remained at relatively constant levels at $S_a > 500$ μm^2 cm^{-3}. Such an S_a dependence of τ(N_2O_5) is consistent with previous observations in Hong Kong (Brown et al., ~~2016a~~2016b). Large variations in τ(N_2O_5) as a function of RH were also observed. As shown in Fig. 3d, the N_2O_5 lifetime decreased by nearly a factor of 5 from 11.3 to 2.2 ~~mins~~minutes as RH increased from 40% to 50%. We noticed that the aerosol surface area exhibits an increase as a function of RH at RH > 40% (Fig. S4). These results suggested that the decrease in τ(N_2O_5) at high RH levels (RH >40%) might be caused by increased N_2O_5 uptake rates due to the higher S_a. In addition, the increasing aerosol liquid water content at high RH might be another reason (Fig. S4). Comparatively, the N_2O_5 lifetime showed an increase as a function of RH at RH< 40%, while the variations in S_a were small, suggesting additional contributions from other factors, for example, aerosol loading and composition (Morgan et al., 2015). Considering that the period of this study is relatively short, long-term measurements are needed in future studies to better characterize the parameterizations of τ(N_2O_5) as a function of S_a and RH.

3.3 Relationship between N_2O_5 and $ClNO_2$

Previous studies have found that N_2O_5 and $ClNO_2$ were generally positively correlated in predominantly continental air masses whereas they were negatively correlated in marine air masses with high chloride content (Bannan et al., 2015). Phillips et al. (2012) also reported large variability in N_2O_5 and $ClNO_2$ correlations and $ClNO_2$-to-N_2O_5 ratios in air masses from continental or marine origins due to the changes in particle Cl^{-}~~.~~$^{-}$. In this study, $ClNO_2$ was well and positively correlated with N_2O_5 during all four nights (Fig. 4, R^2 = 0.~~60~~36 - 0.~~88~~78), and only slight changes in $ClNO_2/N_2O_5$ ratios were observed after sunset. These results are different from previous observations showing large variability in the correlations (Osthoff et al., 2008), which indicates that particulate Cl^{-} was always sufficient for the $ClNO_2$ formation during this study period. The differences in regression ~~slopes~~coefficients among the four nights can be explained by different air masses originating from different regions which were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT, NOAA) model (Draxler and Hess, 1997) (Fig. S5). For example, $ClNO_2$ tracked much better with N_2O_5 after midnight (R^2 = 0.69) than that before midnight (R^2 = 0.16) during P2 (Fig. S6), suggesting the influences of air masses from different regions (Fig. S5). Comparatively, P4 and P1 showed similar tight correlations between $ClNO_2$ and N_2O_5 before and after midnight, consistent with their similar back trajectories during the two different periods.

The $ClNO_2/N_2O_5$ ratios varied significantly throughout the study ranging from 0.3 to 95.5 (30 minute average). The average (±1σ) ratio of $ClNO_2/N_2O_5$ was 6.9 ± 7.4, consistent with the previous studies in NCP, for example, 0.4-131.3 in Jinan and Wangdu (~~Tham et al., 2016;~~ Wang et al., 2017b;Tham et al., 2016). However, the ratios are substantially higher than those measured in other megacities, e.g., Hong Kong (0.1-2.0) ~~(Wang et al., 2016b)~~(Wang et al., 2016), London (0.02-2.4) (Bannan et al., 2015) and Los Angeles, California (0.2-10.0) (Mielke et al., 2013). These results indicate ubiquitously high $ClNO_2/N_2O_5$ ratios in the NCP, consistent with another measurement in suburban Beijing (Wang et al., 2018), which might result from the high $ClNO_2$ production rate due to high aerosol loadings. We also note that the relatively low N_2O_5 associated with high N_2O_5 reactivity might be another possible explanation. Furthermore, we compared the $ClNO_2/N_2O_5$ ratios with particulate concentrations and compositions during the four nights (Fig. 5). P3 showed the highest median ratio of 9.4, which is much higher than those during the rest of three nights (1.0-3.2). This can be explained by the correspondingly high liquid water content that facilitated the N_2O_5 heterogeneous uptake (Morgan et al., 2015). In comparison, the particle chloride concentrations were relatively close during the four nights , with slightly lower concentrations during P4, further supporting that the $ClNO_2/N_2O_5$ ratios were independent of particle chloride in this study due to the sufficient chloride source for the $ClNO_2$ production, e.g., HCl gas-particle partitioning. The lower $ClNO_2/N_2O_5$ ratios during P2 compared with P1 can be explained by the “nitrate effect” which suppressed N_2O_5 uptake (Mentel and

Wahner, 1999) as P2 showed much higher nitrate concentrations than P1 (4.2 vs. 1.4 μg m^{-3}). Note that the $ClNO_2/N_2O_5$ ratios were also characterized with the dependence on Org/SO_4 ratios in our campaign, similar to other studies (Evans and Jacob, 2005; Riemer et al., 2009).

3.4 N_2O_5 uptake coefficient and $ClNO_2$ production yield

To quantity the relative contributions of different pathways to N_2O_5 loss, three periods with relatively stable air masses and concurrent increases in $ClNO_2$ and NO_3^- (Fig. 6, 20:00-23:00 on 12 June, ~~22~~20:00-00:00 on 13 June, and 20:00-22:30 on 14 June) were selected for the calculations of $\gamma_{N_2O_5}$ and ø. The rigorous method as suggested by ~~Phillips et al. (2016)~~Phillips et al. (2016) was used in this study. Briefly, the predicted concentrations of $ClNO_2$ and NO_3^- were derived by integrating $pClNO_2$ and pNO_3^- with average S_a and N_2O_5 over each time step (~15 min) and initial estimations for $\gamma_{N_2O_5}$ and ø. Repeating the integration by changing $\gamma_{N_2O_5}$ and ø until good agreements between observed and predicted values of $ClNO_2$ and NO_3^- were reached. The derived heterogeneous uptake coefficient, $ClNO_2$ yield, and N_2O_5 loss rate k_d following this method are listed in Table 2.

The estimated $\gamma_{N_2O_5}$ for the three selected periods were 0.017-0.09, which was generally comparable to previous values (0.014-0.092) derived from the steady-state assumption method in the NCP (~~Tham et al., 2016;~~ Wang et al., 2017a; Wang et al., 2017b; Tham et al., 2016;Wang et al., 2017c), and also consistent with the recent measurements (0.012-0.055) using the same method in suburban Beijing (Wang et al., 2018). However, the $\gamma_{N_2O_5}$ determined in our campaign was 1-2 orders of magnitude higher than those obtained in laboratory (Thornton et al., 2003), and also much higher than those in Hong Kong and Germany (Brown et al., ~~2016a;~~ 2016b;Phillips et al., 2016). We also found that the parameterized $\gamma_{N_2O_5}$ values (0.0014-0.012) determined from Eq. (9) (the Bertram-Thornton parameterization) were significantly lower than the observed values, suggesting that more field measurements are needed to improve the parameterization schemes. Note that $\gamma_{N_2O_5}$ values appeared to increase with the rising relative humidity, which were also observed at other sites (Wang et al., 2017b;Thornton et al., 2003~~; Wang et al., 2017b~~). For example, $\gamma_{N_2O_5}$ values increased from 0.019 to 0.090 when RH increased from 21.1% to 63.6%. However, the $\gamma_{N_2O_5}$ values were comparable at low RH levels (< 40%) (0.019 vs. 0.017 in Table 2) although RH differed by a factor of 2 (21% vs. 40%). These results further supported that the influences of hygroscopic growth on $\gamma_{N_2O_5}$ were mainly caused by increasing aerosol liquid water content. The direct N_2O_5 loss rates estimated from the uptake coefficient were in the range of 0.00044-0.0034 s^{-1}, which contributed ~~6.9-32.6~~7-33% to the total N_2O_5 loss with the rest being indirect loss. The uncertainty of the direct N_2O_5 loss rates contributions is estimated to be ~40%, associated from S_a (~30%), O_3 and NO_2 (~5%), and N_2O_5 (~17%). Our results indicated that the fast N_2O_5 loss in the nocturnal boundary in urban Beijing was predominantly from the indirect loss of NO_3 rather than the heterogeneous uptake of N_2O_5, mainly due to active NO_3 reaction in summer. Such a conclusion was different from previous results in autumn Beijing that N_2O_5 loss was dominated by N_2O_5 heterogeneous hydrolysis (69.1%-98.8%) (Wang et al., 2017a). Several studies also revealed the importance of heterogeneous N_2O_5 uptake in N_2O_5 loss in the NCP by using the steady-state derived $\gamma_{N_2O_5}$ (Tham et al., 2016; Wang et al., 2017b; Wang et al., 2017c). While the uncertainties in different analysis methods, e.g., the product formation rates or steady-state assumption are one of the reasons, the high NO concentration could be the important reason for the dominant N_2O_5 loss pathway. The high VOCs emissions, particularly biogenic emissions (e.g., isoprene and terpene) in summer than other seasons ~~could~~might be another ~~important~~ reason for the differences in dominant N_2O_5 loss pathway. Indeed, the indirect N_2O_5 loss via NO_3+VOCs was also found to dominate the total loss of N_2O_5 (67%) in summer in suburban Beijing (Wang et al., 2018). Our results highlight the significant nighttime NO_x loss through the reactions of NO_3 with VOCs in summer in urban Beijing.

The $ClNO_2$ yields ø derived for the three cases were 0.35, 0.10 and 0.15, respectively. The production yields in this study are substantially larger than those in urban Jinan (0.014-0.082) ~~(Wang et al., 2017b)~~(Wang et al., 2017b), yet comparable to those reported ~~in Mt. Tai (0.02-0.90) (Wang et al., 2017c)~~at Mt. Tai (0.02-0.90)(Wang et al., 2017c) and continental Colorado (0.07-0.36) (Thornton et al., 2010). However, the significantly lower ø than that in suburban Beiing (0.50-1.0; ~~Wang et al., 2018)~~(Wang et al., 2017b)) indicated more effective $ClNO_2$ production in suburban regions than urban regions to some extent. Indeed, the product of $\gamma_{N_2O_5}$ and ø ($\gamma_{N_2O_5}$ × ø) in this study ranged from 0.006-0.009 and was much lower than those in ~~Wang et al. (2018) (0.008-0.035).~~(Wang et al., 2017b) (0.008-0.035). We noticed that ø were much lower than those paramterized from Eq. (10) (0.55-0.97), indicating that the Bertram-Thornton parameterization scheme might overestimate the $ClNO_2$ yield substantially. Note that $\gamma_{N_2O_5}$ might be overestimated associated with an underestimation of ø if assuming particulate nitrate is completely from the N_2O_5 heterogeneous uptake. Possible contribution from gas-phase

HNO_3 repartitioning to the particulate phase was not considered mainly due to the lack of observational data for HNO_3 and NH_3. Indeed, a recent study found that the nocturnal nitrate formation potential by N_2O_5 heterogeneous uptake was comparable to that formed by gas-phase HNO_3 repartitioning in Beijing (Wang et al., 2017a). In addtion, $\gamma_{N_2O_5} \times \o$ was higher on 13 June than the other two days (e.g., 0.009 vs. 0.003-0.006), which might explain the corresondingly higher $ClNO_2/N_2O_5$ ratio in this day (on average 8.2 vs. 1.2-1.4). Our results overall suggest fast heterogeneous N_2O_5 uptake and high $ClNO_2$ production rate in summer in urban Beijing, which might have great implications for models to improve the simulations for nocturnal nitrate and daytime ozone.

4 Conclusions

We present the simultaneous measurement of gas-phase N_2O_5 and $ClNO_2$ by I-CIMS during the APHH summer campaign to investigate the nocturnal chemistry in urban Beijing. The average (±1σ) mixing ratios of N_2O_5 and $ClNO_2$ were 79.2 ± 157.1 pptv and 174.3 ± 262.0 pptv, with maximum values of 1.17 ppbv and 1.44 ppbv, respectively. Differing from previous studies with negligible N_2O_5 after midnight at surface level, our measurements showed high nocturnal levels of N_2O_5 across the entire night, suggesting a high oxidative capacity in summer in urban Beijing. N_2O_5 and $ClNO_2$ exhibited clear diurnal variations with significant nocturnal formation due to heterogeneous uptake. The average nighttime nitrate radical production rate $p(NO_3)$ was 2.6 ± 2.4 ppbv h^{-1}, and the $\tau(N_2O_5\cancel{)})^{-1}$ was in the range of $0.20\text{-}1.46\times10^{-2}$ s^{-1} corresponding to a nighttime N_2O_5 lifetime of 1.1-10.7 min. We also observed a decrease of $\tau(N_2O_5)$ under high relative humidity (RH > 40%) conditions due to the higher N_2O_5 uptake rates with higher available surface area and liquid water content. N_2O_5 and $ClNO_2$ were positively correlated, although the $ClNO_2/N_2O_5$ ratios changed significantly from 0.3 to 95.5. The high $ClNO_2/N_2O_5$ ratios in this study might result from high $ClNO_2$ production rate and fast N_2O_5 loss due to the sufficient chloride source supply.

The N_2O_5 uptake coefficients estimated on basis of the product formation rates of $ClNO_2$ and NO_3^- were 0.017-0.09 in this study. Correspondingly, the direct N_2O_5 loss rates via the heterogeneous uptake were in the range of 0.00044-0.0034 s^{-1}, contributing 6.9%-32.6% to the total N_2O_5 loss. Our results indicated fast N_2O_5 loss in the nocturnal boundary in urban Beijing was mainly due to the indirect pathways through NO_3 reactions with NO/VOCs rather than the heterogeneous uptake of N_2O_5. We also noticed that the derived $ClNO_2$ production yields (0.10-0.35) were substantially lower than those from the

Bertram-Thornton parameterization, indicating that future studies are needed to address these discrepancies.

Data availability. The data in this study are available from the authors upon request (sunyele@mail.iap.ac.cn).

Competing interests. The authors declare that they have no conflict of interest.

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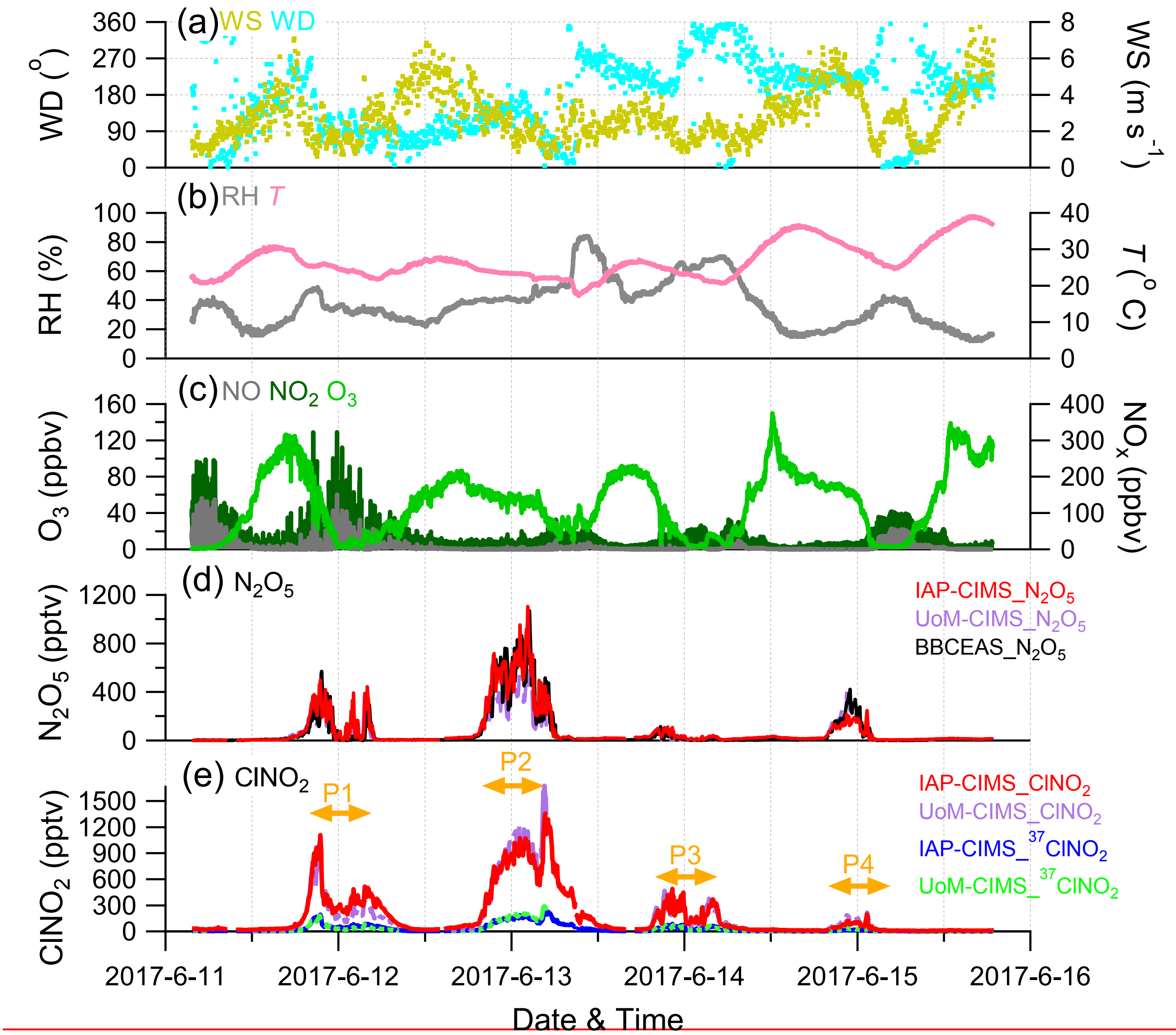
Table 1. Summary of average (±1σ) meteorological parameters (RH, *T*, WS), CIMS species (N_2O_5, $ClNO_2$, the calculated NO_3, nitrate radical production rate $p(NO_3)$, N_2O_5 ~~lifetime (τN_2O_5~~reactivity (τ$(N_2O_5)^{-1}$) and NO_3 ~~lifetime (τNO_3)),~~reactivity (τ$(NO_3)^{-1}$), trace gases (O_3, NO_2, NO), and NR-PM_1 species (NO_3^-, Cl^-) for the entire study and four nighttime periods (i.e., P1, P2, P3 and P4).

	Entire	**P1**	**P2**	**P3**	**P4**
Meteorological parameters					
RH (%)	36.8±15.9	36.3±5.5	41.3±2.5	60.5±6.5	28.0±7.0
T (°C)	26.7±4.9	24.5±1.1	23.2±0.7	23.2±1.4	29.4±2.4
WS (m s^{-1})	2.9±1.4	1.9±0.9	2.3±0.7	1.9±0.6	3.7±1.7
CIMS species					
N_2O_5 (pptv)	79.2±157.1	176.2±137.2	515.8±206.4	37.8±29.0	88.3±68.2
$ClNO_2$ (pptv)	174.3±262.0	427.3±222.5	748.3±220.6	227.7±103.7	57.2±39.0
NO_3(cal) (pptv)	8.9±15.7	7.2±7.3	48.1±26.2	2.0±2.3	18.2±15.2
P (NO_3) (ppbv h^{-1})	3.2±2.3	3.6±4.2	2.8±0.5	1.7±1.2	2.6±1.4
τ$(N_2O_5)^{-1}$ (s^{-1})	0.011±0.017	0.014±0.028	0.0016±0.0008	0.014±0.0063	0.016±0.011
τ$(NO_3)^{-1}$ (s^{-1})	0.34±0.87	0.62±1.66	0.021±0.017	0.42±0.21	0.29±0.30
Gaseous species					
O_3 (ppbv)	51.1±35.4	23.4±23.2	55.6±5.3	17.8±15.3	40.3±28.0
NO_2 (ppbv)	28.1±17.1	56.2±22.4	16.9±3.9	38.2±9.9	28.7±16.0
NO (ppbv)	8.7±16.9	15.6±14.6	0.5±0.7	2.3±3.5	7.1±13.3
NR-PM_1 species					
NO_3^-	2.7±2.4	2.3±1.5	4.3±0.7	4.3±1.6	0.6±0.2
Cl^-	0.10±0.16	0.13±0.14	0.09±0.02	0.08±0.09	0.04±0.07

Table 2. Estimated uptake coefficient of N_2O_5, $ClNO_2$ production yield and related parameters for the selected periods at three nights.

Period	**RH (%)**	**γN_2O_5**	**ø**	**K_d (s^{-1})**	**Percentage (%)**
Case1	39.9	0.017	0.35	0.00044	32.6
Case2	63.6	0.090	0.10	0.0034	20.8
Case3	21.1	0.019	0.15	0.00055	6.9


(a) WS WD
WD (°)
360
270
180
90
0
WS (m s^{-1})
8
6
4
2
0
(b) RH T
RH (%)
100
80
60
40
20
0
T (°C)
40
30
20
10
0
(c) NO NO_2 O_3
O_3 (ppbv)
160
120
80
40
0
NO_x (ppbv)
400
300
200
100
0
(d) N_2O_5
N_2O_5 (pptv)
1200
800
400
0
IAP-CIMS_N_2O_5
UoM-CIMS_N_2O_5
BBCEAS_N_2O_5
(e) $ClNO_2$
$ClNO_2$ (pptv)
1500
1200
900
600
300
0
P1
P2
P3
P4
IAP-CIMS_$ClNO_2$
UoM-CIMS_$ClNO_2$
IAP-CIMS_$^{37}ClNO_2$
UoM-CIMS_$^{37}ClNO_2$
2017-6-11
2017-6-12
2017-6-13
2017-6-14
2017-6-15
2017-6-16
Date & Time

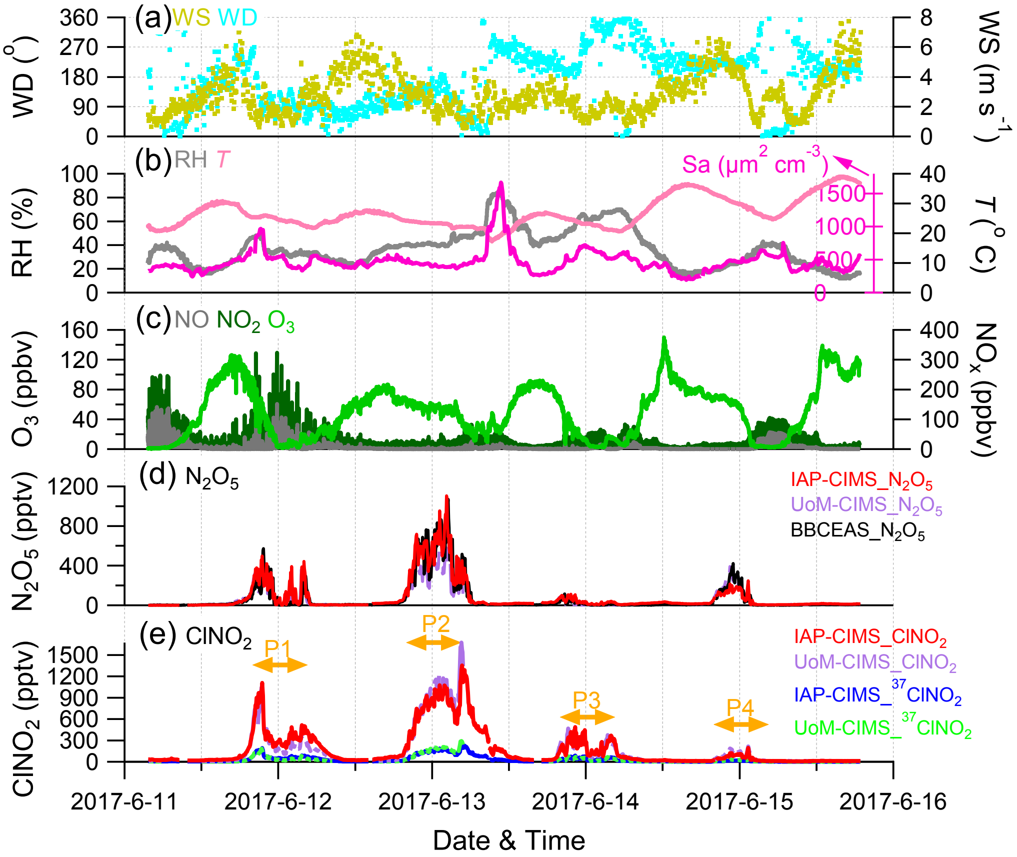
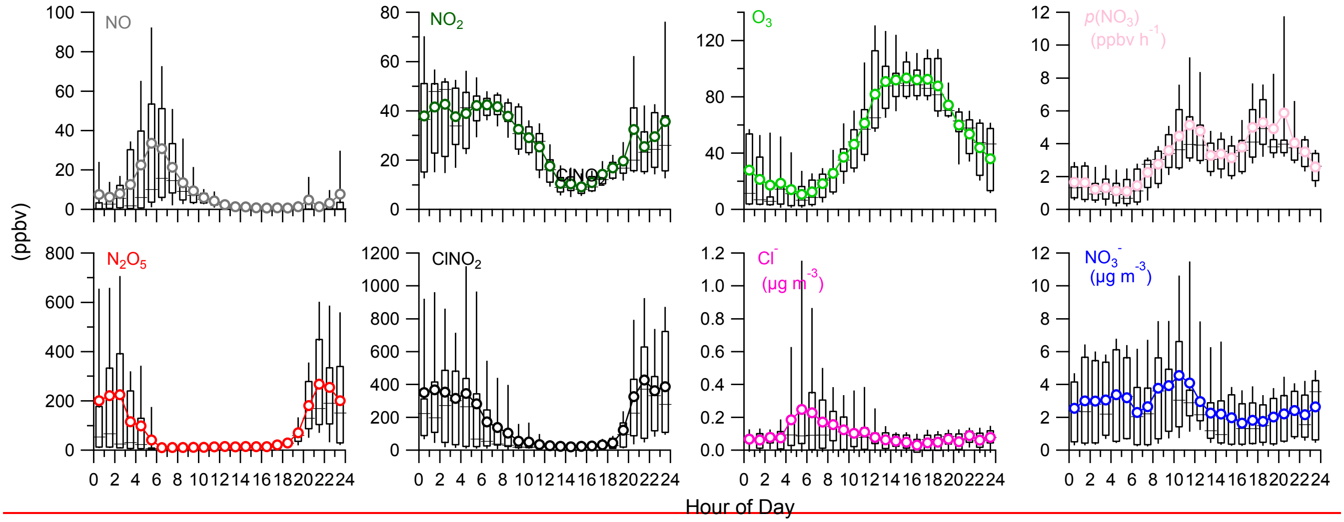


Figure 1. Time series of ~~trace gases (O_3, NO, NO_2),~~ (a-b) meteorological parameters (~~RH, *T*,~~ WS, WD~~),~~, RH, T) and surface area density (*S*a), (c) trace gases (O_3, NO, NO_2), (d-e) IAP-CIMS species (N_2O_5, $ClNO_2$). The UoM-CIMS and BBCEAS measurements are also shown for inter-comparisons. The four nights (i.e., P1, P2, P3 and P4) are marked for further discussions.



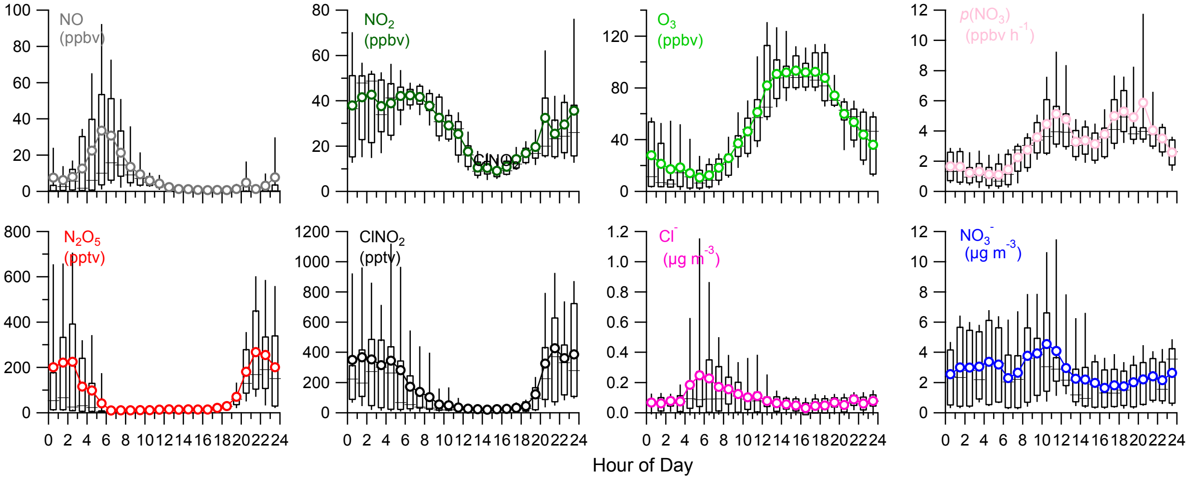


Figure 2. Diurnal variations of trace gases (NO, NO$_2$, O$_3$), IAP-CIMS species (N$_2$O$_5$, ClNO$_2$), nitrate radical production rate p(NO$_3$), and NR-PM$_1$ species (Cl$^-$~~;~~$^-$, NO$_3$$^-$~~).~~

$^{-}$).

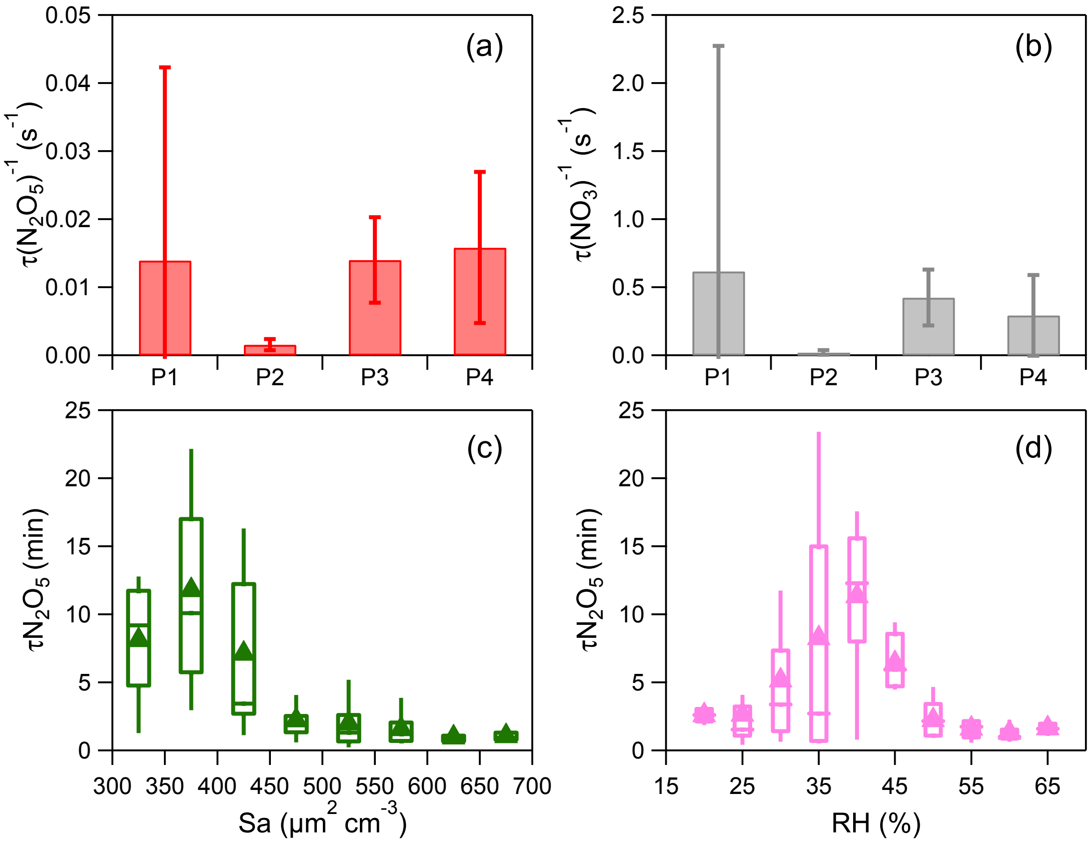
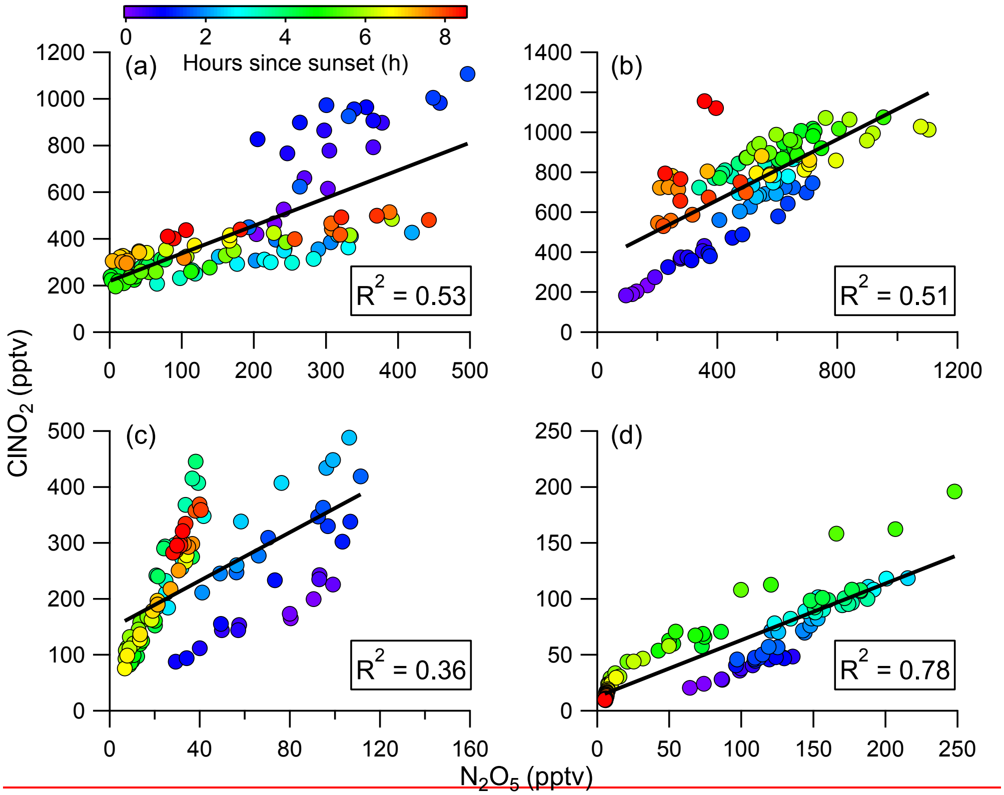


Figure 3. (a-b) Average reactivity of N_2O_5 ($\tau(N_2O_5$~~)~~$)^{-1}$) and NO_3 ($\tau(NO_3$~~)~~$)^{-1}$) for different nights (i.e., P1, P2, P3 and P4). The error bar represents the standard deviation, (c) Variations of the nocturnal $\tau(N_2O_5)$ as a function of aerosol surface area density (S_a), (d) Variations of the nocturnal $\tau(N_2O_5)$ as a function of relative humidity (RH). The data were binned according to S_a (50 μm^2 cm^{-3} increment) or RH (5% increment). Mean (triangle), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are shown for each bin.


0
2
4
6
8
Hours since sunset (h)
(a)
(b)
(c)
(d)
R^2 = 0.53
R^2 = 0.51
R^2 = 0.36
R^2 = 0.78
$ClNO_2$ (pptv)
N_2O_5 (pptv)
0
200
400
600
800
1000
1200
1400
100
300
500
50
150
250
40
80
120
160

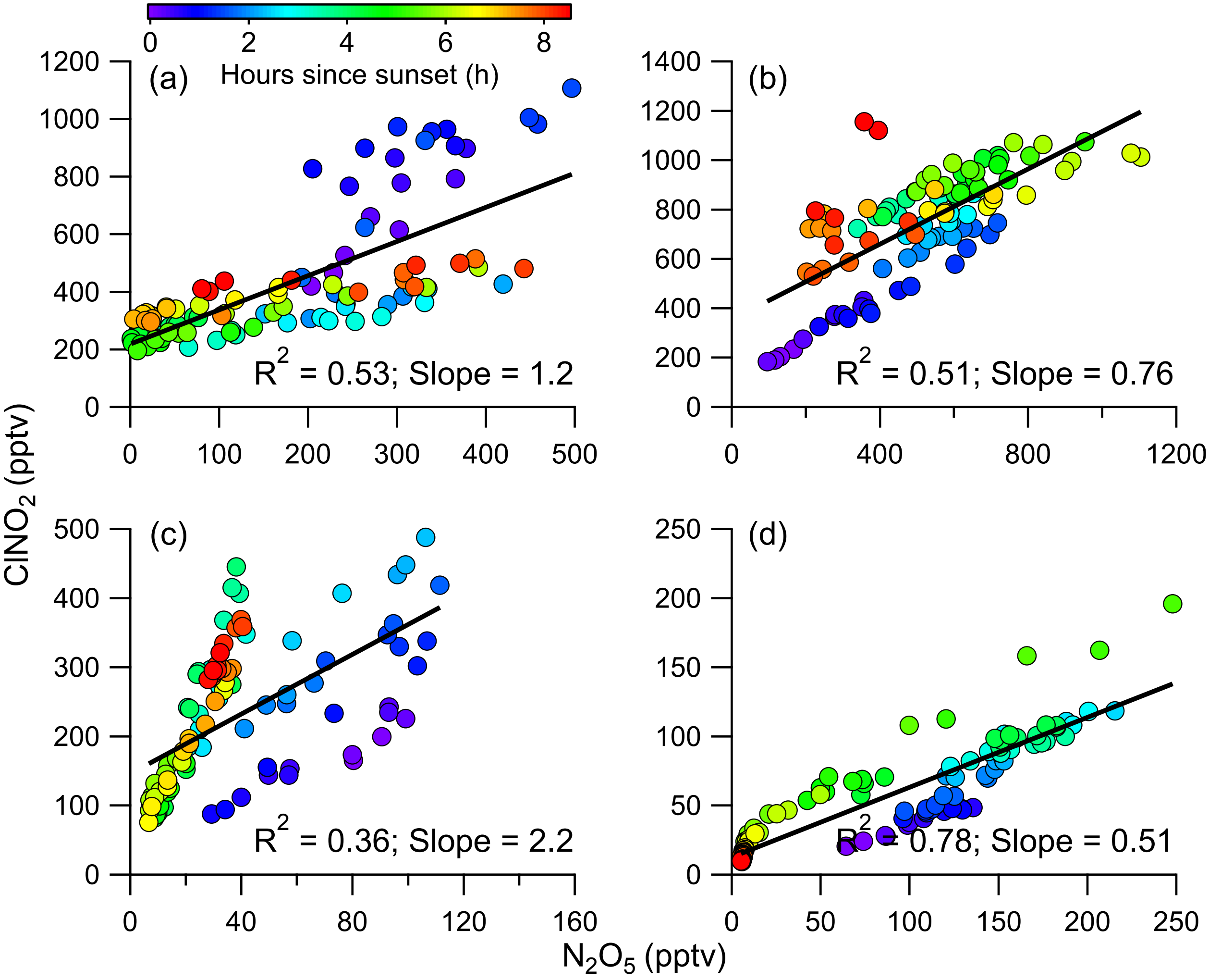


Figure 4. Correlations between ClNO$_2$ and N$_2$O$_5$ for four different nights, i.e., P1, P2, P3 and P4. The data are color-coded by the hours since sunset. Also shown are the correlation coefficients and slopes.

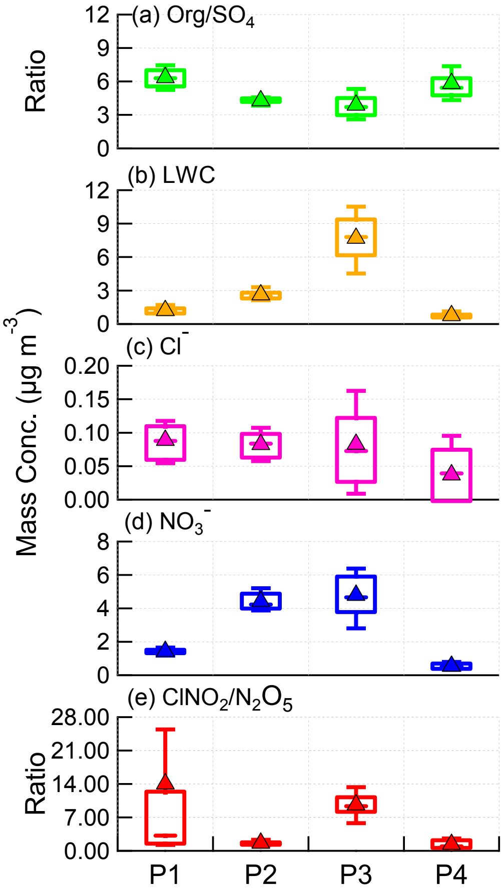


Figure 5. Box plots of (a) Org/SO_4 ratio, (b) LWC, (c) particulate chloride, (d) particulate nitrate, and (e) $ClNO_2/N_2O_5$ ratio for each night, i.e., P1, P2, P3 and P4. The mean (triangle), median (horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are shown.

5

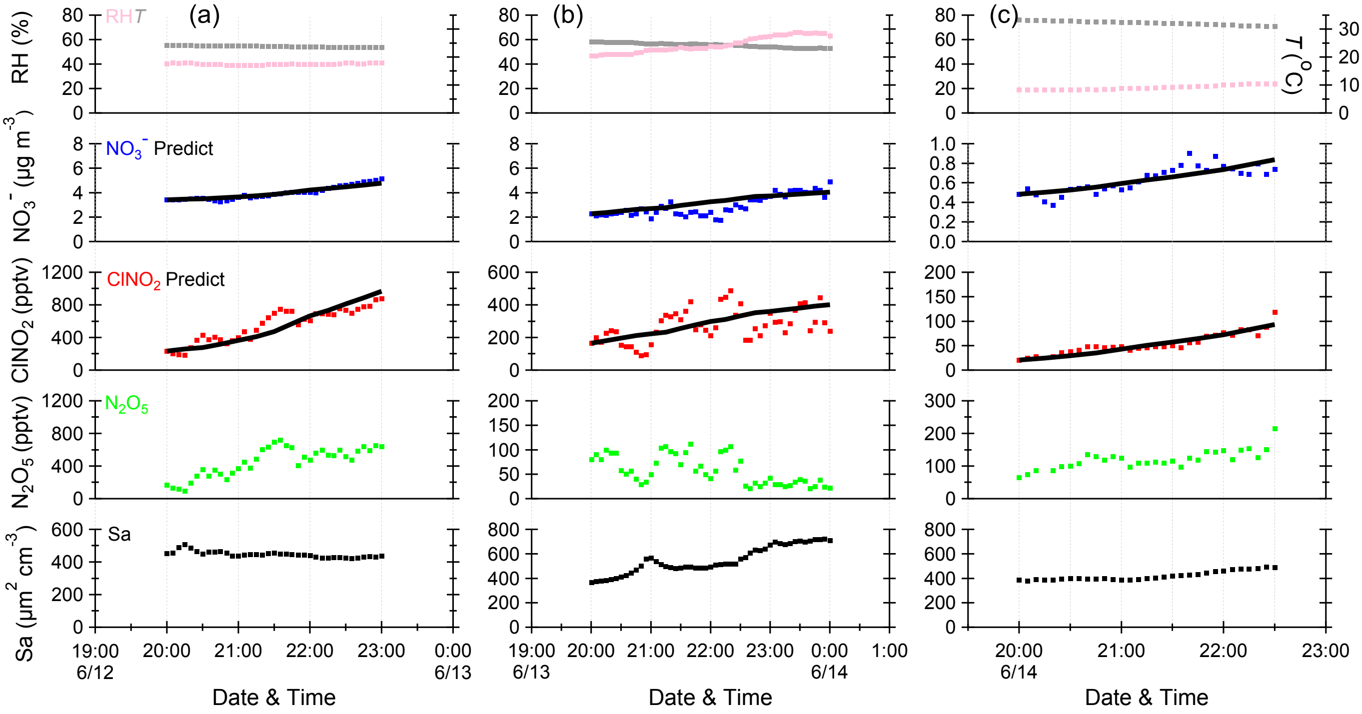


Figure 6. Time series of meteorological parameters (RH, T), particulate nitrate (NO$_3^-$~~),~~ $^-$), mixing ratios of N$_2$O$_5$ and ClNO$_2$, and aerosol surface area density (S_a) for the selected periods at three nights. The black solid lines are the predicted, integration concentrations of NO$_3^-$ and ClNO$_2$ calculated using the estimated method.