Efficient N₂O₅ uptake and NO₃ 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 (N₂O₅) associated with nitryl chloride (ClNO₂) and particulate nitrate (pNO₃⁻) at a suburban site of Beijing in the summer of 2016. High levels of N₂O₅ and ClNO₂ were observed in the outflow of the urban Beijing air masses, with 1 min average maxima of 937 and 2900 pptv, respectively. The N₂O₅ uptake coefficients, γ, and ClNO₂ yield, f, were experimentally determined from the observed parameters. The N₂O₅ 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 N₂O₅ heterogeneous processes in Beijing. The ClNO₂ 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 (NO₃⁻) was calculated assuming that the thermal equilibrium between NO₃ and N₂O₅ was maintained. In NO₃-rich air masses, the oxidation of nocturnal biogenic volatile organic compounds (BVOCs) was dominated by NO₃ rather than O₃. The production rate of organic nitrate (ON) via NO₃ + BVOCs was significant, with an average of 0.10 ± 0.07 ppbv h⁻¹. We highlight the importance of NO₃ 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 (NO₃⁻) and dinitrogen pentoxide (N₂O₅), play a key role in nighttime chemistry (Wayne et al., 1991; Brown and Stutz, 2012). NO₃ is the most important oxidant in the nighttime and can be considered the nighttime analogue of the hydroxyl radical (OH) for certain volatile organic compounds (VOCs; Wayne et al., 1991; Benton et al., 2010). NO₃ can initiate the removal of many kinds of anthropogenic and biogenic emissions after sunset. In NO₃-rich plumes, NO₃ is responsible for the vast majority of the oxidation of biogenic VOCs because of its rapid reactions with unsaturated hydrocarbons (Edwards et al., 2017). NO₃ is predominantly formed by the reaction of NO₂ with O₃ (Reaction R1) and further reacts with NO₂ to produce N₂O₅ (Reaction R2). N₂O₅ is rapidly decomposed back to NO₃ (Reaction R3). NO₃, and N₂O₅ are in dynamic equilibrium in the troposphere.

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R1)}
\]
\[
\text{NO}_2 + \text{NO}_3 + M \rightarrow \text{N}_2\text{O}_5 + M \quad \text{(R2)}
\]
\[
\text{N}_2\text{O}_5 + M \rightarrow \text{NO}_2 + \text{NO}_3 + M \quad \text{(R3)}
\]

Photolysis of NO\(_3\) and the reaction of NO\(_3\) with NO are rapid, which leads 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\(_2\)O\(_5\) heterogeneous hydrolysis because the two terms are the dominating loss pathways of NO\(_3\) and N\(_2\)O\(_5\). The VOC 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% of nocturnal NO\(_3\) loss in Houston (Stutz et al., 2010) and contributed approximately 50% in a forest region in Germany (Geyer et al., 2001). The reactions of NO\(_3\) with several biogenic VOCs (BVOCs) produce considerable amounts of organic nitrates (ONs) with efficient yields, which act as important precursors of secondary organic aerosols (SOAs). The reaction of NO\(_3\) with isoprene has a SOA mass yield of 23.8% (Ng et al., 2008). For the reaction with monoterpenes, 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\(_2\)O\(_5\) produces soluble nitrate (HNO\(_3\) or NO\(_3^-\)) and nitryl chloride (ClNO\(_2\)) on chloride-containing aerosols (Reaction R4) (Finlayson-Pitts et al., 1989). This reaction is known to be an important intermediate in the NO\(_3\) removal processes (Brown et al., 2006). The pseudo-first-order loss rate constant of N\(_2\)O\(_5\) via heterogeneous uptake is given in Eq. (1) (Wahner et al., 1998).

\[
\text{N}_2\text{O}_5 + (\text{H}_2\text{O} \text{ or } \text{Cl}^-) \rightarrow (2 - f)\text{NO}_3^- + f\text{ClNO}_2 \quad \text{(R4)}
\]

\[
k_{\text{N}_2\text{O}_5} = 0.25 \cdot c \cdot \gamma (\text{N}_2\text{O}_5) \cdot S_d
\]

Here c is the mean molecule speed of N\(_2\)O\(_5\), S\(_d\) is the aerosol surface concentration, and \(\gamma (\text{N}_2\text{O}_5)\) is the N\(_2\)O\(_5\) uptake coefficient. N\(_2\)O\(_5\) heterogeneous hydrolysis is one of the major uncertainties of the NO\(_3\) budget since the N\(_2\)O\(_5\) uptake coefficient can be highly variable and difficult to quantify (Brown and Stutz, 2012; Chang et al., 2011; Wang and Lu, 2016). Laboratory and field measurement studies have reported that the N\(_2\)O\(_5\) uptake coefficient has large variability and ranges from < 0.001 to 0.1; the N\(_2\)O\(_5\) uptake coefficient depends on relative humidity (RH), particle morphology, compositions (water content, nitrate, sulfate, and organic or mineral particles), and other factors (Wahner et al., 1998; Mentel et al., 1999; Hallquist et al., 2003; Thornton et al., 2003, 2005; Brown et al., 2006; Bertram and Thornton, 2009; Tang et al., 2012, 2014; Gaston et al., 2014; Gržinić 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 photolyses and liberates the chlorine radical (Cl) and NO\(_2\) after sunrise. Hundreds of parts per trillion by volume to parts per billion by volume of ClNO\(_2\) can lead to several parts per billion by volume 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\(_3\) 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; S. S. Wang et al., 2013; D. Wang et al., 2015). The N\(_2\)O\(_5\) concentration was elevated in Beijing (H. C. Wang et al., 2017a, b) but was moderate in other parts of the 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\(_2\)O\(_5\) uptake coefficients were determined to be very high, even up to 0.1 in the NCP, but the reason is still not well studied (H. C. Wang et al., 2017b; X. F. Wang et al., 2017; Z. Wang et al., 2017).

Reactive N\(_2\)O\(_5\) chemistry was also reported in Hong Kong and showed the highest field-observed N\(_2\)O\(_5\) concentration to date (Wang et al., 2016; Brown et al., 2016). Observations and model simulations revealed that fast heterogeneous uptake of N\(_2\)O\(_5\) is an important pathway of pNO\(_3^-\) formation in China (H. C. Wang et al., 2017b; 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\(_2\)O\(_5\) 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\(_2\)O\(_5\) chemistry to the atmospheric oxidation capacity and the NO\(_3\) removal process in the outflow of urban Beijing, we report the measurement of N\(_2\)O\(_5\), ClNO\(_2\), and related species in the surface layer of a suburban site in Beijing and determine the N\(_2\)O\(_5\) heterogeneous uptake coefficients and ClNO\(_2\) yields. The nighttime NO\(_3\) oxidation of BVOCs and its impact on ON formation in a NO\(_2\)-rich region were diagnosed. Finally, the nighttime NO\(_3\) removal via NO\(_3\) and N\(_2\)O\(_5\) chemistry was estimated and discussed.

2 Method

2.1 The site

Within the framework of a Sino-Sweden Joint Research Programme, “Photochemical Smog in China”, a summer field
A comprehensive suite of trace gas compounds and aerosol properties was measured in the field study, and the details are listed in Table 1. $\text{N}_2\text{O}_5$ was measured using a newly developed cavity-enhanced absorption spectrometer (CEAS; H. C. Wang et al., 2017a). In the CEAS, ambient $\text{N}_2\text{O}_5$ was thermally decomposed to $\text{NO}_3$ in a perfluoroalkoxy alkane (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 $\text{NO}_3$ reacting back to $\text{N}_2\text{O}_5$. 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 s to destroy $\text{NO}_3$ from $\text{N}_2\text{O}_5$ thermal decomposition in a 5 min cycle, and the corresponding measurements were then used as reference spectra. A Teflon polytetrafluoroethylene (PTFE) filter was used in front of the sampling module to remove ambient aerosol particles. The filter was replaced with a fresh one every hour to avoid the decrease in $\text{N}_2\text{O}_5$ 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%.

$\text{ClNO}_2$ and $\text{N}_2\text{O}_5$ 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 min 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 high-resolution thermograms. Formic acid calibrations were first normalized to the campaign formic acid calibrations. The decrease in N₂O₃ from the reaction with NaCl was assumed to be equal to the concentration of ClNO₂ produced (i.e., 100 % yield). The sensitivities of the CIMS to N₂O₃ and ClNO₂ were found to be 9.5 and 1.2 ion counts per pptv Hz⁻¹, respectively, with errors of 23 and 25 % for ClNO₂ and N₂O₃, respectively. The LODs for ClNO₂ and N₂O₃ were 16 and 8 pptv, respectively. An intercomparison of N₂O₃ measurements between the CEAS and FIGAERO-ToF-CIMS showed good agreement; another paper on chlorine photochemical activation during this campaign gives detailed intercomparison results of N₂O₃ measured with the two different techniques (Le Breton et al., 2018).

Submicron aerosol composition (PM₁₀), including nitrate, sulfate, chloride, ammonium, and organic compounds, were measured using 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) were measured with a scanning mobility particle sizer (SMPS, TSI 3936) and an aerosol particle sizer (APS, TSI 3321) (Yue et al., 2009). The SMPS measured the particles in the range between 3.5 and 523.3 nm in diameter, and the APS measured the particles with a diameter range from 597.6 nm to 10.0 µm. Sₐ was calculated based on the dry-state particle number and geometric diameter in each size bin (3.5 nm–2.5 µm). Dry-state Sₐ was corrected to wet-particle-state Sₐ for particle hygroscopicity by a growth factor. The growth factor, f(RH) = 1 + 8.77 × (RH/100)⁰.⁷⁴, 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 with the error from the 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 Sₐ.

VOCs were measured by proton-transfer-reaction mass spectrometry (PTR-MS) with a time resolution of 5 min (de Gouw and Warneke, 2007; Wang et al., 2014). A commercial instrument (Thermo Fisher Scientific model 42i) equipped with a molybdenum catalytic converter was used to monitor NOₓ. The LODs were 60 pptv (1 min) for NO and 300 pptv (1 min) for NO₂, with both at a 20 % precision (Tan et al., 2017). The molybdenum catalytic technique not only converts NO₂ to NO but also converts ambient NOₓ such as peroxyacetyl nitrate (PAN) and HNO₃. Therefore, the measured NO₂ concentration corresponded to NO₂ + NOₓ and was normally higher than the real concentration, especially in an aged air mass with high NOₓ conditions. In this study, we used a factor of 0.6 to correct the nighttime NO₂ concentration (a detailed explanation is in the Supplement Sect. S1 and Fig. 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 the 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 NO₂ is 50 % when further including the associated measurement uncertainty from calibrations. O₃ was measured by a commercial instrument using ultraviolet (UV) absorption (Thermo Fisher Scientific model 49i); the LOD was 0.5 ppbv, with an uncertainty of 5 %. The mass concentration of PM₂.₅ was measured using a standard tapered-element oscillating microbalance (TEOM, 1400A analyzer). Meteorological parameters included relative humidity, temperature, pressure, wind speed, and wind.

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Limit of detection</th>
<th>Methods</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O₃</td>
<td>2.7 pptv (1σ, 1 min)</td>
<td>CEAS</td>
<td>± 19 %</td>
</tr>
<tr>
<td>ClNO₂</td>
<td>16 pptv (2σ, 1 min)</td>
<td>FIGAERO-ToF-CIMS</td>
<td>± 23 %</td>
</tr>
<tr>
<td>NO</td>
<td>60 pptv (2σ, 1 min)</td>
<td>Chemiluminescence</td>
<td>± 20 %</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.3 ppbv (2σ, 1 min)</td>
<td>Mo convert</td>
<td>± 50 %</td>
</tr>
<tr>
<td>O₃</td>
<td>0.5 ppbv (2σ, 1 min)</td>
<td>UV photometry</td>
<td>± 5 %</td>
</tr>
<tr>
<td>Aerosol surface area</td>
<td>(4 min)</td>
<td>SMPS, APS</td>
<td>± 30 %</td>
</tr>
<tr>
<td>VOCs</td>
<td>0.1 ppbv (5 min)</td>
<td>PTR-MS</td>
<td>± 30 %</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>0.1 µg m⁻³ (1 min)</td>
<td>TEOM</td>
<td>± 5 %</td>
</tr>
<tr>
<td>PM₁₀ components</td>
<td>0.15 µg m⁻³ (4 min)</td>
<td>HR-ToF-AMS</td>
<td>± 30 %</td>
</tr>
</tbody>
</table>
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3 Results

3.1 Overview

During the campaign, the meteorological conditions of the site included high temperature and low RH; the temperature ranged from 10 to 34 $^\circ$C and was 23 $\pm$ 5 $^\circ$C on average, and RH ranged from 10 to 80 $\%$, with an average of 37 $\pm$ 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 23 May–5 July 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 3 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 26 May 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 Fig. 2, and nighttime statistical results are listed in Table S1 in the Supplement. 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 UAM period. The nocturnal nitrate radical production rate, $P$(NO$_3$), was large, with an average of 1.2 $\pm$ 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 CNST on the early night of 2 June, when the $P$(NO$_3$) was up to 4 ppbv h$^{-1}$. The average mixing ratio of $N_2O_5$ was 73 $\pm$ 90 pptv, which is much higher than recent measurements reported in northern 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 $N_2O_5$ was up to 7.7 ppbv (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
O3 concentration was low, high levels of NO could occasionally be observed, and N2O5 dropped to zero because of the fast titration by NO, as during the events that occurred in the second half of the nights of 24, 28, and 30 May. The PM2.5 mass concentration was moderate during the measurement period, with an average of 26 ± 21 µg m⁻³, and the average S₄ was 560 ± 340 μm² cm⁻³. Elevated ClNO₂ was observed with a daily maximum of over 800 pptv (1 min average) during the UAM period. The maximum of ClNO₂ in Beijing was comparable with that reported in the NCP (Tham et al., 2016; X. F. Wang et al., 2017; Z. Wang et al., 2017), but slightly higher than that measured at coastal (e.g., Osthoff et al., 2008) and inland sites (e.g., Thornton et al., 2010). Overall, high ClNO₂ observed at this site suggested that fast N₂O₅ heterogeneous hydrolysis and effective ClNO₂ yields are common in Beijing.

### 3.2 Mean diurnal profiles

The mean diurnal profiles of the measured NO₂, O₃, N₂O₅, and ClNO₂ and the particle chloride content are shown in Fig. 3, as well as the calculated NO₃ based on the thermal equilibrium of NO₂, NO₃, and N₂O₅. Figure 3a shows the average results of the BAM period, and Fig. 3b shows those of the UAM period. NO₂ and O₃ from the UAM, as well as the mixing ratios of N₂O₅, NO₃ and ClNO₂, were much higher than those from the BAM, but the daily variation tendencies of those species in the two kinds of air masses were similar. N₂O₅ began to accumulate in the late afternoon and increased sharply after sunset. A peak occurred near 20:00 CNST and decreased below the instrument detection limit at sunrise. The time at which N₂O₅ maxima occurred is similar to our previous observation in urban Beijing (H. C. Wang et al., 2017b). However, the decrease rate of the observed N₂O₅ after the peak time was much slower than that in urban Beijing, where the N₂O₅ dropped to zero in 2–4 h, which suggests a relatively slow N₂O₅ loss rate in suburban Beijing. The daily average peaks of N₂O₅ during the BAM period and the UAM period were 75 and 150 pptv, respectively. The calculated NO₃ diurnal profile was quite similar to N₂O₅, and the daily average peaks of NO₃ during the BAM and UAM periods were approximately 11 and 27 pptv, respectively. The uncertainty of NO₃ calculation was estimated to be 67 % according to Eq. (2), which is dominated by the uncertainty of NO₂ measurement.

\[
\frac{\Delta[NO_3]}{[NO_3]} = \sqrt{\left(\frac{\Delta[NO_3]}{[NO_3]}\right)^2 + \left(\frac{\Delta[NO_2]}{[NO_2]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2 + \left(\frac{\Delta K_{eq}}{K_{eq}}\right)^2}
\]

The observed ClNO₂ concentrations showed a clear increase after sunset; ClNO₂ reached a maximum before sunrise for the BAM period but around midnight for the UAM period. The diurnal peak of ClNO₂ in the BAM period was 125 pptv, whereas the diurnal peak of ClNO₂ 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 ClINO\(_2\) yield on aerosol surface. Higher particle chloride leads to higher ClINO\(_2\) yield and promotes the N\(_2\)O\(_5\) conversion to ClINO\(_2\) (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 ClINO\(_2\), suggesting a continuously nighttime Cl source replenished to support ClINO\(_2\) formation. HYSPLIT showed that the air masses mainly came from the continental, not coastal, regime, suggesting that large amounts of Cl\(^{-}\) were not replenished by NaCl from marine sources, but they possibly replenished by gas-phase HCl through the acid displacement reaction (Ye et al., 2016). Cl\(^{-}\) was found to be strongly correlated with CO and SO\(_4^{2-}\), much higher than NO\(_2\), likely originating 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 ClINO\(_2\) is several parts per billion by volume per night. The required HCl source indicated the ratio HCl / Cl\(^{-}\) is about 10–30, which was found to be 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 urban Beijing in September 2016; we propose that gas-phase HCl was sufficient to support ClINO\(_2\) formation.

After sunrise, ClINO\(_2\) was photolyzed and decreased with the increasing photolysis intensity; however, ClINO\(_2\) can still survive until noon with an averaged daily maximum of \(J(CINO_2)\) of \(1.7 \times 10^{-4}\) s\(^{-1}\). Similar to the studies reported in London, Texas, and Wanzhou (Bannan et al., 2015; Faxon et al., 2015; Tham et al., 2016), we observed sustained elevated ClINO\(_2\) events after sunrise on 5 of 12 days. For example, on the morning of 30 May, ClINO\(_2\) increased fast after sunrise and up to 500 pptv at 08:00 CNST. Such a high ClINO\(_2\) increase was impossible to attribute to the local chemical formation since N\(_2\)O\(_5\) dropped to almost zero and the required N\(_2\)O\(_5\) uptake coefficients were unrealistically high. A previous study suggested that abundant ClINO\(_2\) produced in the residual layer at night and downward transport in the morning may help to explain this phenomenon (Tham et al., 2016).

3.3 Variation in N\(_2\)O\(_5\) 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\(_2\)O\(_5\) formation processes, the limited NO\(_2\) in the high-O\(_3\) region indicates that the variation in NO\(_2\) is more essential to the variation in the N\(_2\)O\(_5\) concentration. As shown in Fig. 4, during the night of 24 May (20:00–04:00 CNST), the local emission of NO was negligible. The O\(_3\) concentration was larger than 25 ppbv, much higher than NO\(_2\) and free of the local NO emissions. The N\(_2\)O\(_5\) concentration was highly correlated with NO\(_2\) \((R^2 = 0.81)\) and the NO\(_3\) production rate \((R^2 = 0.60)\), suggesting the N\(_2\)O\(_5\) concentration was solely a response to the NO\(_2\) concentration in the BAM when enough O\(_3\) was present.

3.4 Elevated ClINO\(_2\)-to-N\(_2\)O\(_5\) ratio

Large day-to-day variabilities in N\(_2\)O\(_5\) and ClINO\(_2\) 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 ClINO\(_2\) to N\(_2\)O\(_5\) to describe the conversion capacity of N\(_2\)O\(_5\) to ClINO\(_2\). Note that the loss of N\(_2\)O\(_5\) by dry deposition would drive up the ClINO\(_2\) : N\(_2\)O\(_5\). The nighttime peak values and mean values of ClINO\(_2\) : N\(_2\)O\(_5\) were used to calculate the daily ratios (Table S2); the calculation period is from 19:30 to 05:00 CNST the next day. The average nighttime ratio ranged from 0.7 to 42.0, with a mean of 7.7 and a median of 6.0. ClINO\(_2\) formation was effective, with ClINO\(_2\) : N\(_2\)O\(_5\) ratios larger than 1 : 1 throughout the campaign, except for the night of 26 May, when the ratio was 0.7 : 1. Previous observations of the ClINO\(_2\) : N\(_2\)O\(_5\) 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 recent studies in the NCP (Tham et al., 2016; X. F. Wang et al., 2017; Z. Wang et al., 2017), which suggests that high ClINO\(_2\) : N\(_2\)O\(_5\) ratios were ubiquitous in the NCP and implies that ClINO\(_2\) yield via N\(_2\)O\(_5\) uptake is efficient.

4 Discussion

4.1 Determination of N\(_2\)O\(_5\) uptake coefficients

A composite term, \(\gamma \times f\), was used to evaluate the production of ClINO\(_2\) from N\(_2\)O\(_5\) heterogeneous hydrolysis (Mielke et al., 2013). \(\gamma \times f\) was estimated by fitting the observed ClINO\(_2\) in a time period when the nighttime concentrations of ClINO\(_2\)
increased continuously. The increased ClNO$_2$ was assumed to be solely from the N$_2$O$_5$ uptake. The fitting was optimized by changing the input of $\gamma \times f$ associated with the measured N$_2$O$_5$ and $S_a$, until the ClNO$_2$ increase was well reproduced (Eq. 3).

$$[\text{ClNO}_2](t) = [\text{ClNO}_2](t_0) + (\gamma \times f) \cdot \int_{t_0}^{t} C \cdot S_a / 4 \cdot [\text{N}_2\text{O}_5] \cdot dr \quad (3)$$

Here $t_0$ and $t$ denote the start time and end time, respectively; the calculation time duration was normally several hours. $[\text{ClNO}_2](t_0)$ is the observed concentration at $t_0$ and set as the fitting offset. Note that the transport leads to the bias of the N$_2$O$_5$ uptake coefficient and ClNO$_2$ yield. But the small variation in the mixing ratio of CO ($<5\%$) during each analysis time period 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 and ranged from 0.008 to 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 an 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 at 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 was higher than in the urban region. The difference of the overall yield between the two regions may be caused by particle properties or other factors (Riemer et al., 2009; Gaston et al., 2014; Gržinič et al., 2015; Bertram and Thornton, 2009).

According to reaction R4, soluble nitrate and ClNO$_2$ were formed by N$_2$O$_5$ heterogeneous uptake, with yields of $2 - f$ and $f$, respectively. Following the recent work of Phillips et al. (2016), we used the observed $p\text{NO}_3^-$ 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$_2$O$_5$ 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 $p\text{NO}_3^-$ and ClNO$_2$ were present ($R^2 > 0.5$), which suggested that, to a good approximation, both ClNO$_2$ and $p\text{NO}_3^-$ are produced only by N$_2$O$_5$ heterogeneous uptake. The reason for excluding other nights with low correction ($R^2 < 0.2$) was that ClNO$_2$ and $p\text{NO}_3^-$ may be affected by the effective transport or other production pathways, and these contributions cannot be well quantified. Therefore the selection of a high correction of ClNO$_2$ with $p\text{NO}_3^-$ may lead to a bias as the contribution from other formation pathways and the transport were neglected. (2) During an increasing period of $p\text{NO}_3^-$, an equivalent or faster increase in ammonium to

### Table 2. Summary of the field-observed ambient ClNO$_2$ / N$_2$O$_5$.

<table>
<thead>
<tr>
<th>Location</th>
<th>Region</th>
<th>ClNO$_2$ / N$_2$O$_5$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China</td>
<td>Inland</td>
<td>0.7–42.0 (5.4)</td>
<td>This work</td>
</tr>
<tr>
<td>Wangdu, China</td>
<td>Inland</td>
<td>0.4–131.3 (29.5)</td>
<td>Tham et al. (2016)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>Marine</td>
<td>25.0–118.0$^b$</td>
<td>X. F. Wang et al. (2017)</td>
</tr>
<tr>
<td>Mt. Tai, China</td>
<td>Marine</td>
<td>~4.0</td>
<td>Z. Wang et al. (2017)</td>
</tr>
<tr>
<td>Hong Kong, China</td>
<td>Marine</td>
<td>0.1–2.0</td>
<td>Wang et al. (2016)</td>
</tr>
<tr>
<td>London, UK</td>
<td>Inland</td>
<td>0.02–2.4 (0.51)</td>
<td>Bannan et al. (2015)</td>
</tr>
<tr>
<td>Frankfurt, Germany</td>
<td>Inland</td>
<td>0.2–3.0</td>
<td>Phillips et al. (2012)</td>
</tr>
<tr>
<td>Colorado, USA</td>
<td>Inland</td>
<td>0.2–3.0</td>
<td>Thornton et al. (2010)</td>
</tr>
<tr>
<td>California, USA</td>
<td>Marine</td>
<td>~0.2–10.0$^c$</td>
<td>Mielke et al. (2013)</td>
</tr>
</tbody>
</table>

$^a$ Daily average results. $^b$ Power plant plume cases at Mt. Tai in Shandong, China. $^c$ Estimated according to Mielke et al. (2013).

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

<table>
<thead>
<tr>
<th>Location</th>
<th>Region</th>
<th>$\gamma \times f$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China</td>
<td>Suburban</td>
<td>0.019 ± 0.009</td>
<td>This work</td>
</tr>
<tr>
<td>Frankfurt, Germany</td>
<td>Suburban</td>
<td>0.014</td>
<td>Phillips et al. (2016)</td>
</tr>
<tr>
<td>Mt. Tai, China</td>
<td>Suburban</td>
<td>0.016</td>
<td>Z. Wang et al. (2017)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>Urban</td>
<td>&lt; 0.008</td>
<td>X. F. Wang et al. (2017)</td>
</tr>
<tr>
<td>California, USA</td>
<td>Urban</td>
<td>0.008</td>
<td>Mielke et al. (2013)</td>
</tr>
</tbody>
</table>
Table 4. List of the $N_2O_5$ uptake coefficients and the yield of CINO$_2$ in this campaign.

<table>
<thead>
<tr>
<th>Start time</th>
<th>End time</th>
<th>$\gamma$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 May, 00:00</td>
<td>25 May, 05:00</td>
<td>0.047 ± 0.023</td>
<td>0.60 ± 0.30</td>
</tr>
<tr>
<td>25 May, 18:30</td>
<td>25 May, 23:00</td>
<td>0.012 ± 0.006</td>
<td>1.0 ± 0.50</td>
</tr>
<tr>
<td>27 May, 19:00</td>
<td>27 May, 20:40</td>
<td>0.040 ± 0.032</td>
<td>0.50 ± 0.40</td>
</tr>
<tr>
<td>28 May, 19:00</td>
<td>28 May, 23:00</td>
<td>0.017 ± 0.009</td>
<td>1.0 ± 0.50</td>
</tr>
<tr>
<td>30 May, 21:00</td>
<td>31 May, 00:00</td>
<td>0.055 ± 0.030</td>
<td>0.55 ± 0.30</td>
</tr>
</tbody>
</table>

$pNO_3^-$ was also observed, 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 gas–particle repartitioning of HNO$_3$ and nighttime-produced HNO$_3$ will result in the overestimation of $\gamma$ and the underestimation of $f$. The daytime-produced HNO$_3$ will soon be in a new equilibrium rapidly on the timescale of total nitrate chemical production, and the nighttime formation of HNO$_3$ is normally not important; thus the nocturnal HNO$_3$ uptake impact is negligible. During this campaign, five nights were eligible for the following analysis. The observational data of $N_2O_5$, CINO$_2$, $pNO_3^-$, and $S_a$ were averaged to 5 min for the following analysis. The formations of $pNO_3^-$ and CINO$_2$ were integrated to reproduce the increasing $pNO_3^-$ and CINO$_2$ by inputting an initial $\gamma$ and $f$. The offset of $pNO_3^-$ and CINO$_2$ is the measured $pNO_3^-$ and CINO$_2$ concentration at the start time. $\gamma$ and $f$ were optimized based on the Levenberg–Marquardt algorithm until good agreement between the observed and predicted concentrations of $pNO_3^-$ and CINO$_2$ was obtained (Phillips et al., 2016). Figure 5 depicts an example of the fitting results on 28 May. The predicted $N_2O_5$ uptake coefficient and CINO$_2$ yield were 0.017 and 1.0, respectively. The uncertainty on each individual fitting is varied from 55 to 100 % due to the variability in and measurement uncertainties of $pNO_3^-$ and CINO$_2$. Five sets of values of $\gamma$ and $f$ obtained are listed in Table 4. $N_2O_5$ uptake coefficients ranged from 0.012 to 0.055, with an average of 0.034 ± 0.018, and the CINO$_2$ 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 CINO$_2$.

The average $\gamma$ value was consistent with the results determined by the same method at 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, including 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 NO$_3$ 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 with 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 about by the differences in 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 for the elevated $N_2O_5$ uptake coefficient present in Beijing, like the results for 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, $pNO_3^-$, 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; Wagner 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 on 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

Figure 5. The best fit of $\gamma$ and $f$ to reproduce the observed CINO$_2$ and $pNO_3^-$ with an offset on 28 May. The black lines are the predicted results of the integrated NO$_3^-$ and CINO$_2$ by using the observed $S_a$ and $N_2O_5$. 

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are comparable to those observed in Germany (Phillips et al., 2016) and are similar to those estimated in the power plant plume in Mt. Tai with high chloride content (Z. Wang et al., 2017).

4.2 N$_2$O$_5$ lifetime and reactivity

The lifetime of N$_2$O$_5$ was estimated using the steady-state method, assuming that the production and loss of N$_2$O$_5$ was in balance after a period following sunset. Equation (4) for the steady-state approximation has been frequently applied in analyzing the fate of N$_2$O$_5$ (Platt et al., 1980; Allan et al., 1999; Brown et al., 2003).

$$\tau_{ss}(N_2O_5) = \frac{1}{L_{ss}(N_2O_5)} = \frac{[N_2O_5]}{k_{NO_2+O_3}[NO_2][O_3]} \quad (4)$$

Here $\tau_{ss}(N_2O_5)$ denotes the steady-state lifetime of N$_2$O$_5$ and $L_{ss}(N_2O_5)$ denotes the loss term of N$_2$O$_5$ 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 Fig. S3. The results show that the steady state can generally be achieved within 30 min. In this study, the steady-state lifetime of N$_2$O$_5$ was only calculated from 20:00 to the next day at 04:00 CNST. The time periods with a NO concentration larger than 0.06 ppbv (instrument LOD) were excluded as the steady state is easily disturbed. The overall N$_2$O$_5$ loss rate ($k(N_2O_5)$) can be calculated by accumulating each individual loss term in Eq. (5), including the N$_2$O$_5$ heterogeneous hydrolysis and the reaction of NO$_3$ with VOCs.

$$k(N_2O_5) = \sum k_{NO_3+VOCs} \cdot [VOCs_i] + C \cdot S_a \cdot \gamma / 4 \quad (5)$$

The NO$_3$ heterogeneous uptake and the loss of N$_2$O$_5$ via gas-phase reactions were assumed to be negligible (Brown and Stutz, 2012). $k_{NO_3+VOCs}$ denotes the reaction rate constants of the reaction of NO$_3$ + VOCs$_i$. Isoprene and monoterpane were used in this calculation.

The N$_2$O$_5$ 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$_2$O$_5$ is shown in Fig. S4. The N$_2$O$_5$ steady-state lifetime ranged from < 5 to 1260 s, with an average of 270 ± 240 s, and large variability was shown during the campaign. The N$_2$O$_5$ lifetimes during the BAM period were higher than those during the UAM period, which is predictable since the clean air mass has lower N$_2$O$_5$ reactivity because of much lower aerosol loading. Two extremely short N$_2$O$_5$ lifetime cases were captured on the nights of 30 May and 3 June, with peak values below 200 s throughout those nights. Figure 6 shows that the N$_2$O$_5$ lifetime had a very clear negative dependence on the ambient $S_a$ when larger than 300 μm$^2$ cm$^{-3}$, which indicates that the N$_2$O$_5$ heterogeneous uptake plays an important role in the regulation of N$_2$O$_5$ lifetime. The study conducted in the residual layer of Hong Kong showed a similar tendency despite the overall N$_2$O$_5$ lifetime being shorter at this site (Brown et al., 2016). Additionally, a negative dependence of N$_2$O$_5$ lifetime on RH was reported in Hong Kong but was not observed in this study (Fig. S5).

Figure 7 shows the time series of the overall N$_2$O$_5$ loss rate constant as well as the N$_2$O$_5$ steady-state loss rate constant. The overall N$_2$O$_5$ loss rate constant was calculated from the individual terms (Eq. 3). The uncertainties of the N$_2$O$_5$ steady-state loss rate constant and the overall $k(N_2O_5)$ are estimated to be 67 and 95 %, respectively (Eqs. 6 and 7). The largest error sources were from the corrected NO$_3$ measurements.

$$\frac{\Delta L_{ss}(N_2O_5)}{L_{ss}(N_2O_5)} = \sqrt{\left(\frac{\Delta[N_2O_5]}{[N_2O_5]}\right)^2 + \left(\frac{\Delta[NO_2]}{[NO_2]}\right)^2 + \left(\frac{\Delta[O_3]}{[O_3]}\right)^2 + \frac{\Delta K_{eq}}{K_{eq}}} \quad (6)$$

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

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 $L_{ss}(N_2O_5)$ values calculated with 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 30 May was approximately 10 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$_2$O$_5$ loss rate
constant and the steady-state N$_2$O$_5$ loss rate constant were comparable, taking into consideration the uncertainties. The average N$_2$O$_5$ loss rate constant contributed by the N$_2$O$_5$ heterogeneous hydrolysis was $8.1 \times 10^{-4}$ s$^{-1}$. The average NO$_3$ loss rate constant by the reaction of NO$_3$ with VOCs was $0.015 \pm 0.007$ s$^{-1}$, which is comparable with the previous results in suburban Beijing in 2006 (H. C. Wang et al., 2017b), in which the contribution to the N$_2$O$_5$ reactivity was $1.63 \times 10^{-3} \pm 0.65 \times 10^{-3}$ s$^{-1}$ on average. Compared with N$_2$O$_5$ 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$_2$O$_5$ loss via NO$_3$ + VOCs may occupy a larger proportion. The overall loss rate constant from NO$_3$ + VOCs and N$_2$O$_5$ uptake was $2.44 \times 10^{-3} \pm 1.5 \times 10^{-3}$ s$^{-1}$ on average, which was reasonably lower than the steady-state N$_2$O$_5$ loss rate constant of $3.61 \times 10^{-3} \pm 2.80 \times 10^{-3}$ s$^{-1}$ on average. The gap may be explained by the unmeasured reactive VOCs or the unaccounted for 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$_3$, or O$_3$, with variation in the ratio of NO$_3$ to BVOCs and that the nighttime oxidation is located in the transition region between NO$_3$ domination and O$_3$ domination in the United States (Edwards et al., 2017). During this campaign, the nocturnal average concentrations of isoprene and monoterpane were 156 ± 88 and 86 ± 42 pptv, respectively. We used isoprene and monoterpane to represent a lower limit mixing ratio of total BVOCs; the average ratio of NO$_3$ / 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$_3$ / BVOC = 0.5) of the transition regime proposed by Edwards et al. (2017), which suggests that the oxidation of BVOCs in Beijing was NO$_3$ 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$_3$ / BVOC region.

The first-order loss rate of VOCs initialized by oxidants, $k$(VOCs$_i$), is defined as VOC reactivity and expressed as Eq. (8). Here, we only consider the reaction of VOCs with O$_3$ and NO$_3$. $k$(NO$_3$+VOCs$_i$) denotes the reaction rate constants of VOCs$_i$ with O$_3$.

$$k$(VOCs$_i$) = $k$(NO$_3$+VOCs$_i$) · [NO$_3$] + $k$(O$_3$+VOCs$_i$) · [O$_3$] \tag{8}$$

During this campaign, VOC reactivity could be determined with the measured O$_3$ and calculated NO$_3$. Figure 8 depicts four kinds of VOC reactivity distribution during nighttime, including the isoprene (ISO), monoterpane (MNT), 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 in Beijing (Ying Liu, personal communication, 2018). Here we assumed α-pinene and β-pinene occupy half and half in the monoterpane with an uncertainty of 50%. The rate coefficients of α-pinene and β-pinene with NO$_3$ were referred to in Atkinson and Arey (2003). The uncertainty of the calculated mixing ratio of NO$_3$ is 67%, and the overall uncertainty of monoterpane reactivity was calculated to be 85% with Gaussian propagation. The uncertainties of other kinds of VOCs was calculated to be 75% by assuming the uncertainty of rate coefficient was 30%. The VOC reactivity was dominated by NO$_3$ oxidation and contributed up to 90% in total; less than 10% of VOCs were oxidized by O$_3$ during the nighttime. Even though the NO$_3$ concentration is in the lower range, NO$_3$ is still responsible for more than 70% nocturnal BVOC oxidation, and the results further confirmed
that the oxidation of BVOCs is controlled by NO$_3$ rather than O$_3$ in summer in Beijing.

For calculating nocturnal ON production from NO$_3$ oxidation of isoprene and monoterpenes, as well as inorganic nitrate production via N$_2$O$_5$ heterogeneous uptake over the same period, the CINO$_2$ 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 monoterpenes was represented by NO$_3$ + α-pinene and was set to 0.16, following Spittler et al. (2006). As α-pinene and β-pinene have very different ON yields, the yield set in the study was an upper limit for α-pinene-initialized ON, but has a relatively low yield for the β-pinene-initialized ON (e.g., Hallquist et al., 1999). Although the yield from the NO$_3$ oxidation of isoprene is much higher than that of monoterpenes, the total ON production was dominated by the oxidation of NO$_3$ with monoterpenes because the reaction of NO$_3$ with monoterpenes 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 estimation.

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 at a suburban site in Beijing in 2006, with an average value of 0.06 ppbv h$^{-1}$ (H. C. Wang et al., 2017c). In the high NO$_x$ / BVOC air masses, the inorganic nitrate formation was proposed to increase with the increase in sunset NO$_x$ / BVOC (Edwards et al., 2017). The formation rate of inorganic nitrate via N$_2$O$_5$ uptake was significant, with an average of 0.43 ± 0.12 ppbv h$^{-1}$, and was much larger than the ON formation. NO$_3$ was mainly removed as the inorganic nitrate format by nocturnal NO$_3$–N$_2$O$_5$ chemistry in Beijing. Overall, the NO$_3$–N$_2$O$_5$ chemistry led to significant NO$_3$ removal, with 0.54 ppbv h$^{-1}$ accounted for by the organic and inorganic nitrates, and the integral NO$_3$ removal was approximately 5 ppbv per night. Since ONs are important precursors of the SOAs, 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$_2$O$_5$ chemistry at a downwind suburban site in Beijing during the summer of 2016. High levels of CINO$_2$ and N$_2$O$_5$ were observed, with maxima of 2.9 and 937 pptv (1 min), respectively. The N$_2$O$_5$ 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 CINO$_2$ yield was derived to be in the range of 0.5–1.0, with an average value of 0.73 ± 0.25. The elevated CINO$_2$ levels and CINO$_2$ / N$_2$O$_5$ ratios are comparable with those in chloride-rich regions in the NCP. The results highlight fast N$_2$O$_5$ heterogeneous hydrolysis and efficient CINO$_2$ formation in the outflow of urban Beijing.

Since the NO$_3$–N$_2$O$_5$ 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$_x$ / BVOC ratios (> 10), our results suggest that the nocturnal NO$_3$ oxidation of BVOCs was NO$_3$ dominated. Because of the extremely high NO$_3$ 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 control of the unsaturated VOCs would moderate O$_3$ pollution and ON particulate matter in parallel. Moreover, reduction of NO$_3$ would also be helpful in reducing the pNO$_3^-$ formation via N$_2$O$_5$ heterogeneous hydrolysis under such high NO$_x$ / BVOC ratios (Edwards et al., 2017).
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**Data availability.** The observational data and meteorological parameters used in this study are available from the corresponding authors upon request (k.lu@pku.edu.cn).

**Supplement.** The supplement related to this article is available online at: https://doi.org/10.5194/acp-18-9705-2018-supplement.

**Author contributions.** SG, MiH, and MaH organized the field campaign. KL and HW designed the experiments on N₂O₅, MiH and MaH organized the field campaign. KL and HW designed the experiments on N₂O₅. All authors contributed to measurements, discussing results, and commenting on the manuscript.

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

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