Dear editor,

Thanks for your careful reading and the suggestion of the detailed corrections for improving our manuscript. We corrected accordingly and all revisions were labelled in red in the following differ version.

*Line 273, 308, 331 and 333, replace "transportation" with transport*
Corrected accordingly.

*Line 320, replace "others" with "other factors."*
Corrected accordingly.

*Line 333, replace "contrition" with "contribution"*
Corrected accordingly.

*Line 335, replace "accompanied" with "also observed"*
Corrected accordingly.

*Line 457, replace "the amount quantification uncertainty" with "an uncertainty"*
Corrected accordingly.

*Line 446, 472 and 810, replaced "initialed" with either "initialized" or "derived"*
Corrected accordingly.

# Efficient $N_2O_5$ Uptake and $NO_3$ Oxidation in the Outflow of Urban Beijing

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**Abstract.** Nocturnal reactive nitrogen compounds play an important role in regional air pollution. Here we present the measurements of dinitrogen pentoxide ($N_2O_5$) associated with nitryl chloride ($ClNO_2$) and particulate nitrate ($pNO_3^-$) in a suburban site of Beijing in the summer of 2016. High levels of $N_2O_5$ and $ClNO_2$ were observed in the outflow of the urban Beijing air masses, with 1-min average maxima of 937 pptv and 2900 pptv, respectively. The $N_2O_5$ uptake coefficients, $\gamma$, and $ClNO_2$ yield, $f$, were experimentally determined from the observed parameters. The $N_2O_5$ uptake coefficient ranged from 0.012 to 0.055, with an average of 0.034 ± 0.018, which is in the upper range of previous field studies reported in North America and Europe but is a moderate value in the North China Plain (NCP), which reflects efficient $N_2O_5$ heterogeneous processes in Beijing. The $ClNO_2$ yield exhibited high variability, with a range of 0.50 to unity and an average of 0.73 ± 0.25. The concentration of the nitrate radical ($NO_3$) was calculated assuming that the thermal equilibrium between $NO_3$ and $N_2O_5$ was maintained. In $NO_x$-rich air masses, the oxidation of nocturnal biogenic volatile organic compounds (BVOCs) was dominated by $NO_3$ rather than $O_3$. The production rate of organic nitrate (ON) via $NO_3$+BVOCs was significant, with an average of 0.10 ± 0.07 ppbv $h^{-1}$. We highlight the importance of $NO_3$ oxidation of VOCs in the formation of ON and subsequent secondary organic aerosols in summer in Beijing.

## 1. Introduction

It has been well recognized that reactive nitrogen compounds, specifically the nitrate radical ($NO_3$) and dinitrogen pentoxide ($N_2O_5$), play a key role in nighttime chemistry (Wayne et al., 1991; Brown and Stutz, 2012). $NO_3$ is the most important oxidant in the nighttime and can be considered the nighttime analogue of the hydroxyl radical (OH) for certain VOCs (Wayne et al., 1991; Benton et al., 2010). $NO_3$ can initiate the removal of many kind of anthropogenic and biogenic emissions after sunset. In $NO_x$-rich plumes, $NO_3$ is responsible for the vast majority of the oxidation of biogenic VOCs because of its rapid reactions with unsaturated hydrocarbons (Edwards et al., 2017). $NO_3$ is predominantly formed by the reaction of $NO_2$ with $O_3$ (R1) and further reacts with $NO_2$ to produce $N_2O_5$ (R2). $N_2O_5$ is rapidly decomposed back to $NO_3$ (R3), $NO_3$ and $N_2O_5$ are in dynamic equilibrium in the troposphere.

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

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad \text{(R2)}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \quad \text{(R3)}$$

Photolysis of $NO_3$ and the reaction of $NO_3$ with NO are rapid, which lead to a daytime $NO_3$ lifetime being shorter than 5 s with extremely low concentrations, whereas in low-NO air masses, the fate of $NO_3$ is mainly controlled by the mixing ratios of various VOCs and $N_2O_5$ heterogeneous hydrolysis because the two terms are the dominating loss pathways of $NO_3$ and $N_2O_5$. The VOCs reaction is significant downwind of an urban area or a strongly urban-influenced forested area in summer. The $NO_3$ oxidation of VOCs was responsible for more than 70% nocturnal $NO_3$ loss in Houston (Stutz et al., 2010) and contributed approximately 50% in the forest region in Germany (Geyer et al., 2001). The reactions of $NO_3$ with several BVOCs produce considerable amounts of organic nitrates (ON) with efficient yields, which act as important precursors of secondary organic aerosols (SOA). The reaction of $NO_3$ with isoprene has a SOA mass yield of 23.8% (Ng et al., 2008). For the reaction with monoterpene, such as limonene, the SOA mass yield can reach 174% at ambient temperatures (Boyd et al., 2017). The reactions of $NO_3$+BVOCs are critical to the studies of aerosols on regional and global scales (Fry et al., 2009; Rollins et al., 2009; Pye et al., 2010; Ng et al., 2017). For example, ON had extensive percentages of fine particulate nitrate ($pNO_3^-$) (34% - 44%) in Europe (Kiendler-Scharr et al., 2016).

The heterogeneous hydrolysis of $N_2O_5$ produces soluble nitrate ($HNO_3$ or $NO_3^-$) and nitryl chloride ($ClNO_2$) on chloride-containing aerosols (R4) (Finlayson-Pitts et al., 1989). This reaction is known to be an important intermediate in the $NO_x$ removal processes (Brown et al., 2006). The pseudo-first order loss rate constant of $N_2O_5$ via heterogeneous uptake is given in Eq. 1 (Wahner et al., 1998).

$$N_2O_5 + (H_2O \text{ or } Cl^-) \rightarrow (2 - f)\, NO_3^- + f\, ClNO_2 \quad \text{(R4)}$$

$$k_{N2O5} = 0.25 \cdot c \cdot \gamma(N_2O_5) \cdot S_a \quad \text{(Eq. 1)}$$

Where $c$ is the mean molecule speed of $N_2O_5$, $S_a$ is the aerosol surface concentration and $\gamma(N_2O_5)$ is the $N_2O_5$ uptake coefficient. $N_2O_5$ heterogeneous hydrolysis is one of the major uncertainties of the $NO_3$ budget since the $N_2O_5$ uptake coefficient can be highly variable and difficult to quantify (Brown and Stutz, 2012; Chang et al., 2011; H. C. Wang et al., 2016). Laboratory and field measurement studies

have reported that the $N_2O_5$ uptake coefficient has large variability and ranges from <0.001 to 0.1; the $N_2O_5$ uptake coefficient depends on relative humidity (RH), particle morphology, compositions (water content, nitrate, sulfate, organic or mineral particles) and other factors (Wahner et al., 1998; Mentel et al., 1999; Hallquist et al., 2003; Thornton et al., 2003; Thornton et al., 2005; Brown et al., 2006; Bertram and Thornton, 2009; Tang et al., 2012, 2014; Gaston et al., 2014; Grzinic et al., 2015; Tang et al., 2017). The coupled chemical mechanisms in ambient conditions are still not well understood. $ClNO_2$ forms and accumulates with a negligible sink during the night and further photolyzes and liberates the chlorine radical (Cl) and $NO_2$ after sunrise. Hundreds of pptv to ppbv of $ClNO_2$ can lead to several ppbv of $O_3$ enhancement and significant primary $RO_x$ production (Osthoff et al., 2008; Thornton et al., 2010; McLaren et al., 2010; Riedel et al., 2014; Sarwar et al., 2014; Tham et al., 2016).

Large amounts of $NO_x$ have been emitted for the past several decades in China, but comprehensive field studies of the nighttime chemical processes of reactive nitrogen oxides remain sparse. Previous studies have found high mixing ratios of $NO_3$ associated with high $NO_3$ reactivity in the megacities in China, including Shanghai, the Pearl River Delta (PRD) and Beijing (Li et al., 2012; Wang et al., 2013; Wang et al., 2015). The $N_2O_5$ concentration was elevated in Beijing (H. C. Wang et al., 2017a; H. C. Wang et al., 2017c) but was moderate in other places of North China Plain (NCP), such as Wangdu, Jinan and Mount Tai (Tham et al., 2016; X. F. Wang et al., 2017; Z. Wang et al., 2017). Recently, the $N_2O_5$ uptake coefficients were determined to be very high, even up to 0.1 in NCP, but the reason is still not well studied (H. C. Wang et al., 2017c; X. F. Wang et al., 2017; Z. Wang et al., 2017). Reactive $N_2O_5$ chemistry was also reported in Hong Kong, and showed the highest field-observed $N_2O_5$ concentration to date (T. Wang et al., 2016; Brown et al., 2016). Observations and model simulations revealed that fast heterogeneous uptake of $N_2O_5$ is an important pathway of $pNO_3^-$ formation in China (H. C. Wang et al., 2017b; H. C. Wang et al., 2017c; Z. Wang et al., 2017; Su et al., 2017); the reaction also contributed significantly to removal (Z. Wang et al., 2017; Brown et al., 2016). Moreover, chlorine activation from $N_2O_5$ uptake had a significant effect on daytime photolysis chemistry in China (Xue et al., 2015; Li et al., 2016; Tham et al., 2016; T. Wang et al., 2016).

In this study, to quantify the contribution of $NO_3$ and $N_2O_5$ chemistry to the atmospheric oxidation capacity and the $NO_x$ removal process in the outflow of urban Beijing, we report the measurement of $N_2O_5$, $ClNO_2$, and related species in the surface layer of a suburban site in Beijing and determine the $N_2O_5$ heterogeneous uptake coefficients and $ClNO_2$ yields. The nighttime $NO_3$ oxidation of biogenic VOCs and its impact on the ON formation in the $NO_x$-rich region were diagnosed. Finally, the nighttime $NO_x$ removal via $NO_3$ and $N_2O_5$ chemistry was estimated and discussed.

## 2. Method

### 2.1 The site

Within the framework of a Sino-Sweden joint research project, “Photochemical Smog in China”, a summer field campaign was conducted in Beijing to enhance our understanding of the secondary chemistry via photochemical smog and the heterogeneous reactions (Hallquist et al., 2016). The data presented here were collected at a regional site, PKU-CP (Peking University Changping campus), from 23 May to 5 June 2016. The measurement site is located in the northern rural area of Beijing, approximately 45 km from the city center; the closest road is approximately 1 km to the south, and there are no major industry in the surroundings (Figure. 1). The site is surrounded to the north, east

and west by mountains. The general feature of this site is that it captures air masses with strong influences from both urban and biogenic emissions. Instruments were set up on the fifth floor of the main building of the campus with inlets approximately 12 m above the ground. Time is given in this paper as CNST (Chinese National Standard Time = UTC+8 h). During the campaign, sunrise was at 05:00 CNST and sunset was at 19:30 CNST.

## 2.2 Instrument setup

A comprehensive suite of trace gas compounds and aerosol properties was measured in the field study, and the details are listed in Table 1. $N_2O_5$ was measured by a newly developed cavity enhanced absorption spectrometer (CEAS; H. C. Wang et al., 2017a). In the CEAS, ambient $N_2O_5$ was thermally decomposed to $NO_3$ in a perfluoroalkoxy alkanes (PFA) tube (length: 35 cm, I.D.: 4.35 mm) heated to 120 °C and was then detected within a PFA resonator cavity; the cavity was heated to 80 °C to prevent $NO_3$ reacting back to $N_2O_5$. Ambient gas was sampled with a 1.5-m sampling line (I.D.: 4.35 mm) with a flow rate of 2.0 L $min^{-1}$. NO was injected for 20 seconds to destroy $NO_3$ from $N_2O_5$ thermal decomposition in a 5-minute cycle, and the corresponding measurements were then used as reference spectra. A Teflon polytetrafluoroethylene (PTFE) filter was used in the front of the sampling module to remove ambient aerosol particles. The filter was replaced with a fresh one every hour to avoid the decrease of $N_2O_5$ transmission efficiency due to aerosol accumulation on the filter. The limit of detection (LOD) was 2.7 pptv (1σ), and the measurement uncertainty was 19%.

$ClNO_2$ and $N_2O_5$ were also detected using a Time of Flight Chemical Ionization Mass Spectrometer (ToF-CIMS) with the Filter Inlet for Gas and AEROsols (FIGAERO; Lopez-Hilfiker et al., 2014; Bannan et al., 2015). Briefly, the gas phase species were measured via a 2-m-long, 6-mm-outer-diameter PFA inlet while the particles were simultaneously collected on a Teflon filter via a separate 2-m-long, 10-mm-outer-diameter copper tubing inlet; both had flow rates of 2 L $min^{-1}$. The gas phase was measured for 25 minutes at 1 Hz, and the FIGAERO instrument was then switched to place the filter in front of the ion molecule region; it was then heated incrementally to 200 °C to desorb all the mass from the filter to be measured in the gas phase, which resulted in high-resolution thermograms. Formic acid calibrations were performed daily using a permeation source maintained at 40 °C. Post-campaign laboratory calibrations of $N_2O_5$ were first normalized to the campaign formic acid calibrations to account for any change in sensitivity (Le Breton et al., 2014). Then, $ClNO_2$ measurements were quantified by passing the $N_2O_5$ over a wetted NaCl bed to produce $ClNO_2$. The decrease in $N_2O_5$ from the reaction with NaCl was assumed to be equal to the concentration of $ClNO_2$ produced (i.e., 100% yield). The sensitivities of the CIMS to $N_2O_5$ and $ClNO_2$ were found to be 9.5 and 1.2 ion counts per pptv $Hz^{-1}$, respectively, with errors of 23% and 25% for $ClNO_2$ and $N_2O_5$, respectively. The LOD for $ClNO_2$ and $N_2O_5$ were 16 and 8 pptv, respectively. An intercomparison of $N_2O_5$ measurements between the CEAS and FIGAERO-ToF-CIMS showed good agreement; a companion paper on chlorine photochemical activation during this campaign gives detailed intercomparison results of $N_2O_5$ measured by the two different techniques (Le Breton et al., 2018).

Sub-micron aerosol composition ($PM_{1.0}$), including nitrate, sulfate, chloride, ammonium and organic compounds, were measured by a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (De Carlo et al, 2006, Zheng et al., 2017). Particle number and size distribution (PNSD) was measured by a scanning mobility particle sizer (SMPS, TSI 3936) and an aerosol particle

sizer (APS, TSI 3321) (Yue et al., 2009). SMPS measured the particles in the range between 3.5 nm and 523.3 nm in diameter, and APS measured the particles with a diameter range from 597.6 nm to 10.0 μm. $S_a$ was calculated based on the dry-state particle number and geometric diameter in each size bin (3.5 nm - 2.5 μm). Dry-state $S_a$ was corrected to wet particle-state $S_a$ for particle hygroscopicity by a growth factor. The growth factor, $f(RH)=1 + 8.77 \times (RH/100)^{9.74}$, was derived from the measurement of aerosol extinction as a function of RH in autumn in Beijing and is valid for 30% < RH < 90% (Liu et al., 2013). The uncertainty of the wet aerosol surface areas was estimated to be ~30%, associated from the error from dry PNSD measurement (~20%) and the growth factor (~20%). During this measurement, fine particles below 500 nm contributed to more than 90% of the total $S_a$.

VOCs were measured by Proton Transfer Reaction Mass Spectrometry (PTR-MS) with a time resolution of 5 minutes (de Gouw and Warneke et al., 2007; Wang et al., 2014). A commercial instrument (Thermo Electron model 42i) equipped with a molybdenum-catalytic converter was used to monitor $NO_x$. The LODs were 60 pptv (1 min) for NO and 300 pptv (1 min) for $NO_2$, with both at a 20% precision (Tan et al., 2017). The molybdenum-catalytic technique not only converts $NO_2$ to NO but also converts ambient $NO_y$ such as peroxyacetyl nitrate (PAN) and $HNO_3$. Therefore, the measured $NO_2$ concentration corresponded to $NO_2 + NO_y$ and was normally higher than the real concentration, especially in an aged air mass with high $NO_x$ conditions. In this study, we used a factor of 0.6 to correct the nighttime $NO_2$ concentration (a detailed explanation is in the Support Information Text S1 and Figure S1). The correction factor (0.6) is the average 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). If this uncertainty is extended to the nighttime correction factor, the resulting uncertainty of the nighttime correction is 45%. The uncertainty of $NO_2$ is 50% when further included the associated measurement uncertainty from calibrations. $O_3$ was measured by a commercial instrument using ultraviolet (UV) absorption (Thermo Electron model 49i); the LOD was 0.5 ppbv, with an uncertainty of 5%. The mass concentration of $PM_{2.5}$ was measured using a standard Tapered Element Oscillating Microbalance (TEOM, 1400A analyzer). Meteorological parameters included relative humidity, temperature, pressure, wind speed, and wind direction and were available during the campaign. Photolysis frequencies were calculated from the spectral actinic photon flux density measured by a spectroradiometer (Bohn et al., 2008).

## 3. Results

### 3.1 Overview

During the campaign, the meteorological conditions of the site was high temperature and low relative humidity (RH); the temperature ranged from 10 - 34 °C and was 23 ± 5 °C on average, and RH ranged from 10% - 80%, with an average of 37% ± 15%. Because of the special terrain of the observation site, the local wind was measured by the in situ meteorological stations; the site has a typical mountain-valley breeze that cannot reflect the general air mass movement patterns at slightly higher altitudes. Figure S2 shows the calculated backward trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). These images show the 24-h backward particle dispersion trajectories for 12:00 local time (CNST) as the starting time during May 23 - July 5, 2016. The arrivals of air masses were mainly from the northwest and the south. Therefore,

we meteorologically separated the measurement period into two parts. The first three days show that the air masses came from the north or northwest; the air masses represent the background region (defined as Background Air Mass, BAM). The air masses after May 26 originated from the polluted NCP and passed over urban Beijing; they were characterized by large $NO_x$ emissions and severe photochemical pollution (defined as Urban Air Mass, UAM).

The time series of $N_2O_5$, $ClNO_2$ and other relevant species are shown in Figure 2, and nighttime statistical results are listed in Table S1. The daily 8-h maximum of $O_3$ concentration exceeded 93 ppbv (Chinese national air quality standard) for 8 of 12 days, and all the $O_3$-polluted air masses came from the urban region. When the air masses were from the background region, the daily maximum of $O_3$ was only approximately 60 ppbv, much lower than that from the urban region. The $NO_2$ concentration was elevated, with a nocturnal average value over 10 ppbv during the urban air mass period. The nocturnal nitrate radical production rate, $P(NO_3)$, was large, with an average of 1.2 ± 0.9 ppbv $h^{-1}$, which is comparable with rates previously reported in the NCP and Hong Kong (Tham et al., 2016; Brown et al., 2016; Z. Wang et al., 2017; X. F. Wang et al., 2017). The daily peaks of $N_2O_5$ were 100-500 pptv most nights; the maximum of 937 pptv in a 1-min average was observed near 20:00 on the early night of June 2, when the $P(NO_3)$ was up to 4 ppbv $h^{-1}$. The average mixing ratio of $N_2O_5$ was 73 ± 90 pptv, which is much higher than recent measurements reported in North China (Tham et al., 2016; X. F Wang et al., 2017; Z. Wang et al., 2017), but much lower than that observed in the residual layer of the outflow from the PRD region, where the $N_2O_5$ was up to 7.7 ppbv (T. Wang et al., 2016). With an elevated $O_3$ mixing ratio in the first half of the night, the NO lifetime was only several minutes, and the mixing ratio of NO concentration was observed below the detection limit. During the second half of the night when the $O_3$ concentration was consumed to low concentration, high levels of NO could occasionally be observed, and $N_2O_5$ dropped to zero because of the fast titration by NO, such as the events that occurred on the second half of the nights of May 24, 28, 30. The $PM_{2.5}$ mass concentration was moderate during the measurement period, with an average of 26 ± 21 μg $m^{-3}$, and the average $S_a$ was 560 ± 340 $\mu m^2$ $cm^{-3}$. Elevated $ClNO_2$ was observed with a daily maximum over 800 pptv (1-min average) during the urban air masses period. The maximum of $ClNO_2$ was observed with 2900 pptv on the morning (05:30) of May 31. The observed $ClNO_2$ in Beijing was comparable with those reported in NCP (Tham et al., 2016; X. Wang et al., 2017; Z. Wang et al., 2017), but slightly higher than that measured in coastal (e.g., Osthoff et al., 2008) and inland sites (e.g., Thornton et al., 2010). Overall, high $ClNO_2$ observed in this site suggested fast $N_2O_5$ heterogeneous hydrolysis and effective $ClNO_2$ yields are common in Beijing.

### 3. 2 Mean diurnal profiles

The mean diurnal profiles of the measured $NO_2$, $O_3$, $N_2O_5$, $ClNO_2$ and the particle chloride content are shown in Figure 3, as well as the calculated $NO_3$ based on the thermal equilibrium of $NO_2$, $NO_3$ and $N_2O_5$. The left panel show the average results of the BAM period, and the right panels show those of the UAM period. $NO_2$ and $O_3$ from the UAM were much higher than those from the BAM, as well as the mixing ratios of $N_2O_5$, $NO_3$ and $ClNO_2$, but the daily variation tendencies of those species in the two kinds of air masses were similar. $N_2O_5$ began to accumulate in the late afternoon and increased sharply after sunset. A peak occurred near 20:00 and decreased below the instrument detection limit at sunrise. The time that $N_2O_5$ maxima occurred is similar to our previous observation in urban Beijing

(H. C. Wang et al., 2017c). However, the decrease rate of the observed $N_2O_5$ after the peak time was much slower than that in urban Beijing, where the $N_2O_5$ dropped to zero in 2-4 hours, which suggests a relatively slow $N_2O_5$ loss rate in suburban Beijing. The daily average peaks of $N_2O_5$ during the BAM period and the UAM period were 75 pptv and 150 pptv, respectively. The calculated $NO_3$ diurnal profile was quite similar to $N_2O_5$, and the daily average peaks of $NO_3$ during the BAM and UAM periods were approximately 11 pptv and 27 pptv, respectively. The uncertainty of $NO_3$ calculation was estimated to be 67% according to Eq. 2, which is dominated by the uncertainty of $NO_2$ measurement.

$$\frac{\Delta[NO_3]}{[NO_3]} = \sqrt{\left(\frac{\Delta[N_2O_5]}{[N_2O_5]}\right)^2+\left(\frac{\Delta[NO_2]}{[NO_2]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2 + \left(\frac{\Delta K_{eq}}{K_{eq}}\right)^2} \quad \text{(Eq. 2)}$$

The observed $ClNO_2$ concentrations showed a clear increase after sunset, $ClNO_2$ reached a maximum before sunrise for BAM period but around midnight for the UAM period. The diurnal peak of $ClNO_2$ in the BAM period was 125 pptv, whereas the diurnal peak of $ClNO_2$ was over 780 pptv in the UAM period, and 6 times as high as that in the UAM period. Particulate chloride ($Cl^-$) is a key factor that affects the $ClNO_2$ yield on aerosol surface. Higher particle chloride leads to higher $ClNO_2$ yield and promotes the $N_2O_5$ conversion to $ClNO_2$ (e.g., Finlayson-Pitts et al., 1989; Behnke et al., 1997), whereas the particle chloride content during the measurement was below 60 pptv and was much lower than the mixing ratio of $ClNO_2$, suggest a nighttime continuously Cl source replenished to support the $ClNO_2$ formation. The HYSPLIT showed that the air masses mainly came from continental, not from the coastal regime, suggested that large amounts of the $Cl^-$ were not replenished by NaCl from marine sources, but possibly replenished by gas-phase HCl through the acid displacement reaction (Ye et al., 2016). $Cl^-$ was found to be correlated strongly with CO and $SO_2$, likely to originate from an anthropogenic source, such as power plants or combustion sources (Le Breton et al., 2018). According to the mass balance, the gas phase HCl for supporting the production of $ClNO_2$ is several ppbv per night. The required HCl source indicated the ratio HCl/$pCl^-$ is about 10-30, which was found consistent with the following observation in Beijing. Although the HCl measurement was not available in this study, note that up to 10 ppbv of HCl was observed in the urban Beijing in September, 2016, we purpose that the gas phase HCl was sufficient to support the $ClNO_2$ formation.

After sunrise, $ClNO_2$ was photolyzed and decreased with the increasing photolysis intensity; However, the $ClNO_2$ can still survive until noon with the averaged daily maximum of $J(ClNO_2)$ to be $1.7\times10^{-4}$ $s^{-1}$. Similar to the studies reported in London, Texas and Wangdu (Bannan et al., 2015; Faxon et al., 2015; Tham et al., 2016), we observed sustained elevated $ClNO_2$ events after sunrise in 5 of 12 days. For example, on the morning of May 30, $ClNO_2$ increased fast after sunrise and up to 500 pptv at 8:00 am. Such high $ClNO_2$ increasing was impossible attribute to the local chemical formation since $N_2O_5$ dropped to almost zero and the needed $N_2O_5$ uptake coefficients were unrealistically high. Previous study suggested that abundant $ClNO_2$ produced in the residual layer at night and downward transport~~ation~~ in the morning may help to explain this phenomenon (Tham et al., 2016).

### 3.3 Variation of $N_2O_5$ in the background air masses

During the BAM period, the $O_3$ concentration was well in excess of $NO_2$. In the $NO_3$ and $N_2O_5$ formation processes, the limited $NO_2$ in high $O_3$ region indicates that the variation of $NO_2$ is more essential to the variation of the $N_2O_5$ concentration. As shown in Figure 4, during the night of May 24 (20:00 - 04:00), the local emission of NO was negligible. $O_3$ concentration was larger than 25 ppbv, much higher than $NO_2$ and free of the local NO emission. The $N_2O_5$ concentration was highly correlated with $NO_2$ ($R^2$ = 0.81) and the $NO_3$ production rate ($R^2$ = 0.60), suggests the $N_2O_5$ concentration was solely response to the $NO_2$ concentration in the background air mass when enough $O_3$ is presented.

### 3.4 Elevated $ClNO_2$ to $N_2O_5$ ratio

Large day-to-day variabilities of $N_2O_5$ and $ClNO_2$ were observed during the measurement period. Following the work of Osthoff et al. (2008), Mielke et al. (2013), Phillips et al. (2012) and Bannan et al. (2015), we used the concentration ratio of $ClNO_2$ to $N_2O_5$, to describe the conversion capacity of $N_2O_5$ to $ClNO_2$. Although $N_2O_5$ is lost to dry deposition in near surface measurements and would drive up the $ClNO_2$:$N_2O_5$. The nighttime peak values and mean values of $ClNO_2$: $N_2O_5$ were used to calculate the daily ratios (Table S2), the calculation period is from 19:30 to the next day 05:00. The average nighttime ratio ranged from 0.7 to 42.0, with a mean of 7.7 and a median of 6.0. The $ClNO_2$ formation was effective, with $ClNO_2$:$N_2O_5$ ratios larger than 1:1 throughout the campaign, except for the night of May 26, when the ratio was 0.7:1. Previous observations of the $ClNO_2$:$N_2O_5$ ratios are summarized in Table 2. Compared with the results conducted in similar continental regions in Europe and America (0.2 - 3.0), the ratios in this work were significantly higher and consistent with the recent studies in the NCP (Tham et al., 2016; X. F. Wang et al., 2017; Z. Wang et al., 2017), which suggests that high $ClNO_2$: $N_2O_5$ ratios were ubiquitous in the NCP and implies that the $ClNO_2$ yield via $N_2O_5$ uptake is efficient.

## 4. Discussion

### 4.1 Determination of $N_2O_5$ uptake coefficients

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). $\gamma \times f$ was estimated by fitting the observed $ClNO_2$ in a time period when the nighttime concentrations of $ClNO_2$ increased continuously at night. 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. 3).

$$[\mathrm{ClNO_2}](t) = [\mathrm{ClNO_2}](t_0) + (\gamma \times f) \cdot \int_{t_0}^{t} \frac{C \cdot S_a}{4} [\mathrm{N_2O_5}]\,\mathrm{dt} \qquad \text{(Eq. 3)}$$

Here $t_0$ and $t$ denote the start time and end time, respectively, the calculation time duration was normally several hours. $[ClNO_2](t_0)$ is the observed concentration at $t_0$ and set as the fitting offset. Note that the transport~~ation~~ leads to the bias of $N_2O_5$ uptake coefficient and $ClNO_2$ yield. But the small variation of the mixing ratio of CO (< 5%) during each analysis time periods suggested the transport

process is not important to the increasing $ClNO_2$. The derived $\gamma \times f$ was found to be constant with small uncertainties for optimization (see Table S3). The $\gamma \times f$ had moderate variability, ranged from 0.008 - 0.035 with an average of 0.019 ± 0.009. Table 3 summarizes the $\gamma \times f$ values derived in the previous field observations. The value in suburban Germany was between 0.001 and 0.09, with the average of 0.014 (Phillips et al., 2016), and the average value in Mt. Tai, China, was approximately 0.016 (Z. Wang et al., 2017). The average $\gamma \times f$ in this study was comparable with that of the two suburban sites, whereas in an urban site of Jinan, China (X. F. Wang et al., 2017), the value was lower than 0.008 and comparable with that in the CalNex-LA campaign. The three sets of $\gamma \times f$ values from suburban regions were about twice as large as those in urban regions, which implies that the $ClNO_2$ formation efficiency in the aged air masses in suburban regions were more efficient than in the urban region. The difference of the overall yield between the two regions may be caused by particle properties or other factors~~s~~ (Riemer et al., 2009; Gaston et al., 2014; Grzinic et al., 2015; Bertram and Thornton, 2009).

According to reaction R4, soluble nitrate and $ClNO_2$ were formed by $N_2O_5$ heterogeneous uptake, with yields of 2 - *f* and *f*, respectively. Following the recent work of Phillips et al., (2016), we used the observed $pNO_3^-$ and $ClNO_2$ formation rates to derive individual $\gamma$ and *f*. The calculations assumed that the relevant properties of the air mass are conserved and that the losses of produced species are negligible; additionally, the $N_2O_5$ uptake coefficients and the $ClNO_2$ yield are independent of particle size. The nights characterized by the following two features were chosen for further analysis: (1) significant correlations between $pNO_3^-$ and $ClNO_2$ were present ($R^2 > 0.5$), which suggested that, to a good approximation, both $ClNO_2$ and $pNO_3^-$ are produced only by $N_2O_5$ heterogeneous uptake. The reason for excluding other nights with low correction ($R^2 < 0.2$) was $ClNO_2$ and $pNO_3^-$ may be affected by the effective transport~~ation~~ or other production pathways, and these contributions can't be well quantified. Therefore the selection of high correction of $ClNO_2$ with $pNO_3^-$ may be lead a bias as the contribution~~contrition~~ from other formation pathways and the transport~~ation~~ were neglected. (2) During an increasing period of $pNO_3^-$, an equivalent or faster increase of ammonium molar ratio to $pNO_3^-$ was~~–~~ also observed~~accompanied~~, which means enough gas-phase ammonia was repartitioned to form ammonium nitrate and suppress the release of $HNO_3$. The ammonia rich conditions (22 ± 9 ppbv on average) in Beijing demonstrated that the degassing of $HNO_3$ at night can be effectively buffered by the high concentrations of ammonia presented in the NCP (Liu et al., 2017). Both the gas-particle repartitioning of $HNO_3$ or nighttime produced $HNO_3$ will result in the overestimation of $\gamma$ and the underestimation of *f*. The daytime produced $HNO_3$ will be soon in a new equilibrium rapidly on the time scale of total nitrate chemical production, and the nighttime formation of $HNO_3$ are normally not important, so the nocturnal $HNO_3$ uptake impact is negligible. During this campaign, five nights were eligible for the following analysis. Based on the observational data of $N_2O_5$, $ClNO_2$, $pNO_3^-$ and $S_a$ in 5 minutes average. The formations of $pNO_3^-$ and $ClNO_2$ were integrated to reproduce the increasing $pNO_3^-$ and $ClNO_2$ by input an initial $\gamma$ and *f*. The offset of $pNO_3^-$ and $ClNO_2$ is the measured $pNO_3^-$ and $ClNO_2$ concentration at the start time. The $\gamma$ 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). Figure 5 depicts an example of the fitting results on May 28. The predicted $N_2O_5$ uptake coefficient and $ClNO_2$ yield were 0.017 and 1.0, respectively. The uncertainty on each individual fitting is varied from 55% - 100% due to the variability and measurements uncertainties of $pNO_3^-$ and $ClNO_2$. Five sets of values of $\gamma$ and *f* obtained are listed in Table 4. $N_2O_5$ uptake coefficients ranged from 0.012 - 0.055, with an average of 0.034 ± 0.018, and

the $ClNO_2$ yield ranged from 0.50 to unity, with an average of 0.73 ± 0.25. The errors from each derivation were 55% and came from the field measurements of $S_a$, $N_2O_5$, $pNO_3^-$ and $ClNO_2$.

The average $\gamma$ value was consistent with the results determined by the same method in a rural site in Germany (Phillips et al., 2016), but was higher than those in the UK and North America where they used other derivation methods, included the steady state lifetime method (Morgan et al., 2015; Brown et al., 2006, 2009), the iterated box model (Wagner et al., 2013) and direct measurement based on an aerosol flow reactor (Bertram et al., 2009; Riedel et al., 2012). The steady state lifetime method is very sensitive to $NO_2$ concentration, and since the $NO_2$ measurement suffered with ambient NOy interference, we did not apply the steady state lifetime method in this study (Brown et al., 2003). Nonetheless, the derived $\gamma$ in Beijing showed good agreement with the recent results derived by the steady state method in Jinan and Mt. Tai (X. F. Wang et al., 2017; Z. Wang et al., 2017). The consistency eliminates the discrepancy possibly brought by the differences of analysis methods. Therefore, we suggest that fast $N_2O_5$ uptake was a ubiquitous feature that existed in the NCP. In this study, sulfate is the dominant component of $PM_{1.0}$, accounting for more than 30% of its mass concentration, which may be the reason of elevated $N_2O_5$ uptake coefficient presented in Beijing, like the result in high sulfate air mass over Ohio and western Pennsylvania (Brown et al., 2006). Previous studies have shown that the $N_2O_5$ uptake coefficient strongly depends on the liquid water content, the $pNO_3^-$ and organic mass. Liquid water content promotes $N_2O_5$ uptake, whereas $pNO_3^-$ and organic mass inhibit $N_2O_5$ uptake (e.g., Thornton et al., 2003, Wahner et al., 1998; Bertram and Thornton, 2009). Because of the limited data set of $N_2O_5$ uptake coefficients in this work, the function dependence studies about the determined $N_2O_5$ uptake coefficients with the parameters mentioned above were not convincing. More valid data are needed in the further studies of the $N_2O_5$ uptake mechanism. With respect to *f*, the values are comparable with that observed in Germany (Phillips et al., 2016) and are similar to that estimated in the power plant plume in Mt. Tai with high chloride content (Z. Wang et al., 2017).

### 4.2 $N_2O_5$ lifetime and reactivity

The lifetime of $N_2O_5$ was estimated by the steady state method, assuming that the production and loss of $N_2O_5$ was in balance after a period following sunset. Eq. 4 for the steady state approximation has been frequently applied in analyzing the fate of $N_2O_5$ (Platt et al., 1980; Allan et al., 1999; Brown et al., 2003).

$$\tau_{ss}(N_2O_5) = \frac{1}{L_{ss}(N_2O_5)} = \frac{[N_2O_5]}{k_{NO2+O3}[NO_2][O_3]} \qquad \text{(Eq. 4)}$$

Here $\tau_{ss}(N_2O_5)$ denotes the steady state lifetime of $N_2O_5$ and $L_{ss}(N_2O_5)$ denotes the loss term of $N_2O_5$ corresponding to the steady state lifetime. A numerical model was used to check the validity of the steady state approximation (Brown et al., 2003); details are given in Figure S3. The results show that the steady state can generally be achieved within 30 minutes. 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 as the steady state is easily disturbed. The overall $N_2O_5$ loss rate ($k(N_2O_5)$) can be calculated by accumulating each individual loss term in Eq. 5, including the $N_2O_5$ heterogeneous hydrolysis and the reaction of $NO_3$ with VOCs.

$$k(N_2O_5) = \frac{\sum k_{NO3+VOCs_i}\cdot[VOCs_i]}{k_{eq}\cdot[NO_2]} + \frac{c\cdot S_a\cdot\gamma}{4} \quad \text{(Eq. 5)}$$

The $NO_3$ heterogeneous uptake and the loss of $N_2O_5$ via gas-phase reactions were assumed to be negligible (Brown and Stutz, 2012). $k_{NO3+VOCs_i}$ denotes the reaction rate constants of the reaction of $NO_3$+$VOCs_i$. Isoprene and monoterpene were used in this calculation.

The $N_2O_5$ loss rate coefficient by heterogeneous hydrolysis was calculated by using an average $\gamma$ of 0.034. The time series of the steady state lifetime of $N_2O_5$ is shown in Figure S4. The $N_2O_5$ 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. The $N_2O_5$ lifetimes during the BAM period were higher than those during the UAM period, which is predictable since the clean air mass has lower $N_2O_5$ reactivity because of much lower aerosol loading. Two extremely short $N_2O_5$ lifetime cases were captured on the nights of May 30 and June 3, with peak values below 200 s throughout those nights. Figure 6 shows that the $N_2O_5$ lifetime had a very clear negative dependence on the ambient $S_a$ when larger than 300 $\mu m^2\ cm^{-3}$, which indicates that the $N_2O_5$ heterogeneous uptake plays an important role in the regulation of $N_2O_5$ lifetime. The study conducted in the residual layer of Hong Kong showed a similar tendency despite the overall $N_2O_5$ lifetime being shorter at this site (Brown et al., 2016). Additionally, a negative dependence of $N_2O_5$ lifetime on RH was reported in Hong Kong but was not observed in this study (Figure S5).

Figure 7 shows the time series of the overall $N_2O_5$ loss rate constant as well as the $N_2O_5$ steady state loss rate constant. The overall $N_2O_5$ loss rate constant was calculated from the individual terms (Eq.3). The uncertainties of the $N_2O_5$ steady state loss rate constant and the overall $k(N_2O_5)$ are estimated to be 67% and 95%, respectively (Eq. 6 and Eq. 7). The largest error sources were from the corrected $NO_2$ measurements.

$$\frac{\Delta Lss(N_2O_5)}{Lss(N_2O_5)} = \sqrt{(\frac{\Delta[N_2O_5]}{[N_2O_5]})^2 + (\frac{\Delta[NO_2]}{[NO_2]})^2 + (\frac{\Delta[O_3]}{[O_3]})^2 + (\frac{\Delta K_{eq}}{K_{eq}})^2} \quad \text{(Eq. 6)}$$

$$\frac{\Delta k(N_2O_5)}{k(N_2O_5)} = \sqrt{(\frac{\Delta[N_2O_5]}{[N_2O_5]})^2 + (\frac{\Delta[S_a]}{[S_a]})^2 + (\frac{\Delta[\gamma]}{[\gamma]})^2 + (\frac{\Delta[NO_2]}{[NO_2]})^2 + (\frac{\Delta[O_3]}{[O_3]})^2 + (\frac{\Delta[VOC_s]}{[VOC_s]})^2 + (\frac{\Delta K_{eq}}{K_{eq}})^2} \quad \text{(Eq. 7)}$$

On the night of 29 May, the steady state loss rate constant was much lower than the overall $k(N_2O_5)$; on the nights of 28, May and 3 June, the $L_{ss}(N_2O_5)$ calculated by the steady state method were much higher than the overall $k(N_2O_5)$, but these discrepancies were in the range of the uncertainties. The steady state loss rate constant in the case of May 30 was approximately ten times larger than the overall loss rate constant, and this difference was outside of the range of uncertainty. The reason for the larger difference on this night is not understood from the available measurements. In general, the overall $N_2O_5$ loss rate constant and the steady state $N_2O_5$ loss rate constant were comparable taking into considerations of the uncertainties. The average $N_2O_5$ loss rate constant contributed by the $N_2O_5$ heterogeneous hydrolysis was $8.1\times10^{-4}\ s^{-1}$. The average $NO_3$ loss rate constant by the reaction of $NO_3$ with VOCs was 0.015 ± 0.007 $s^{-1}$, which is comparable with the previous results in suburban Beijing in 2006 (H. C. Wang et al., 2017c), in which the contribution to the $N_2O_5$ reactivity was $1.63\times10^{-3}$ ± $0.65\times10^{-3}\ s^{-1}$ on average. Compared with $N_2O_5$ loss via direct heterogeneous hydrolysis, the indirect loss via $NO_3$+VOCs was dominant, accounting for approximately 67%. Because only a subset of the

suite of organic species at the site was measured, the calculated loss rate constant via $NO_3$+VOCs represents a lower limit. Therefore, the $N_2O_5$ loss via $NO_3$+VOCs may occupy a larger proportion. The overall loss rate constant from $NO_3$+VOCs and $N_2O_5$ uptake was $2.44\times10^{-3} \pm 1.5\times10^{-3}$ $s^{-1}$ on average, which was reasonably lower than the steady state $N_2O_5$ loss rate constant of $3.61\times10^{-3} \pm 2.80\times10^{-3}$ $s^{-1}$ on average. The gap may be explained by the unmeasured reactive VOCs or the unaccounted NO that was near the instrumental limit of detection.

### 4.3 $NO_3$-induced nocturnal oxidation of VOCs

Recent studies have suggested that the fate of BVOCs after sunset is dominated by $NO_x$ or $O_3$, with variation of the ratio of $NO_x$ to BVOCs and that the nighttime oxidation is located in the transition region between $NO_x$-domination and $O_3$-domination in the United States (Edwards et al., 2017). During this campaign, the nocturnal average concentrations of isoprene and monoterpene were 156 ± 88 pptv and 86 ± 42 pptv, respectively. We used isoprene and monoterpene to represent a lower limit mixing ratio of total BVOCs; the average ratio of $NO_x$/BVOCs was larger than 10 and exhibited small variation during the BAM and UAM periods. The value was much higher than the critical value ($NO_x$ /BVOC = 0.5) of the transition regime proposed by Edwards et al. (2017), which suggests that the oxidation of BVOCs in Beijing was $NO_x$-dominated and the nighttime fate of BVOCs was controlled by $NO_3$. Since the reaction of $NO_3$ with BVOCs has a high mass yield, the nocturnal ON production may be important in the high $NO_x$/BVOCs region.

The first order loss rate of VOCs initialized~~initialed~~ by oxidants, $k(VOCs_i)$, is defined as VOCs reactivity and expressed as Eq. 8. Here, we only consider the reaction of VOCs with $O_3$ and $NO_3$. $k_{O_3+VOCs_i}$ denotes the reaction rate constants of $VOCs_i$ with $O_3$.

$$k(VOCs_i) = k_{NO_3+VOCs_i} \cdot [NO_3] + k_{O_3+VOCs_i} \cdot [O_3] \qquad \text{(Eq. 8)}$$

During this campaign, VOCs reactivity could be determined with the measured $O_3$ and calculated $NO_3$. Figure 8 depicts four kinds of VOCs reactivity distribution during nighttime, including the isoprene (ISO), monoterpene (MNT), the double bond at the end or terminal position of the molecule (OLT) and alkenes with the double bond elsewhere in the molecule (OLI). The reaction rates were cited from the regional atmospheric chemistry mechanism version 2 (RACM2, Goliff et al., (2013)). 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 occupies half and half in the monoterpene with an uncertainty ~~the amount quantification uncertainty~~ of 50%. The rate coefficients of *α*-pinene and *β*-pinene with $NO_3$ were referred to Atkinson and Arey, (2003). The uncertainty of calculated mixing ratio of $NO_3$ is 67%, and the overall uncertainty of monoterpene reactivity was calculated to be 85% by Gaussian propagation. The uncertainties of other kinds of VOCs was calculated to be 75% by assuming the uncertainty of rate coefficient was 30%. The VOCs reactivity were dominated by $NO_3$ oxidation and contributed up to 90% in total; less than 10% VOCs were oxidized by $O_3$ during the nighttime. Even the $NO_3$ concentration in the lower range, $NO_3$ still responsible for more than 70% nocturnal BVOCs oxidation, the results further confirmed that the oxidation of BVOCs is controlled by $NO_3$ rather than $O_3$ in summer Beijing.

For calculating nocturnal ON production from $NO_3$ oxidation of isoprene and monoterpene, as well as inorganic nitrate production via $N_2O_5$ heterogeneous uptake over the same period, the $ClNO_2$ yield was set to the determined average value of 0.55. The organic nitrate yield of the reaction of $NO_3$ with isoprene was set to 0.7, from Rollins et al. (2009). The yield from the reaction of $NO_3$ with monoterpene was represented by $NO_3$ +α-pinene and was set to 0.16, following Spittler et al. (2006). As the *α*-pinene and *β*-pinene have very different ON yields, the yield set in the study was an upper limit for *α*-pinene initialed ON, but is relative low yield for the *β*-pinene initialized~~initialed~~ ON (e.g., Hallquist et al., 1999). Although the yield from the $NO_3$ oxidation of isoprene is much higher than that of monoterpene, the total ON production was dominated by the oxidation of $NO_3$ with monoterpene because the reaction of $NO_3$ with monoterpene is much faster than that with isoprene. Because of the lack of measurement of alkenes and other VOCs that can react with $NO_3$ and form ON, the calculated nighttime ON production rate analyzed here served as a lower estimations.

Figure 9 depicts the mean diurnal profiles of the nocturnal formation rates of inorganic nitrates and ON. The average production rate of ON was up to 0.10 ± 0.07 ppbv $h^{-1}$, which was higher than that predicted in a suburban site in Beijing in 2006, with an average value of 0.06 ppbv $h^{-1}$ (H.C. Wang et al., 2017b). In the high $NO_x$/BVOCs air masses, the inorganic nitrate formation was proposed to increase with the increase of sunset $NO_x$/BVOCs (Edwards et al., 2017). The formation rate of inorganic nitrate via $N_2O_5$ uptake was significant, with an average of 0.43 ± 0.12 ppbv $h^{-1}$, and was much larger than the ON formation. $NO_x$ was mainly removed as the inorganic nitrate format by nocturnal $NO_3$-$N_2O_5$ chemistry in Beijing. Overall, the $NO_3$-$N_2O_5$ chemistry led to significant $NO_x$ removal, with 0.54 ppbv $h^{-1}$ accounted for by the organic and inorganic nitrates, and the integral $NO_x$ removal was approximately 5 ppbv per night. Since ON are important precursors of the secondary organic aerosols (SOA), the $NO_3$ oxidation was very important from the perspective of organic aerosol formation and regional particulate matter (e.g., Ng et al., 2008).

## 5. Conclusion

We reported an intensive field study of $NO_3$-$N_2O_5$ chemistry at a downwind suburban site in Beijing during the summer of 2016. High levels of $ClNO_2$ and $N_2O_5$ were observed, with maxima of 2.9 ppbv and 937 pptv (1-min), respectively. The $N_2O_5$ uptake coefficient was estimated to be in the range of 0.010-0.055, with an average value of 0.034 ± 0.018, and the corresponding $ClNO_2$ yield was derived to be in the range of 0.5-1.0, with an average value of 0.73 ± 0.25. The elevated $ClNO_2$ levels and $ClNO_2$/$N_2O_5$ ratios are comparable with those in chloride-rich regions in the NCP. The results highlight fast $N_2O_5$ heterogeneous hydrolysis and efficient $ClNO_2$ formation in the outflow of urban Beijing.

Since the $NO_3$-$N_2O_5$ chemical equilibrium favors $NO_3$ in summer with high temperature, the elevated $NO_3$ dominated the nocturnal degradation of BVOCs and could lead to efficient ON formation. Because the air masses in Beijing featured high $NO_x$/BVOCs ratios (>10), our results suggest that the nocturnal $NO_3$ oxidation of BVOCs was $NO_x$-dominated. Because of the extremely high $NO_x$ emissions, the formation of ON may not be sensitive to the reduction of $NO_x$ but rather to the change of unsaturated VOCs (e.g., BVOCs), which is similar to the daytime photochemical $O_3$ pollution (e.g., Lu et al., 2010) diagnosed for this area. This suggests that the control of the unsaturated VOCs would moderate the $O_3$ pollution and ON particulate matter in parallel. Moreover, the reduction of $NO_x$ would

also be helpful to reduce the $pNO_3^-$ formation via $N_2O_5$ heterogeneous hydrolysis under such high $NO_x$/BVOCs ratios (Edwards et al., 2017).

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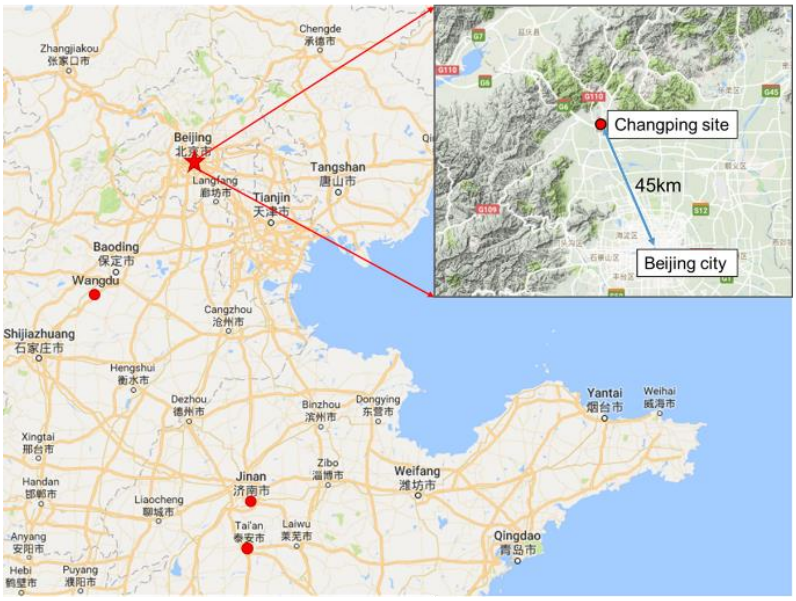
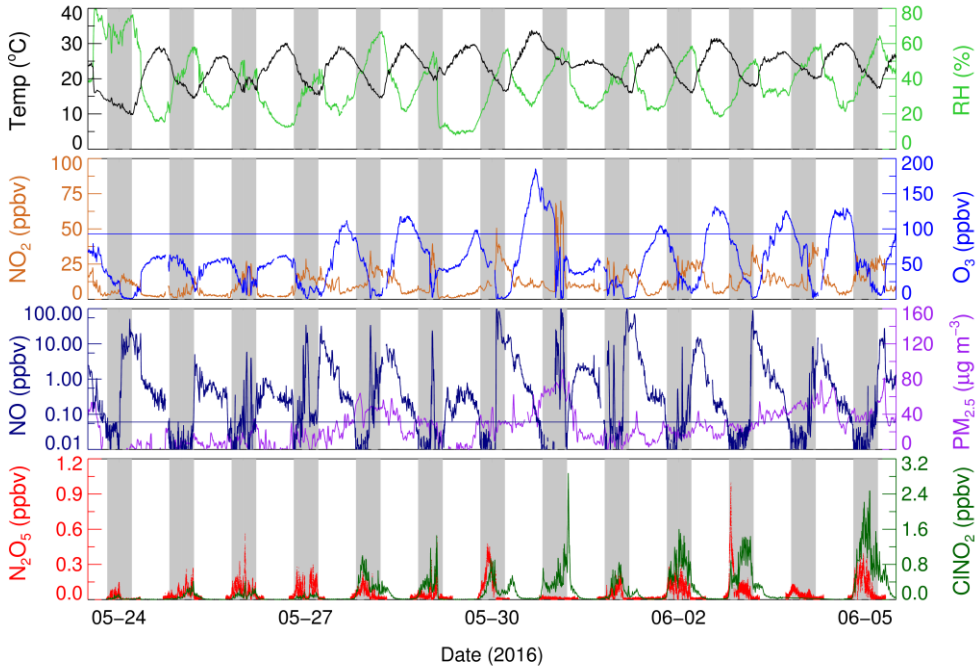


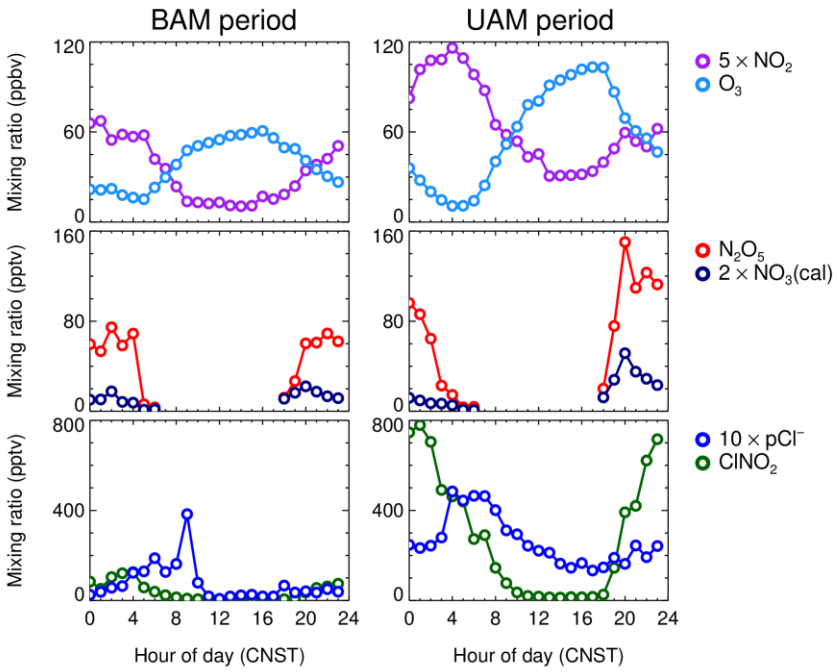

780

781 **Figure 1.** Map of Beijing and surrounding area. The red star shows the location of the Changping site,
782 and red dots show other sites where previous $N_2O_5$ measurements were conducted in the North China
783 Plain (NCP), including Wangdu, Jinan and Mt. Tai (Tai' an).



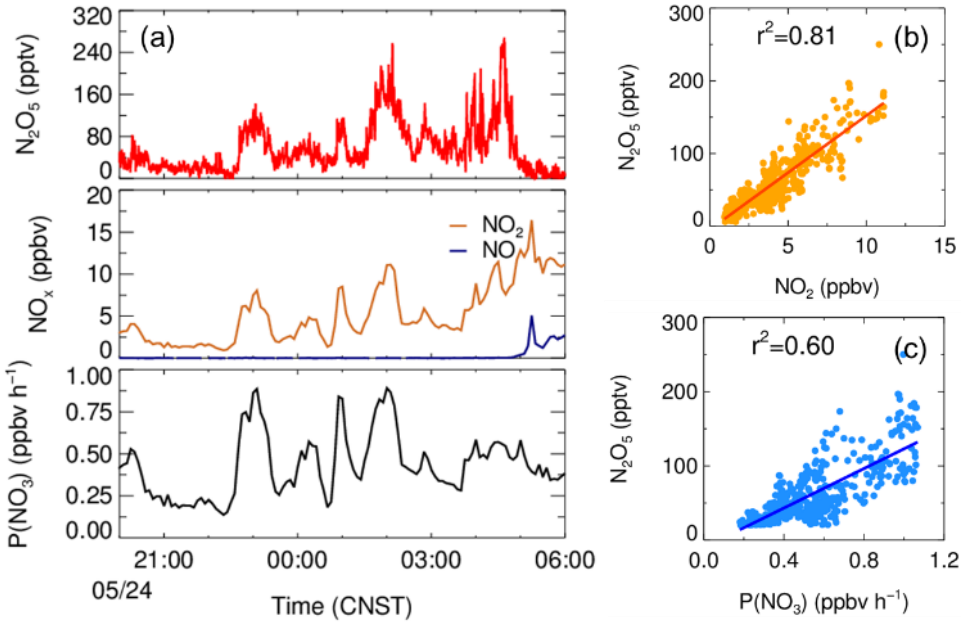

784

785 **Figure 2.** Time series of $N_2O_5$, $ClNO_2$ and other relevant parameters. The blue line in the $O_3$ panel
786 denotes Chinese national air quality standard for $O_3$ (ca. 93 ppbv for the surface conditions). The
787 black line in the NO panel denotes 0.06 ppbv.




788

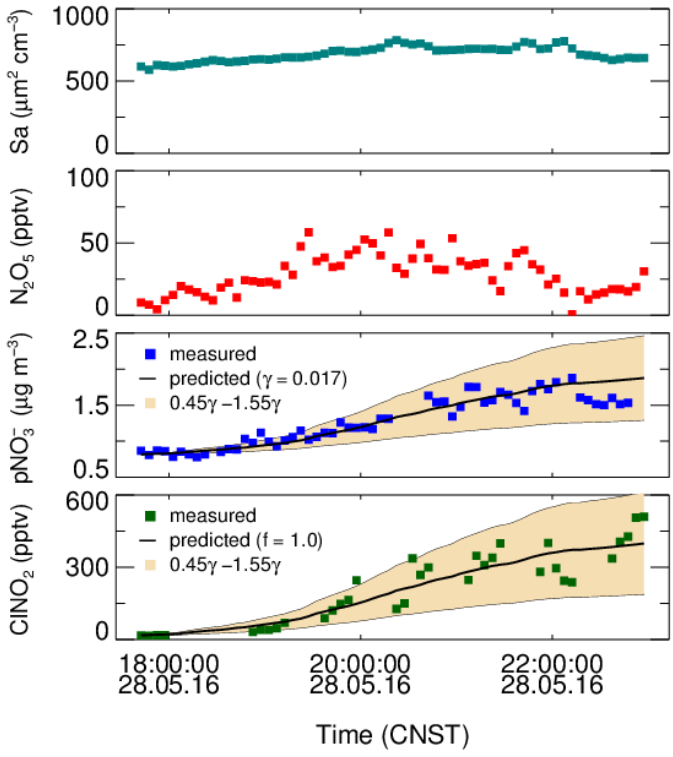
789 **Figure 3.** Mean diurnal profiles of 5×$NO_2$, $O_3$, $N_2O_5$, 2×$NO_3$ (calculated), $ClNO_2$, and 10×$pCl^-$. The
790 left three panels depict the background air mass (BAM) period and the right three panels depict the
791 urban air mass (UAM) period.




792

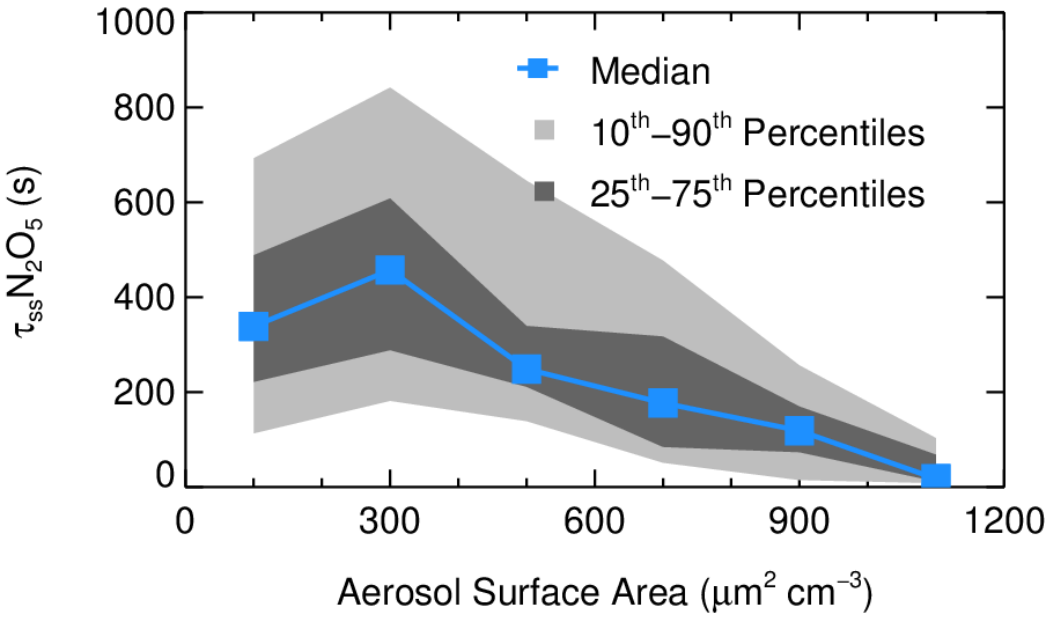
793 **Figure 4.** The correlation of the mixing ratio of $N_2O_5$ and $NO_2$ and the production rate of $NO_3$ on the
794 night of May 24.

795



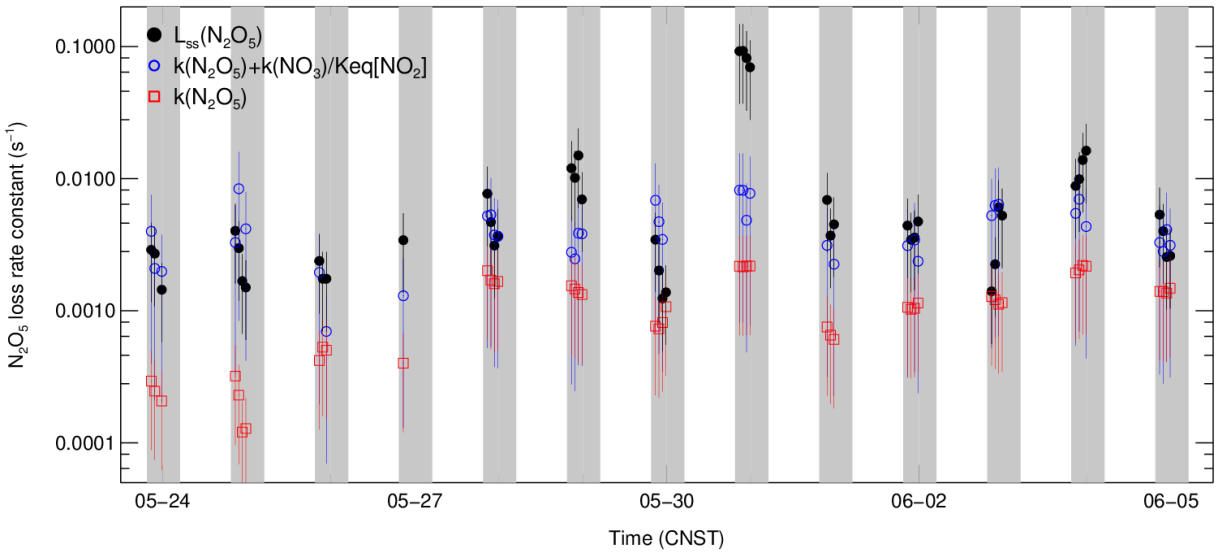

796

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




800

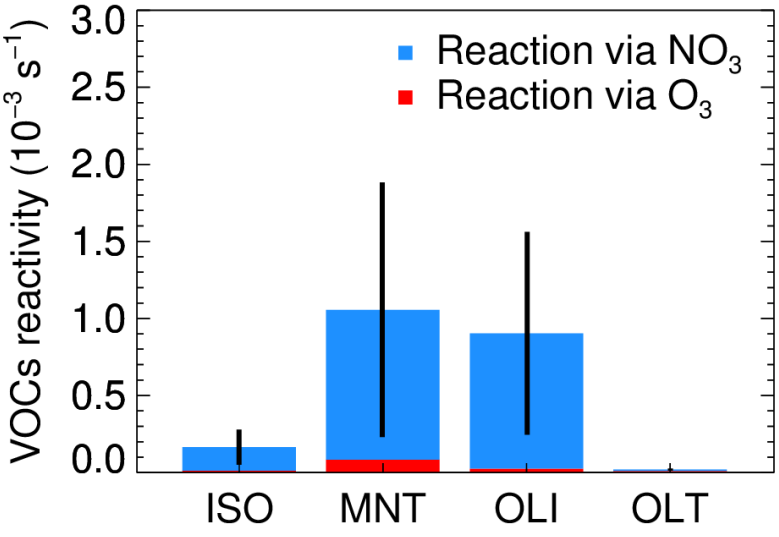
801 **Figure 6.** The dependence of $N_2O_5$ lifetime on aerosol surface area. Data were selected from 20:00 to
802 04:00 and are shown as medians, 25 - 75$^{th}$ percentile ranges, and 10 - 90$^{th}$ percentile ranges, as shown
803 in the legend.




804

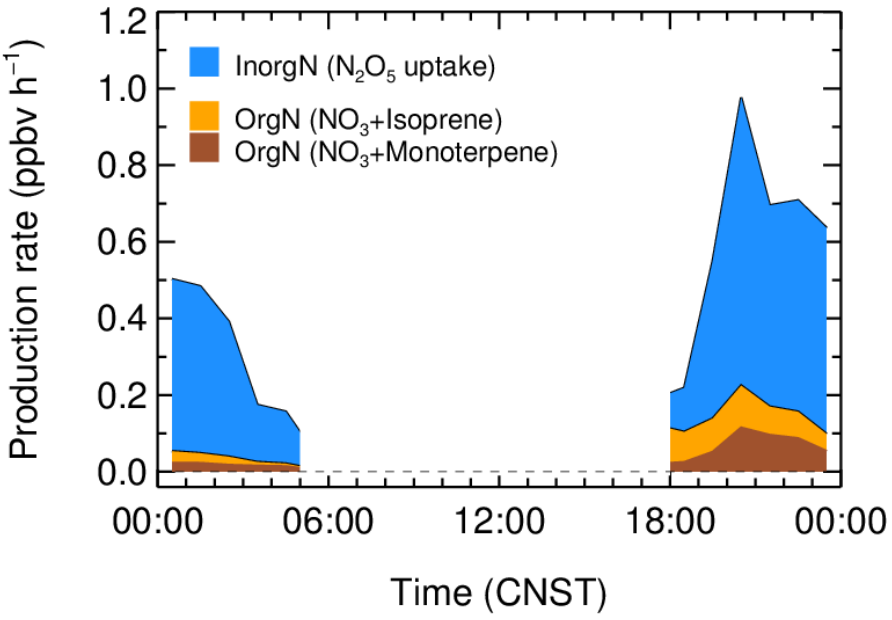
805 **Figure 7**. Time series of the individual $N_2O_5$ loss terms and the loss rate constant of $N_2O_5$ in steady
806 state (*Lss*($N_2O_5$)).

807




808

809 **Figure 8.** The nighttime VOCs reactivity of $NO_3$ and $O_3$ (defined as the first order loss rate of VOCs
810 initialized~~initialed~~ by oxidants, include $NO_3$ and $O_3$); the VOCs are classified as isoprene (ISO),
811 monoterpene (MNT), the terminal alkenes (OLT) and the internal alkenes (OLI). The data were
812 selected from 20:00 to the next day 04:00.




813

814 **Figure 9.** The nighttime production rate of organic and inorganic nitrates; the inorganic nitrates were
815 calculated from the $N_2O_5$ heterogeneous hydrolysis, and the ON were calculated by the $NO_3$ reacted
816 with isoprene and monoterpene.

817

818

819 **Table 1.** The observed gas and particle parameters used in this analysis during the campaign.

| Species | Limit of detection | Methods | Accuracy |
|---|---|---|---|
| $N_2O_5$ | 2.7 pptv (1$\sigma$, 1 min) | CEAS | ± 19% |
| $ClNO_2$ | 16 pptv (2$\sigma$, 1 min) | FIGAERO-ToF-CIMS | ± 23% |
| NO | 60 pptv (2σ, 1 min) | Chemiluminescence | ± 20% |
| $NO_2$ | 0.3 ppbv (2σ, 1 min) | Mo convert | ± 50% |
| $O_3$ | 0.5 ppbv (2σ, 1 min) | UV photometry | ± 5% |
| Aerosol surface area | - (4 min) | SMPS, APS | ± 30% |
| VOCs | 0.1 ppbv (5 min) | PTR-MS | ± 30% |
| $PM_{2.5}$ | 0.1 μg $m^{-3}$ (1 min) | TEOM | ± 5% |
| $PM_{1.0}$ components | 0.15 μg $m^{-3}$ (4 min) | HR-ToF-AMS | ± 30% |

820

821 **Table 2.** Summary of the field observed ambient $ClNO_2/N_2O_5$.

| Location | Region | $ClNO_2/N_2O_5$ [a] | References |
|---|---|---|---|
| Beijing, China | Inland | 0.7 – 42.0 (5.4) | This work |
| Wangdu, China | Inland | 0.4 - 131.3 (29.5) | Tham et al., 2016 |
| Jinan, China | Marine | 25.0 - 118.0 [b] | X. F. Wang et al., 2017 |
| Mt. Tai, China | Marine | ~ 4.0 | Z. Wang et al., 2017 |
| Hong Kong, China | Marine | 0.1 - 2.0 | T. Wang et al., 2016 |
| London, UK | Inland | 0.02 - 2.4 (0.51) | Bannan et al., 2015 |
| Frankfurt, Germany | Inland | 0.2 - 3.0 | Phillips et al., 2012 |
| Colorado, USA | Inland | 0.2 - 3.0 | Thornton et al., 2010 |
| California, USA | Marine | ~ 0.2 - 10.0 [c] | Mielke et al., 2013 |

822 Note: [a] Daily average results; [b] Power plant plume cases at Mt. Tai in Shandong, China; [c] Estimated according to Mielke
823 et al., (2013).

824 **Table 3.** Summary of the average $\gamma \times f$ values derived in the field observations.

| Location | Region | $\gamma \times f$ | References |
|---|---|---|---|
| Beijing, China | suburban | 0.019 ± 0.009 | This work |
| Frankfurt, Germany | suburban | 0.014 | Phillips et al., 2016 |
| Mt. Tai, China | suburban | 0.016 | Z. Wang et al., 2017 |
| Jinan, China | urban | <0.008 | X. F. Wang et al., 2017 |
| California, USA | urban | 0.008 | Mielke et al., 2013 |

825

826 **Table 4.** List of the $N_2O_5$ uptake coefficients and the yield of $ClNO_2$ in this campaign.

| Start time | End time | $\gamma$ | $f$ |
|---|---|---|---|
| 05/25 00:00 | 05/25 05:00 | 0.047 ± 0.023 | 0.60 ± 0.30 |
| 05/25 18:30 | 05/25 23:00 | 0.012 ± 0.006 | 1.0 ± 0.50 |
| 05/27 19:00 | 05/27 20:40 | 0.040 ± 0.032 | 0.50 ± 0.40 |
| 05/28 19:00 | 05/28 23:00 | 0.017 ± 0.009 | 1.0 ± 0.50 |
| 05/30 21:00 | 05/31 00:00 | 0.055 ± 0.030 | 0.55 ± 0.30 |

827