

Response to Referees

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

Referee #2

Wang et al present measurements of N_2O_5 , $ClNO_2$ and ancillary species in the urban outflow of Beijing and thereby analyze nocturnal rates of oxidation of VOCs, NO_x lifetimes and chlorine activation via heterogeneous reaction of N_2O_5 on chloride containing particles. N_2O_5 uptake coefficients were in the "usual" range and $ClNO_2$ yields were high, implying abundant sources of chlorine. The authors use established expressions to analyze their data and the manuscript contributes to the growing literature on nighttime VOC oxidation, NO_x loss and $ClNO_2$ formation without providing significant new insight. Detracting from this work, much of the referencing seems to be an arbitrary selection (often self-citation) of related work and the estimation (or presentation) of uncertainties in derived parameters is largely missing. The following points should be addressed (some are major) and the English language corrected (some suggestions are listed below) before re-review.

Thanks for the referee's careful and constructive comments. We checked and cited the references carefully in the revised manuscript. The uncertainties analysis was added as suggested.

1. L61 State how the yield of SOA (23.8 % or 174 %) is defined.

These are the mass yields, and we revised accordingly in the text. Change in the revised text: "The reaction of NO_3 with isoprene has a SOA mass yield of 23.8% (Ng et al., 2008). For the reaction with a monoterpene, such as limonene, the SOA mass yield can reach 174% at ambient temperatures (Boyd et al., 2017)."

2. L70 kN_2O_5 is not a rate coefficient. Its best to call it a pseudo-first order loss rate constant to avoid confusing it with rate constants for gas-phase reactions.

We change accordingly.

3. L70 Eq. (1) was certainly not derived by Tang et al in 2017. Use an appropriate (earlier) reference.

We cited the reference: “[Wahner et al., 1998](#)”.

4. L175 The correction factor of 0.6 (independent of time of day, day of campaign, NO_x , or air mass-age) is clearly a poor assumption given that the NO_x to NO_y ratio is highly variable in time and space. The assumption that the correction factor in Wangdu is the same as in Changping is without real basis. Note also that the photo-stationary state between NO , NO_2 and O_3 will break down in the presence of other oxidants (e.g. RO_2) so that measurement of NO and O_3 (and j - NO_2) cannot replace NO_2 measurements. The authors must estimate the uncertainty related to this correction factor (and thus with the NO_2 measurements) if they wish to use NO_2 data in any quantitative sense. This applies to section 4.2 where they calculate N_2O_5 lifetimes in steady state via calculation of the N_2O_5 production term, which requires NO_2 mixing ratios. It also applies to the calculation of NO_3 from the N_2O_5 and NO_2 measurements and the equilibrium constant and this impacts on the results of section 4.2 where NO_3 concentrations are used to calculate oxidation rates of VOCs. In principal, the lack of accurate NO_2 measurements during this campaign reduces many conclusions of this paper to a qualitative level.

According to the reviewer’s suggestions, we now extensively evaluated the influence of the uncertainty of the used NO_2 concentrations on the deduced VOCs (+ NO_3) and N_2O_5 reactivity.

Line 177: “The correction factor (0.6) used to be the averaged scaled value of the correction factors during nighttime, the standard deviation of the daytime correction factor for all the air masses experienced at Changping site was determined to be 0.27 (1σ), which extended to nighttime and result in an uncertainty of correction to be 45%. The uncertainty of NO_2 is therefore about 50% when further included the associated measurement uncertainty from calibrations.”

According to a Gaussian error propagation approach (see the following equations), the uncertainties of the calculated steady state lifetime, the overall $k(N_2O_5)$ and the NO_3 concentration were determined to be 67%, 95% and 67%, respectively.

We revised the paper correspondingly as follows:

Firstly, changed in line 242: “the uncertainty of NO₃ calculation was estimated to be 67% according to Eq. 2 which is dominated by uncertainty of the NO₂ concentrations.

$$\frac{\Delta[\text{NO}_3]}{[\text{NO}_3]} = \sqrt{\left(\frac{\Delta[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]}\right)^2 + \left(\frac{\Delta[\text{NO}_2]}{[\text{NO}_2]}\right)^2 + \left(\frac{\Delta[\text{O}_3]}{[\text{O}_3]}\right)^2 + \left(\frac{\Delta K_{\text{eq}}}{K_{\text{eq}}}\right)^2} \quad (\text{Eq. 2})$$

Secondly, the N₂O₅ loss rate constant was revised in Figure 7, the error bar was added to denote the uncertainties of N₂O₅ steady state loss constant and the overall N₂O₅ loss rate constant (as NO₂ concentration affected the contribution of NO₃ oxidation).

Changed in line 390: “Figure 7 shows the time series of the overall N₂O₅ loss rate constant as well as the N₂O₅ steady state loss rate constant. The overall N₂O₅ loss rate constant was calculated from the individual terms (Eq.3). The uncertainties of the N₂O₅ steady state loss rate constant and the overall k(N₂O₅) are estimated to be 67% and 95%, respectively (Eq. 7 and Eq. 8). The largest error sources were from the corrected NO₂ measurements so that it is really important to have accurate NO₂ measurement instrument involved in the future campaigns.

$$\frac{\Delta L_{\text{ss}}(\text{N}_2\text{O}_5)}{L_{\text{ss}}(\text{N}_2\text{O}_5)} = \sqrt{\left(\frac{\Delta[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]}\right)^2 + \left(\frac{\Delta[\text{NO}_2]}{[\text{NO}_2]}\right)^2 + \left(\frac{\Delta[\text{O}_3]}{[\text{O}_3]}\right)^2 + \left(\frac{\Delta K_{\text{eq}}}{K_{\text{eq}}}\right)^2} \quad (\text{Eq. 7})$$

$$\frac{\Delta k(\text{N}_2\text{O}_5)}{k(\text{N}_2\text{O}_5)} = \sqrt{\left(\frac{\Delta[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]}\right)^2 + \left(\frac{\Delta[\text{S}_a]}{[\text{S}_a]}\right)^2 + \left(\frac{\Delta[\gamma]}{[\gamma]}\right)^2 + \left(\frac{\Delta[\text{NO}_2]}{[\text{NO}_2]}\right)^2 + \left(\frac{\Delta[\text{O}_3]}{[\text{O}_3]}\right)^2 + \left(\frac{\Delta[\text{VOC}_s]}{[\text{VOC}_s]}\right)^2 + \left(\frac{\Delta K_{\text{eq}}}{K_{\text{eq}}}\right)^2} \quad (\text{Eq. 8})$$

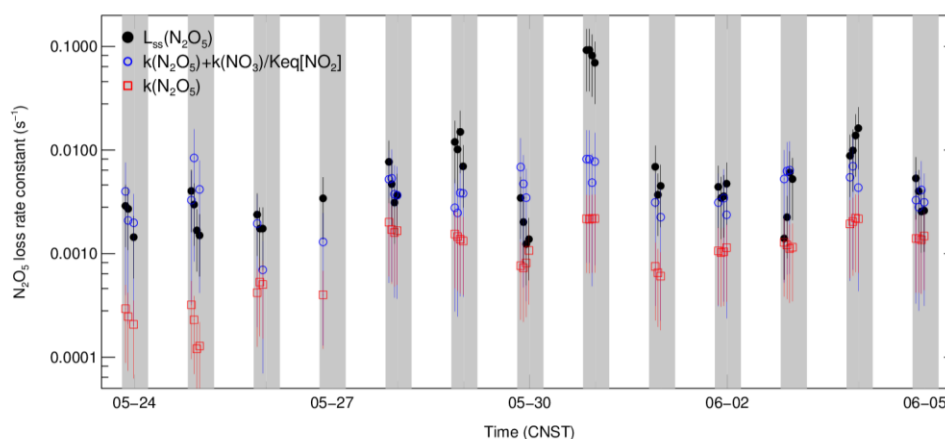


Figure 7. Time series of the individual N₂O₅ loss terms and the loss rate constant of N₂O₅ in steady state ($L_{\text{ss}}(\text{N}_2\text{O}_5)$).

Thirdly, the uncertainty of VOCs loss rate by NO₃ was added in the Figure 8. Changed in line 422: “Previous measurement indicated the main detectable monoterpenes were α-pinene and β-pinene in summer Beijing (personal communication with Ying Liu). Here we assumed α-pinene and β-pinene contributes

equally to the mixing ratios of the monoterpenes. The average value of the rate coefficients of α -pinene and β -pinene with NO_3 (Atkinson and Arey, 2003) was used as the rate coefficient of monoterpene with NO_3 . The uncertainty of the monoterpene + NO_3 rate coefficient in these air masses is thus estimated to be 50%. Since the uncertainty of calculated NO_3 is estimated to be 67%, the overall uncertainty of monoterpene reactivity toward NO_3 was calculated to be 85% according to a Gaussian propagation method, the uncertainties of other VOCs reactivity toward NO_3 was calculated to be 75% by assuming the uncertainties of the corresponding bimolecular rate constants to be 30%.”

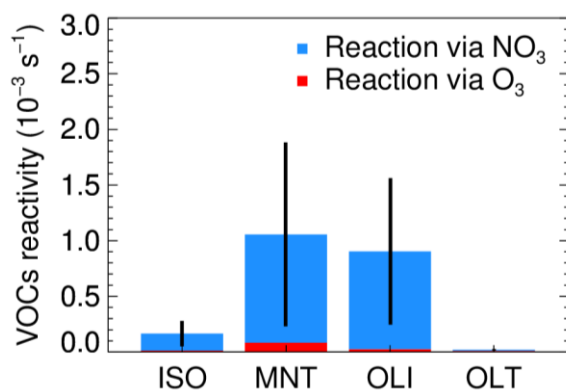


Figure 8. The nighttime VOCs reactivity of NO_3 and O_3 (defined as the pseudo first order loss rate of VOCs initiated by oxidants, include NO_3 and O_3); the VOCs classified as isoprene (ISO), monoterpene (MNT), the terminal alkenes (OLT) and the internal alkenes (OLI). The data were selected from 20:00 to the next day 04:00.

5. L191 “Figure 2 shows the calculated backward trajectories using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model”. As far as I can tell, this is the first and last mention of air-mass trajectories. I would suggest that the Figure can be relegated to the SI.

We changed accordingly.

6. L235 “The single peak (in N_2O_5) occurred near 20:00 and then gradually decreased“. Is this a reproducible feature of the campaign or a bias of the mean due to one or two events. Taking the median rather than the mean would resolve this. Also, why (line 236) does the N_2O_5 increase before sunrise (or do the authors mean “at sunrise“)?

Thanks for the suggestion, we checked the median value of N_2O_5 and NO_3 , the peak also occurred near 20:00. Therefore, we rewrote the description as following: “A peak occurred near 20:00 and decreased below the instrument detection limit at sunrise”. We corrected to “at sunrise” in Line 236 accordingly.

7. L243-246 “ClNO₂ accumulated corresponding to N₂O₅ after sunset but ClNO₂ peaked in the middle or the second half of the night since the nocturnal sinks of ClNO₂ were negligible to our knowledge.” I’m not sure what the authors are trying to say here.

We rewrote the sentence as following: “The observed ClNO₂ concentrations showed a clear increase after sunset and reached a maximum before sunrise for BAM period while reached a maximum around midnight for the UAM period.”

There are many examples that show great variability in the N₂O₅-to-ClNO₂ ratio. The interesting part of this section (lines 243 to 267) is the discussion of the sources of chloride needed to drive the ClNO₂ formation in this continental region. In principal, the chloride content of the aerosol can be calculated from the yield of ClNO₂ and the appropriate expression that defines the parameter "f". I suggest the authors do this.

Thanks for the suggestion. We added the following discussion in the revised text: “The required nocturnal source of Cl⁻ to support the ClNO₂ production is further estimated through its loss rate. The $\gamma \times f$ was set to the campaign average value (0.019) (see Sect. 4.1), and real-time Cl⁻ loss rate via N₂O₅ can be calculated based on the measured N₂O₅ and Sa by Eq.3.

$$L[Cl^-] = (\gamma \times f) \cdot \int_{t_{\text{sunset}}}^{t_{\text{sunrise}}} \frac{C \cdot S_a}{4} [N_2O_5] dt \quad (\text{Eq. 3})$$

Here the $L(Cl^-)$ denotes the integral Cl⁻ loss to form the ClNO₂ per night. The required source term of the Cl⁻ need to support the ClNO₂ formation during the campaign was range from (0.5 - 4.0 ppbv per night) with $(1.7 \pm 2.3 \text{ ppbv per night})$ on average. The gas phase HCl predicted by the ISORROPIA II model showed that the HCl concentration near sunset period was high enough (much larger than 2 ppbv) to support the ClNO₂ formation (Figure. S3).

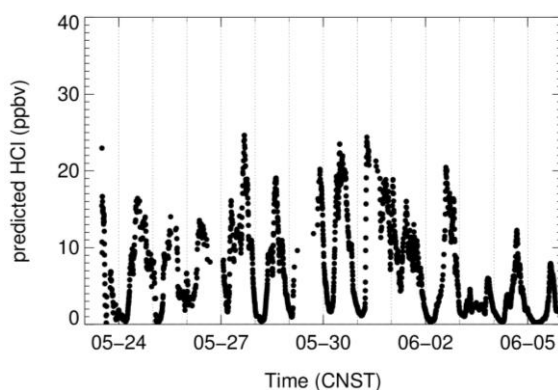


Figure S3. The predicted gas phase HCl concentrations by ISORRPIA II model.”

L249 and promoted the N_2O_5 conversion to $ClNO_2$ (e.g., Roberts et al., 2009). Why this citation? The formation of $ClNO_2$ from N_2O_5 was known (and quantified) long before 2009. Cite the appropriate literature.

Corrected the citation as following: “Finlayson-Pitts et al., 1989; Behnke et al., 1997”

8. L279 In lines 280-290. It is not clear whether we are dealing with ratios of the concentrations of $ClNO_2$ and N_2O_5 or ratios in their production rates (L282). If relative rates are calculated we need to know over which period they were derived.

The daily average or median ratio of the mixing ratio of $ClNO_2$ to N_2O_5 was calculated from 20:00 to the next day 04:00, and the ratio of their production rates was not calculated here.

Revised the description as following: “We used the concentration ratio of $ClNO_2$ to N_2O_5 , to describe the conversion capacity of N_2O_5 to $ClNO_2$. The nighttime peak values and mean values of $ClNO_2$: N_2O_5 were used to calculate the ratios are listed in Table S2, the calculation period is from 19:30 to the next day 05:00.”

9. L295 A composite term, $\gamma \times f$, was used to evaluate the overall $ClNO_2$ yield (f).

The sentence was rewrote as following: “A composite term, $\gamma \times f$, was used to evaluate the production of $ClNO_2$ from N_2O_5 heterogeneous hydrolysis (Mielke et al., 2013)”

10. L296 How and over what period was the production rate of $ClNO_2$ determined? How stable were N_2O_5 and S_a in this period? L296 the term was estimated by considering. Give the expression used to derive the composite term from the observables.

In the revised paper, we added the expression and the corresponding explanation to derive the composite term, $\gamma \times f$, as the following:

“The term, $\gamma \times f$, was estimated by fitting the observed $ClNO_2$ in a time period when the nighttime concentrations of $ClNO_2$ kept increasing. The increased $ClNO_2$ was assumed to be solely from the N_2O_5 uptake. The fitting was optimized by changing the input of $\gamma \times f$ associated with the measured N_2O_5 and S_a , until the $ClNO_2$ increasing was well reproduced (Eq. 4). Here t_0 and t denote the start time and end

time, respectively, $[\text{ClNO}_2](t_0)$ is the observed concentration at t_0 and set as the fitting offset. The calculation time duration was normally several hours, and the derived $\gamma \times f$ was found to be constant with small uncertainties for optimization (see Table S3) (e.g., a case showed in the following Figure A1). It is worth to be noticed that both the N_2O_5 and S_a is not necessary to be stable in this calculation due to the use of integration.

$$[\text{ClNO}_2](t) = [\text{ClNO}_2](t_0) + (\gamma \times f) \cdot \int_{t_0}^t \frac{C \cdot S_a}{4} [\text{N}_2\text{O}_5] dt \quad (\text{Eq. 4})$$

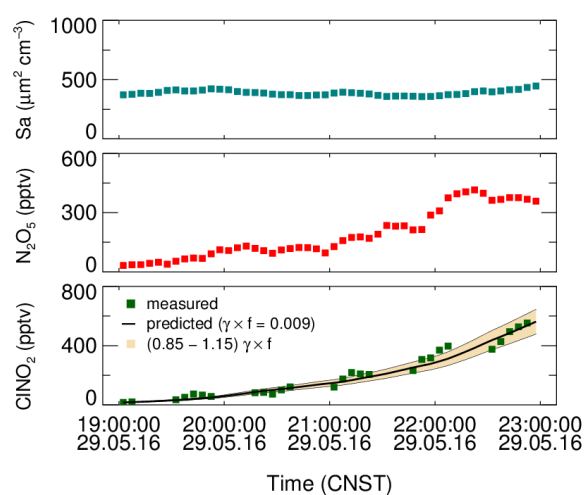


Figure A1. The reproduction of ClNO_2 by observed N_2O_5 and S_a .

11. L300 and 301 (and Table 3) the average values need to be listed with standard deviations to enable comparison. The same applies to Table 4.

The standard deviation of this study was added in both Table 3 and Table 4.

12. L313 uptake coefficients are derived from analysis of particulate nitrate and ClNO_2 concentrations. Only those nights were chosen when a clear covariance between these parameters was observed. The authors should explain how they define “clear covariance” and why, on other nights, covariance did not exist.

Here the “clear covariance” is pointing to the conditions when the square of the correlation coefficient is larger than 0.5 ($R^2 > 0.5$). Changed in line 313: “For some nights, significant correlations between pNO_3^- and ClNO_2 were presented ($R^2 > 0.5$); while on the other nights, the R^2 were always smaller than 0.2, which is not meet the theoretical hypothesis of this method. In this case, we chose the nights with high correlations.”

The reasons for the significant different correlations presented between the two groups of nights are still unclear. We did not find any observed parameters to explain the difference.

Surely the formation of $ClNO_2$ must always be accompanied by formation of particle nitrate? A major issue in this analysis is the assumption that the particulate nitrate is only formed from N_2O_5 uptake and not influenced by (temperature dependent) HNO_3 repartitioning. It appears that there were no measurements of gas-phase HNO_3 or ammonia to support the contentions that this was not important. The authors must assess this rigorously and state how the uptake coefficients would be influenced by HNO_3 uptake.

Unfortunately, we did not have the gas-phase HNO_3 or ammonia during this campaign. Our deduction on this point is as the follows,

Firstly, the daytime produced HNO_3 will soon be in equilibrium with the particulate nitrate within a time scale of about hundred seconds so that the daytime influence will be removed at the very beginning at night (cf. Figure A2, the observations of HNO_3 at summer Beijing in 2015).

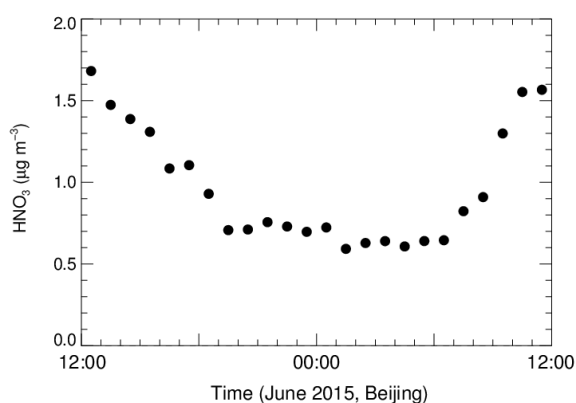


Figure A2. The mean diurnal variation of HNO_3 during a campaign conducted in June 2016 in urban Beijing.

Secondly, we think the nighttime production of HNO_3 is very small mainly due to the small nighttime OH concentrations. Since the available nighttime OH measurements were still under big discussions (e.g., Tan et al., ACP, 2017), we think the nighttime production of HNO_3 from $OH+NO_2$ can be neglected according to the modeled OH concentrations (of about $1 \times 10^5 \text{ cm}^{-3}$). Nevertheless, the unknown nighttime OH chemistry and the possible nighttime produced HNO_3 sheds an

uncertainty on our current analysis. The impact will be the possible overestimation of the uptake coefficient of N_2O_5 in the current analysis framework. We now extensively discussed the possible influence of the nighttime production of HNO_3 and repartitioning in the revised text as: “The daytime produced HNO_3 will be soon in a new equilibrium with the particulate nitrate within a time scale of about hundred seconds; the nighttime source of HNO_3 are normally negligible except there are significant unknown OH sources at night. Both the gas-particle repartitioning of HNO_3 and nighttime produced HNO_3 will result in the overestimation of γ and underestimation of f .”

Reference: Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häsel, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO_2 and RO_2 radicals, *Atmos. Chem. Phys.*, 17, 663-690, 10.5194/acp-17-663-2017, 2017.

13. L327 “the most rigorous analysis was used in this study”. I do not understand what this implies. Most rigorous compared to what?

In Phillips et al., (2016), the first and simplest method is to derive f only by using longer time periods (several hours or the whole night) where plots of ClNO_2 and NO_3^- are approximately linear. The second method is to calculate absolute production rates of NO_3^- and ClNO_2 in shorter periods (1-3 h), when NO_3^- and ClNO_2 concentrations both increase during a period of relatively constant composition and environmental variables, such as temperature and RH. In this case, values of pClNO_2 and pNO_3^- and average values of S_a and N_2O_5 are used to derive γ and f . The last and rigorous method is to avoid the use of the averaged S_a and N_2O_5 in the calculation, the measured N_2O_5 , ClNO_2 , S_a , R, T and NO_3^- were used directly in the calculation in a way of integration (the time step of the calculation were chose to be as small as possible, i.e., the time resolution of the associated measurement parameters). In this study, we used the last method to calculate the N_2O_5 uptake and ClNO_2 yield. In the revised manuscript, we changed the description and rewrote this part in line 349 as following: “Based on the observational data of N_2O_5 , ClNO_2 , pNO_3^- and S_a with the time resolution of 5 minutes, the formations of pNO_3^- and ClNO_2 were calculated and integrated to reproduce the increasing of pNO_3^- and ClNO_2 with estimated values for γ and f . The offset of particle nitrate and ClNO_2 is the measured particle nitrate and ClNO_2 concentration at the start time. The γ and f were optimized based on the

Levenberg-Marquardt algorithm until good agreement between the observed and predicted concentrations of pNO_3^- and ClNO_2 was obtained (Phillips et al., 2016).”

14. L330 Figure 6 would be improved by adding the result of a calculation with lower (factor two?) and higher (factor two?) uptake coefficients to test the sensitivity of the data to the derived parameter. Also, what is the source of the offset in the particle nitrate? How does the particle nitrate look over the diel period? This is essential information when trying to understand the effects of HNO_3 re-partitioning (see comment above).

Thanks for the suggestion, we estimated that the uncertainty of the determined N_2O_5 uptake coefficient was about 55% - 100% (55% shows below as Figure 5), and the scatter of the observed data points could then be explained by the uncertainty of the uptake coefficients. The offset of particle nitrate and ClNO_2 is the measured particle nitrate and ClNO_2 concentration at the start time point. Normally, the calculation period was the particle nitrate with increasing tendency. We checked the mean diurnal variation of particle nitrate (shows in the Figure A3), which is increased throughout the whole night and continued to the midday. The change of the particulate nitrate is not always follow the re-partitioning due to the temperature change. Nevertheless, we deduced that the impact of HNO_3 re-partitioning shall be small at night as presented in our answer to comment 12.

Changed in line 351: “The offset of particle nitrate and ClNO_2 is the measured particle nitrate and ClNO_2 concentration at the start time.”

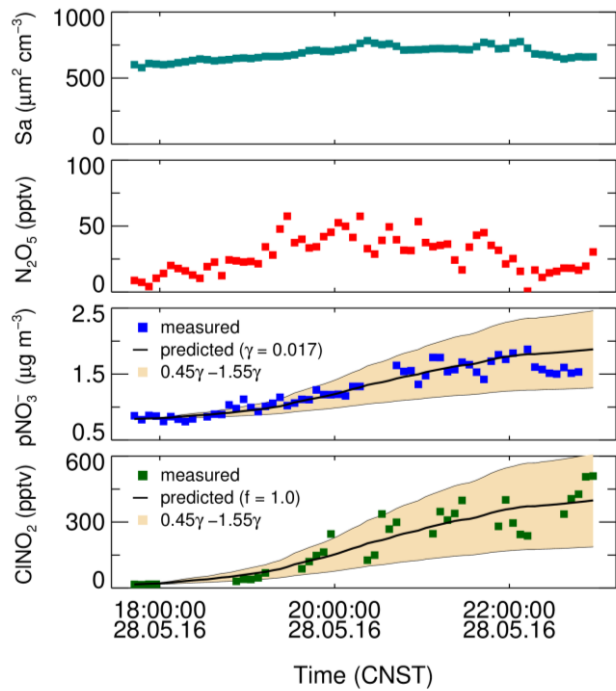


Figure 5. The best fit of γ and f to reproduce the observed ClNO_2 and pNO_3^- with an offset on May 28. The black lines are the predicted results of the integrated NO_3^- and ClNO_2 by using the observed S_a and N_2O_5 .

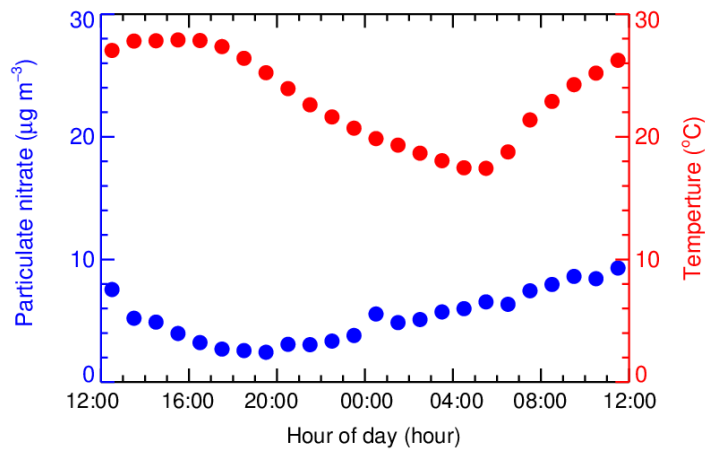


Figure A3. The mean diurnal variation of particulate nitrate during the campaign.

15. L331 “the predicted N_2O_5 uptake coefficient and ClNO_2 yield were 0.017 and 1.0, respectively.” What are the uncertainties?

The uncertainties added in Table 4, and we added the description: “The uncertainty on each individual fitting is varied from 55% - 100% due to the variability and measurements uncertainties of pNO_3^- and ClNO_2 .”

16. L334 “The errors from each derivation were 30% - 50% and came from the field measurements of S_a , N_2O_5 , pNO_3^- and $ClNO_2$.” Using the uncertainties listed in Table 1 results in total uncertainty (propagated in quadrature) of $> 50\%$. I do not understand how the quoted 30-50 % was derived.

As suggested, the propagated uncertainty was added up to 55% according to a Gaussian error propagation approach, here we corrected to “approximately 55%”.

17. L369 “The time periods with NO concentration larger than 0.1 ppbv were excluded”. Why was this threshold chosen? The lifetime of NO_3 at 0.1 ppbv of NO is about 10-20 s.

The data selection through NO concentrations is based on the assumption that the observed NO smaller than 0.1 ppbv are very small (close to zero). This assumption is plausible as shown by the following analysis. According to a histogram analysis of the observed NO and O_3 concentrations for the conditions of NO smaller than 0.1 ppbv (see the following figure A3), the O_3 concentrations are always larger than 10 ppbv and the NO concentrations are nicely fitting to the Gaussian Distribution, suggesting most of the NO concentration below 0.1 ppbv are instrument noise and the actual value shall be very close to zero. For more rigorous analysis, we constrain the NO concentration of 0.06 ppbv (instrument LOD) in the steady state analysis of the revised text.

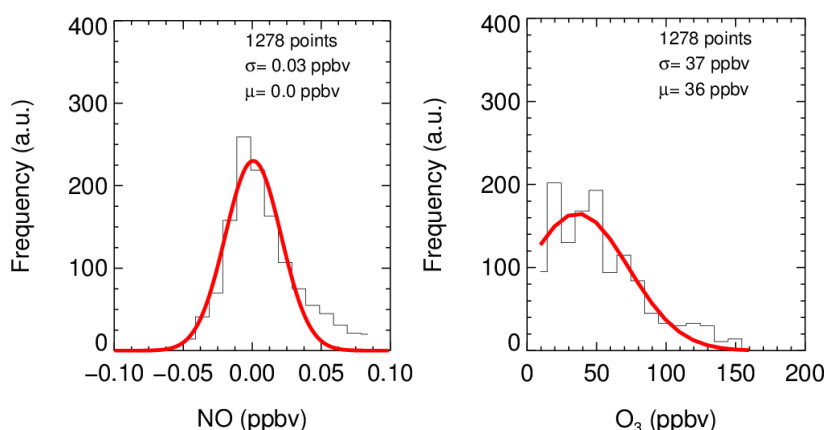


Figure A3. The histogram plot of measured NO concentration below 0.1 ppbv.

Changed line 369: “In this study, the steady state lifetime was only calculated from 20:00 to the next day 04:00. The time periods with NO concentration larger than 0.06 ppbv (instrument LOD) were excluded because the steady state is easily disturbed.”

Changed line 378: “The N₂O₅ steady state lifetime ranged from <5 s to 1260 s, with an average of 270 ± 240 s, and large variability was shown during the campaign.”

18. L389 the uncertainties in the N₂O₅ loss rate need to be calculated. As this involves NO₂ measurements, the uncertainty will be very large.

Added the following description in the revised text: “Figure 7 shows the time series of the overall N₂O₅ loss rate constant as well as the N₂O₅ steady state loss rate constant. The overall N₂O₅ loss rate constant was calculated from the individual terms (Eq.3). The uncertainties of the N₂O₅ steady state loss rate constant, the overall k(N₂O₅) are estimated to be 67% and 95%, respectively (Eq. 7 and Eq. 8). The largest error sources were from the corrected NO₂ measurements so that it is really important to have accurate NO₂ measurement instrument involved in the future campaigns.

$$\frac{\Delta L_{SS}(N_2O_5)}{L_{SS}(N_2O_5)} = \sqrt{\left(\frac{\Delta[N_2O_5]}{[N_2O_5]}\right)^2 + \left(\frac{\Delta[NO_2]}{[NO_2]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2 + \left(\frac{\Delta K_{eq}}{K_{eq}}\right)^2} \quad (\text{Eq. 7})$$

$$\frac{\Delta k(N_2O_5)}{k(N_2O_5)} = \sqrt{\left(\frac{\Delta[N_2O_5]}{[N_2O_5]}\right)^2 + \left(\frac{\Delta[S_a]}{[S_a]}\right)^2 + \left(\frac{\Delta[Y]}{[Y]}\right)^2 + \left(\frac{\Delta[NO_2]}{[NO_2]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2 + \left(\frac{\Delta[VOC_s]}{[VOC_s]}\right)^2 + \left(\frac{\Delta K_{eq}}{K_{eq}}\right)^2} \quad (\text{Eq. 8}).”$$

19. L403 This section deals with oxidation of VOCs and loss of NO_x to nitrates (inorganic and organic). NO₃ was not measured but calculated from N₂O₅ and NO₂ (the latter also not measured properly). The NO₃ concentrations derived are therefore associated with great uncertainty. This needs to be assessed and used in the subsequent discussion and comparison with O₃-induced oxidation.

We carefully performed the uncertainty analysis of the calculated NO₃ concentrations as suggested. We found the uncertainty of calculated NO₃ is 67% associated with the uncertainties of NO₂ and N₂O₅. We also added the following description in the revised text. Added in line 403: “Even the NO₃ concentration in the lower range, NO₃ still responsible for more than 70% nocturnal BVOCs oxidation. The results further confirmed that the oxidation of BVOCs is controlled by NO₃ rather than O₃ in summer Beijing.”

20. L416 Similar to k(OH). . . . I’m not sure why OH is being mentioned here.

Deleted the “Similar to k(OH),”.

21. L422 Terpenes were measured using PTRMS, i.e. no speciation. What is the basis

for assuming that alpha-pinene can be used as surrogate for NO₃ + terpene reactivity in these air masses?

The speciation measurements of monoterpene are still quite sparse in China. We have now discussed with an expert on this topic. We learnt that the major monoterpene species in Summer Beijing were α -pinene and β -pinene according to GC-MS measurements.

Changed in line 422: “Previous measurement indicated the main detectable monoterpenes were α -pinene and β -pinene in summer Beijing (personal communication with Ying Liu). Here we assumed α -pinene and β -pinene contributes equally to the mixing ratios of the monoterpenes. The average value of the rate coefficients of α -pinene and β -pinene with NO₃ (Atkinson and Arey, 2003) was used as the rate coefficient of monoterpene with NO₃. The uncertainty of the monoterpene + NO₃ rate coefficient in these air masses is thus estimated to be 50%.”

22. *Figure 9 Needs uncertainties on the two terms being compared.*

Thanks for the suggestion, we added the error bar in the Figure 9, the uncertainty of NO₃ calculation initiated by NO₂ was discussed in Question NO. 4

23. *Some (certainly not exhaustive) suggestions for improvement of the English. L18 Nocturnal reactive nitrogen compounds play an important role in regional air pollution*

Changed accordingly.

24. *L27 The concentration of the nitrate radical (NO₃) was calculated assuming that. . .*

Changed accordingly.

25. *L34 which indicates that reduction of NO_x emissions cannot help reduce the nocturnal formation of ONs.*

Changed accordingly.

26. *L42 NO₃ can initiate the removal of many kind of anthropogenic*

Changed accordingly.

27. L58 *the reactions of NO₃ with several BVOCs produce considerable amounts of organic nitrates.*

Changed accordingly.

28. L207. *Nocturnal nitrate radical production rate, P(NO₃), was large, with an average. . .*

Changed accordingly.

29. L61 *The reaction of NO₃ with isoprene has a SOA yield of 23.8% (Ng et al., 2008). For the reaction with a monoterpene, such as limonene, the yield can reach 174% at ambient temperatures (Boyd et al., 2017).*

Changed as following; “The reaction of NO₃ with isoprene has a SOA mass yield of 23.8% (Ng et al., 2008). For the reaction with monoterpene, such as limonene, the SOA mass yield can reach 174% at ambient temperatures (Boyd et al., 2017)”.

30. L97 *the reaction also contributed significantly to NO_x.*

Changed accordingly.

31. L259 *by acid displacement*

Changed accordingly.

32. L260 *“however, the photolysis with profound ClNO₂ was still maintained until noon“. I think the authors are trying to say that ClNO₂ survived until noon? In this context they should mention the J-values of ClNO₂.*

Yes, we are trying to say the ClNO₂ survived until noon. The campaign average J-values of ClNO₂ around noon is about $1.7 \times 10^{-4} \text{ s}^{-1}$. The text changed as following: “However, the ClNO₂ can still survive until noon with the averaged daily maximum of $J(\text{ClNO}_2)$ to be $1.7 \times 10^{-4} \text{ s}^{-1}$.”

33. L273-276. *This part needs rewriting. I think the gist if this is that the N₂O₅*

concentration depends on the NO₂ level more than on the O₃ concentration. If so, please explain why.

The sentence was rewritten as follows: “The N₂O₅ concentration was highly correlated with NO₂ ($R^2 = 0.81$) and the NO₃ production rate ($R^2 = 0.60$), suggesting the N₂O₅ concentration was solely a response to the NO₂ concentration in the background air mass when enough O₃ is present.”

34. L305. *Which implies that the ClNO₂ formation efficiency.*

Changed accordingly.

35. L403 *The title of this section is misleading. NO₃ is not oxidized, but the VOCs. I suggest “NO₃-induced nocturnal oxidation of VOCs” or similar.*

Thanks for the suggestion and changed accordingly.

36. L429 *for calculating nocturnal ONs production from NO₃ oxidation of isoprene and monoterpene, as well as inorganic nitrate production via N₂O₅ heterogeneous uptake over the same period.*

Changed accordingly.