Fast heterogeneous N$_2$O$_5$ uptake and ClNO$_2$ production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain

Zhe Wang$^{1}$, Weihao Wang$^{1}$, Yee Jun Tham$^{1,a}$, Qinyi Li$^{1}$, Hao Wang$^{2}$, Liang Wen$^{2}$, Xinfeng Wang$^{2}$, and Tao Wang$^{1}$

$^{1}$Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China
$^{2}$Environment Research Institute, Shandong University, Jinan, China
$^{a}$now at: Department of Physics, University of Helsinki, Helsinki, Finland

Correspondence to: Zhe Wang (z.wang@polyu.edu.hk) and Tao Wang (ctewang@polyu.edu.hk)

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Abstract. Dinitrogen pentoxide (N$_2$O$_5$) and nitryl chloride (ClNO$_2$) are key species in nocturnal tropospheric chemistry and have significant effects on particulate nitrate formation and the following day’s photochemistry through chlorine radical production and NO$_x$ recycling upon photolysis of ClNO$_2$. To better understand the roles of N$_2$O$_5$ and ClNO$_2$ in the high-aerosol-loading environment of northern China, an intensive field study was carried out at a high-altitude site (Mt. Tai, 1465 m a.s.l.) in the North China Plain (NCP) during the summer of 2014. Elevated ClNO$_2$ plumes were frequently observed in the nocturnal residual layer with a maximum mixing ratio of 2.1 ppbv (1 min), whilst N$_2$O$_5$ was typically present at very low levels (< 30 pptv), indicating fast heterogeneous N$_2$O$_5$ hydrolysis. Combined analyses of chemical characteristics and backward trajectories indicated that the ClNO$_2$-laden air was caused by the transport of NO$_x$-rich plumes from the coal-fired industry and power plants in the NCP. The heterogeneous N$_2$O$_5$ uptake coefficient (γ) and ClNO$_2$ yield (ϕ) were estimated from steady-state analysis and observed growth rate of ClNO$_2$. The derived γ and ϕ exhibited high variability, with means of 0.061 ± 0.025 and 0.28 ± 0.24, respectively. These values are higher than those derived from previous laboratory and field studies in other regions and cannot be well characterized by model parameterizations. Fast heterogeneous N$_2$O$_5$ reactions dominated the nocturnal NO$_x$ loss in the residual layer over this region and contributed to substantial nitrate formation of up to 17 µg m$^{-3}$. The estimated nocturnal nitrate formation rates ranged from 0.2 to 4.8 µg m$^{-3}$ h$^{-1}$ in various plumes, with a mean of 2.2 ± 1.4 µg m$^{-3}$ h$^{-1}$. The results demonstrate the significance of heterogeneous N$_2$O$_5$ reactivity and chlorine activation in the NCP and their unique and universal roles in fine aerosol formation and NO$_x$ transformation, and thus their potential impacts on regional haze pollution in northern China.

1 Introduction

Nitrogen oxides (NO$_x$ = NO + NO$_2$) play central roles in the oxidative capacity of the atmosphere and photochemical air pollution. Dinitrogen pentoxide (N$_2$O$_5$) is an important reactive intermediate in the oxidation of NO$_x$ and exists in rapid thermal equilibrium with nitrate radical (NO$_3$) formed via the reaction between NO$_2$ and O$_3$. The heterogeneous hydrolysis of N$_2$O$_5$ has been recognized as a key step in nocturnal NO$_x$ removal and can affect regional air quality by regulating the reactive nitrogen budget and nitrate aerosol formation (e.g., Brown et al., 2006; Abbatt et al., 2012). The heterogeneous reaction of N$_2$O$_5$ on and within atmospheric aerosols, fog, or cloud droplets produces soluble nitrate (HNO$_3$ or NO$_3^-$) and nitryl chloride (ClNO$_2$) when chloride is available in the aerosols (Finlayson-Pitts et al., 1989).

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{het}) \rightarrow 2\text{HNO}_3(\text{aq}) \]  \hspace{1cm} (R1)

\[ \text{N}_2\text{O}_5 + \text{Cl}(\text{het}) \rightarrow \text{NO}_3(\text{aq}) + \text{ClNO}_2 \]  \hspace{1cm} (R2)

The rate coefficient of the heterogeneous N$_2$O$_5$ reactions is governed by the available reaction surface and N$_2$O$_5$ reaction
probability (also known as the uptake coefficient $\gamma_{\text{N}_2\text{O}_5}$), and it can be described by the following expression when the gas-phase diffusive effect is negligible.

$$k(\text{N}_2\text{O}_5)_{\text{het}} = \frac{1}{4}C_{\text{N}_2\text{O}_5} \gamma_{\text{N}_2\text{O}_5} S_a$$  \hspace{1cm} (1)

Here, $C_{\text{N}_2\text{O}_5}$ is the mean molecular speed of $\text{N}_2\text{O}_5$, and $S_a$ is the aerosol (or cloud) surface area density. The yield of CINO$_2$ ($\phi$) is defined as the amount of CINO$_2$ formed per loss of $\text{N}_2\text{O}_5$, representing the fraction to CINO$_2$ formation. Hence, the net reaction of Reactions (R1) and (R2) can be written as follows:

$$\text{N}_2\text{O}_5 + (\text{H}_2\text{O} \text{ or Cl}) \text{ (het)} \rightarrow (2 - \phi)\text{NO}_3^-(\text{aq}) + \phi\text{CINO}_2. \hspace{1cm} (R3)$$

The $\gamma_{\text{N}_2\text{O}_5}$ has been experimentally measured on various types of aerosol surfaces (including sulfate, nitrate, black carbon, organic carbon, organic coating sulfate, sea salts, and dust) in the laboratory, and different parameterizations based on aerosol composition have been proposed in varying degrees of complexity (e.g., Evans and Jacob, 2005; Anttila et al., 2006; Davis et al., 2008; Bertram and Thornton, 2009; Griffiths et al., 2009; Riemer et al., 2009; Roberts et al., 2009; Simon et al., 2009; Foley et al., 2010; Chang et al., 2011; Ammann et al., 2013; Tang et al., 2014). Recently, field studies have been carried out to measure ambient $\text{N}_2\text{O}_5$ and to derive $\gamma_{\text{N}_2\text{O}_5}$ from atmospheric observations (e.g., Bertram et al., 2009b; Brown et al., 2009, 2016; Morgan et al., 2015; Chang et al., 2016; Phillips et al., 2016). These field-derived/measured $\gamma_{\text{N}_2\text{O}_5}$ values were found to vary considerably, and the observed range was found to be significantly larger than that from laboratory studies using synthetic aerosols (Chang et al., 2011; Phillips et al., 2016). Furthermore, inconsistencies between $\gamma_{\text{N}_2\text{O}_5}$ values derived from field measurements and parameterizations were observed in some locations, which implies that $\gamma_{\text{N}_2\text{O}_5}$ has a complex dependence on the aerosol composition, physicochemical characteristics, and environmental parameters (Chang et al., 2011, and references therein). Similarly, for the CINO$_2$ yield, the field-determined values exhibited significant variability, ranging from 0.01 to close to unity (Thornton et al., 2010; Riedel et al., 2013; Wagner et al., 2013; Phillips et al., 2016), which could not be well reproduced (exhibiting a 10-fold difference in some cases) by parameterization based on only aerosol chloride and water content (Wagner et al., 2013; X. Wang et al., 2017). There are only few studies on the determination of $\phi$ from field measurement, and the possible effects of real atmospheric aerosols (including organic composition, mixing state, and chloride partitioning between particle sizes) have not been well characterized (Mielke et al., 2013; Phillips et al., 2016). This incomplete understanding suggests the necessity of more field measurements of $\gamma$ and $\phi$ in various environments to facilitate the validation and construction of parameterizations suitable for use in air quality models.

CINO$_2$ formed from nocturnal heterogeneous $\text{N}_2\text{O}_5$ uptake can potentially affect the atmospheric oxidative capacity via the production of highly reactive chlorine radicals (Cl) and the recycling of NO$_3$ after photolysis (Simpson et al., 2015). Elevated CINO$_2$ mixing ratios were firstly observed in several polluted coast regions (for instance, the coasts of Texas and California, and the Los Angeles Basin), resulting from the strong emission of NO$_3$ and abundant chloride from sea salt aerosols (Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013; Tham et al., 2014). Recently, significant CINO$_2$ production was also observed in some inland areas (such as Colorado, Hessen, and Alberta), with a mixing ratio of up to several hundreds of pptv or even exceeding 1.0 ppbv (e.g., Thornton et al., 2010; Mielke et al., 2011, 2016; Phillips et al., 2012; Riedel et al., 2013; Faxon et al., 2015). Anthropogenic sources of chlorine including coal combustion in power plants, industries, and biomass burning may potentially facilitate CINO$_2$ production (Riedel et al., 2013). The highest CINO$_2$ mixing ratio yet reported (4.7 ± 0.8 ppbv, 1 min average) was recently observed in the regional plumes at a mountaintop site in southern China, indicating the importance of $\text{N}_2\text{O}_5$/CINO$_2$ chemistry in polluted environments (Wang et al., 2016). Large anthropogenic emissions of NO$_x$ and increasing O$_3$ concentrations have been reported in many urban cluster regions in China (Wang et al., 2006; T. Wang et al., 2017). Hence, in these regions, nocturnal nitrogen chemistry may be particularly important in the transformation of NO$_3$ and the subsequent effects on daytime photochemistry and secondary aerosol formation. In the areas downwind of Beijing and Shanghai, high concentrations of particulate nitrate (up to 40 µg m$^{-3}$) have been observed and attributed to heterogeneous $\text{N}_2\text{O}_5$ uptake on acidic aerosols (Pathak et al., 2009, 2011). During a more recent field study in a rural site in the North China Plain (NCP), elevated fine nitrate concentrations were observed at night and in the early morning, with hourly maxima of up to 87.2 µg m$^{-3}$ and a 30% contribution to PM$_{2.5}$, which was mainly attributed to the heterogeneous hydrolysis of $\text{N}_2\text{O}_5$ (Wen et al., 2015). Active heterogeneous $\text{N}_2\text{O}_5$ chemistry has been recently characterized in both rural and urban areas of the NCP via direct measurements of NO$_2$ and CINO$_2$. Rapid heterogeneous $\text{N}_2\text{O}_5$ loss and efficient CINO$_2$ production were observed, with a maximum CINO$_2$ mixing ratio of 2.07 ppbv at Wangdu and 0.77 ppbv at Jinan (Tham et al., 2016; X. Wang et al., 2017). Moreover, sustained CINO$_2$ peaks were observed after sunrise in the region, and the downward mixing of CINO$_2$-rich air in the residual layer was proposed to be the cause of morning peaks (Tham et al., 2016). To confirm these findings and better characterize the chemistry of $\text{N}_2\text{O}_5$/CINO$_2$ and their impacts on regional air quality, it is of great interest to conduct direct field measurements of $\text{N}_2\text{O}_5$/CINO$_2$ in the polluted residual layer.

In the present study, we measured the concentrations of $\text{N}_2\text{O}_5$, CINO$_2$, and related species at a mountaintop site in...
the NCP during the summer of 2014 and characterized the nighttime nitrogen chemistry within the residual layer over a polluted region of northern China. We examined the frequently intercepted ClNO\(_2\)-rich plumes at this high-elevation site and investigated nocturnal N\(_2\)O\(_5\) reactivity to determine the heterogeneous N\(_2\)O\(_5\) uptake coefficients and ClNO\(_2\) yields in a variety of air masses, which were also compared to parameterizations utilized in existing models. The effects of heterogeneous N\(_2\)O\(_5\) chemistry on particulate nitrate formation and nocturnal NO\(_x\) loss were then evaluated based on the observation data.

2 Methodology

2.1 Field study site

The measurement site was located on Mount Tai (36.25° N, 117.10° E, 1465 m a.s.l. – above sea level) in Shandong Province, China. Mt. Tai is located between the two most developed regions in China (Jing–Jin–Ji and the Yangtze River Delta), and its peak (1545 m a.s.l.) is the highest point within the NCP. Figure 1 shows the location of the measurement site in relation to the surrounding topography. Mt. Tai is 230 km away from the Bohai and Yellow seas, and the cities of Tai’an and Jinan (the capital of Shandong Province) are located 15 km south and 60 km north of the measurement site, respectively. The altitude of the measurement site is near the top of the boundary layer in the daytime during the summer and is typically in the residual layer or, occasionally, in the free troposphere at night. This mountaintop site has been previously used in many atmospheric chemistry field studies (e.g., Gao et al., 2005; Wang et al., 2011; Guo et al., 2012; Sun et al., 2016). Previous studies at this site indicated that the site is regionally representative without significant local anthropogenic emissions and affected by the regional aged air masses and occasional combustion plumes from fossil fuel or biomass in the region (e.g., Zhou et al., 2009; Wang et al., 2011; Guo et al., 2012). Intensive measurements were performed from 24 July to 27 August 2014. During this period, the prevailing winds originated from the northeast and northwest. Shandong province is the largest producer of thermal power in China, and dozens of coal-fired industry and power plants are situated within a radius of 200 km from the mountain site.

2.2 Instrumentation

N\(_2\)O\(_5\) and ClNO\(_2\) were measured concurrently using iodide ion chemical ionization mass spectrometry (CIMS) with a quadrupole mass spectrometer (THS Instruments Inc., USA). The principle and detailed calibration of this CIMS system have been described previously by Wang et al. (2016) and Tham et al. (2016). The same configuration was used in the present study. Briefly, N\(_2\)O\(_5\) and ClNO\(_2\) were detected as I(N\(_2\)O\(_5\))\(^-\) and I(ClNO\(_2\))\(^-\) clusters via reaction with iodide ions (I\(^-\)), which were generated from a mixture of CH\(_3\)I (0.3 % in volume) and N\(_2\) using an alpha radioactive source, \(^{210}\)Po (NRD, P-2031-2000). The inlet was installed ~1.5 m above the roof of a single-story building, and the sampling line was a 5.5 m PFA-Teflon tubing (1/4 in o.d.) which was replaced daily in the afternoon before sunset and washed in the ultrasonic bath to minimize wall loss caused by deposited particles (Wang et al., 2016). A small proportion (1.7 SLPM) of total sampling flow (~11 SLPM) was diverted to the CIMS system to reduce the residence time of the air samples in the sampling line. A standard addition of N\(_2\)O\(_5\) into
the ambient inlet was performed before and after the tubing replacement to monitor the transmission efficiency, and this practice limited the loss of N$_2$O$_3$ in the inlet to $<10\%$ in the “clean” tubing and about $30\%$ in the next afternoon. Manual calibrations of N$_2$O$_3$ and Clino$_2$ were conducted daily to determine the instrument sensitivity, the average of which was $2.0\pm0.6$ for N$_2$O$_3$ and $2.2\pm0.6$ Hz pptv$^{-1}$ for Clino$_2$, respectively, during the observation period. The N$_2$O$_3$ standard was synthesized online from the reaction between NO$_2$ and O$_3$, and the produced N$_2$O$_3$ was determined from the decrease in NO$_2$ (Wang et al., 2014). This method has been validated with a cavity ring-down spectrometer (CRDS) measurement in a previous campaign (Wang et al., 2016). The Clino$_2$ was produced by passing a known concentration of N$_2$O$_3$ through a NaCl slurry, assuming unity conversion efficiency (Roberts et al., 2009) and negligible Clino$_2$ loss in the system (Wang et al., 2016). The field background was determined by passing the ambient sample through a filter packed with activated carbon, with average levels of $7.8\pm1.9$ and $6.0\pm1.6$ Hz for N$_2$O$_3$ and Clino$_2$, respectively. The reported concentrations were derived by subtracting the background levels. The detection limit was 4 pptv for both N$_2$O$_3$ and Clino$_2$ ($2\sigma$, 1 min averaged data), and the uncertainty of the nighttime measurement was estimated to be $\pm25\%$ (Tham et al., 2016).

The related trace gases and aerosol compositions were also measured concurrently during the campaign. All of the instruments were used in our previous field studies, and the setup, precision, and accuracies of these instruments were described previously (Wen et al., 2015; Tham et al., 2016; Wang et al., 2016; X. Wang et al., 2017). Briefly, NO and NO$_2$ were measured using a chemiluminescence analyzer equipped with a blue-light converter (TEI, Model 42I-TL). Total gaseous reactive nitrogen (NO$_x$) was determined using a chemiluminescence analyzer with an external molybdenum oxide (MoO) catalytic converter (TEI, Model 42CY) with an inlet filter. The NO$_x$ described here is different from that in previous reports (Tham et al., 2016; Wang et al., 2016), because the particulate nitrate was not included but removed by the filter in the present study. O$_3$, SO$_2$, and CO were measured using the ultraviolet photometry, pulsed-UV fluorescence, and IR (infrared) photometry techniques (TEI, Model 49I, 43C, and 48C), respectively. Zero and span calibrations for trace gases were performed weekly during the campaign. Water-soluble ionic compositions of PM$_2.5$ (including NH$_4^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$) were measured hourly by a monitor for aerosols and gases in ambient air (MARGA ADI 2080, Applikon–ECN) using online ion chromatography.

The particle number and size distribution (5 nm to 10 µm) were measured using a wide-range particle spectrometer (WPS, model 1000XP, MSP Corporation, USA). The particle diameters were corrected for particle hygroscopicity to determine the actual ambient aerosol surface density, and the wet diameters were calculated using growth factors from a size-resolved $\kappa$-Köhler function obtained in a rural site in the NCP (Ma et al., 2016; Tham et al., 2016). The uncertainties associated with the aerosol surface area determination was estimated to be around $30\%$ (Liu et al., 2010; Tham et al., 2016). Meteorological data, including temperature, relative humidity (RH), wind vectors, and photolysis frequency of NO$_2$ ($J_{NO_2}$), were measured by an automated meteorological station (PC-4, JZYG) and a filter radiometer (Metcon, Germany). In addition, a Lagrangian particle dispersion model, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYPLIT) model (Draxler and Hess, 1998; Wang et al., 2016), driven by high spatial and temporal meteorological fields from the Weather Research and Forecasting (WRF) Model, was used to investigate potential source regions of the air masses intercepted at the measurement site. The HYPLIT model was run 12 h backward with 2500 particles released at the measurement site. Detailed parameterization and setup of the HYPLIT and WRF models were previously described by Wang et al. (2016) and Tham et al. (2016).

3 Results and discussion

3.1 Overview of N$_2$O$_3$ and Clino$_2$ measurement

The temporal variations of Clino$_2$, N$_2$O$_3$, related trace gases, aerosol properties, and selected meteorological parameters during the field study at Mt. Tai are depicted in Fig. 2. Overall, the observed mixing ratios of Clino$_2$ were higher than those of N$_2$O$_3$ and exhibited significant variations. The average mixing ratios of N$_2$O$_3$ and Clino$_2$ were $6.8\pm7.7$ and $54\pm106$ pptv, respectively. The maximum mixing ratio of N$_2$O$_3$ (167 pptv) was observed at 21:00 LT on 26 August 2014, and most of the other nights during the observation period exhibited peak N$_2$O$_3$ mixing ratios below 30 pptv. The average nighttime mixing ratios of O$_3$ and NO$_2$ were 77 and 3.0 ppbv, respectively, with an average nitrate radical production rate $p$(NO$_3$) of $0.45\pm0.40$ ppbv h$^{-1}$, which is indicative of potentially active NO$_3$ and N$_2$O$_3$ chemistry during the study period. However, the low N$_2$O$_3$ mixing ratios observed during most of the nights suggest a rapid loss of N$_2$O$_3$, which is consistent with the observed high aerosol surface area ($S_a$), which varied from 100 to 7800 µm$^2$ cm$^{-3}$ with a mean value of 1440 µm$^2$ cm$^{-3}$. The higher RH during nighttime and the frequent occurrence of clouds at the mountaintop site could also account for low N$_2$O$_3$ concentrations, because of the rapid heterogeneous loss of N$_2$O$_3$ on cloud droplets.

The highest Clino$_2$ mixing ratio of 2065 pptv was observed on 8 August 2014, and on 8 of the 35 nights the peak Clino$_2$ mixing ratios were higher than 500 pptv. The simultaneous increases of SO$_2$, NO$_x$, and CO with the Clino$_2$ peaks suggest these air masses originated from coal combustion sources, such as industry and power plants, which will be further discussed in the next section. The elevated Clino$_2$
levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016) but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world. During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 µg cm^-3, accounting for 29.5 and 12.0 % of PM2.5 mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and the USA. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 µg cm^-3, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of ClNO2.

The mean diurnal variations of N2O5, ClNO2, and other relevant chemical species during the study period are shown in Fig. 3. Ozone exhibited a typical diurnal pattern for a polluted mountaintop site (Sun et al., 2016), and it began to increase in the late morning and reached an afternoon peak of 88.6 (±16.6) ppbv, with a daily average rise of 24.4 ppbv. The average O3 remained at elevated levels after sunset and did not begin to decrease until 22:00 LT, and NOx exhibited a diel maximum of 6.1 ppbv before sunset, resulting in a peak in $p$(NO3) just before sunset and relatively high levels in the early night. Gaseous NOy reached a maximum of 16.4 (±6.1) ppbv in the morning and remained stable at a high level during the daytime; the air masses were more aged during the daytime, as indicated by the persistent low NOx/NOy ratios (0.2–0.25). Small N2O5 peaks were observed immediately after sunset, resulting from the abundant O3 and NO2, and N2O5 was present at low levels near the detection limit of the CIMS throughout the rest of the night. ClNO2 exhibited clear nighttime elevations resulting from the heterogeneous production after sunset and reached a diel maximum around midnight. The low N2O5 and high ClNO2 concentrations observed at Mt. Tai are similar to the measurement at a rural surface site within the NCP (Tham et al.,

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**Figure 2.** Time series for N2O5, ClNO2, related trace gases, aerosol properties, and meteorological data measured at Mt. Tai from 24 July to 27 August 2014.
2016), suggesting rapid heterogeneous loss of N$_2$O$_5$ and production of CINO$_2$ in this region.

It was also noted that a small N$_2$O$_5$ peak (∼10 pptv) with larger variability was present in the early afternoon. A simplified photostationary analysis following Brown et al. (2005, 2016) was performed to predict the daytime steady-state N$_2$O$_5$ concentrations for the few cases with daytime peaks. The predicted concentrations all showed increasing trends in the afternoon, similar to the observation pattern. However, for individual cases, the predicted values around 15:00 LT were much lower than the observation under clean sky condition, but of the same magnitude as the observation for reduced photolysis and foggy conditions with higher NO$_3$ production rate (cf. Fig. S1 in the Supplement). Daytime N$_2$O$_5$ signals with few pptv have also been observed by a CRDS at a mountain site in southern China (Brown et al., 2016), where the concentrations were in accord with steady-state estimation in an average sense. Because daily maintenance and calibrations of the CIMS were usually performed during early afternoon periods, the limited daytime data in the present study were not sufficient to make clear whether there were any day-time interferences or sensitivity fluctuations. Thus, additional studies are needed to validate the daytime phenomenon and examine the potential reasons, and the following analysis in the present work will mostly focus on nocturnal processes.

3.2 High-CINO$_2$ plumes from power plants and industry

As described above, several plumes with elevated CINO$_2$ concentrations (>500 pptv) were observed during the measurement period. Figure 4a illustrates the high-CINO$_2$ case observed during the night of 30–31 July 2014. The CINO$_2$ concentration peaked sharply at 1265 pptv, which was accompanied by a steep rise in the concentrations of SO$_2$, NO$_x$, and CO. The SO$_2$/NO$_x$ ratio increased from ∼0.1 to 0.6 in the plume center, with a ΔSO$_2$/ΔNO$_x$ slope of 0.57, indicating the coal combustion source of the plume. The coincident increase in CO/NO$_x$ ratio from ∼30 to 90 suggests that it likely originated from coal-fired industry facilities, such as cement and steel production plants, which is the largest emitting sector of CO in north China (Streets et al., 2006; Zhang et al., 2009). The 12 h backward particle dispersion trajectories calculated from the HYSPLIT model revealed that the air masses mostly moved slowly from the west and passed over the region with the cement and steel production industry and power plants before arriving at the measurement site. Figure 5a shows the highest CINO$_2$ case (2065 pptv) observed on the night of 8 August 2014. The simultaneous increases in SO$_2$, NO$_x$, and CO concentrations, together with the higher SO$_2$/NO$_x$ ratio (∼0.5) compared to that outside of the plume (∼0.1) and the campaign average (0.24), again indicate the coal combustion origin of the plume. The relatively lower CO/NO$_x$ ratio (∼50) possibly suggests the plume affected by power plant emission, as shown by the derived backward particle dispersion trajectories. Table 1 summarizes the chemical characteristics of the eight cases of high-CINO$_2$ plumes from power plants and industry during the study period. In these cases, the average SO$_2$ mixing ratios ranged from 2.3 to 18.7 ppbv, and the maximum CINO$_2$ and N$_2$O$_5$ mixing ratios ranged from 534 to 2065 pptv and 7.3 to 40.1 pptv, respectively, with corresponding CINO$_2$/N$_2$O$_5$ ratios of 25 to 118. The mixing ratios for O$_3$ and NO$_2$ ranged from 60 to 106 ppbv and 2.8 to 11.8 ppbv, respectively, resulting in high p(NO$_3$) values of 0.60 to 1.59 ppbv h$^{-1}$. The aerosol chloride concentration ranged from 1.01 to 2.34 µg m$^{-3}$, which was higher than the nighttime average (0.89 µg m$^{-3}$) and conducive to CINO$_2$ production from Reaction (R3).

NO$_x$ emissions from the coal combustion sources contain abundant NO, which is oxidized rapidly to NO$_2$ by ambient O$_3$. Thus, the anti-correlation between O$_3$ and NO$_2$ within the observed plumes (cf. Figs. 4b and 5b) can be another indicator of the large combustion sources (such as coal-fired power or industry plants). Furthermore, the slope of a plot of O$_3$ vs. NO$_2$ for nighttime plumes can be considered as an

Figure 3. Diurnal variations of N$_2$O$_5$, CINO$_2$, NO$_x$, NO$_3$, O$_3$, particulate nitrate, nitrate radical production rate $p$(NO$_3$), and meteorological parameters during the study period at Mt. Tai. Shaded area in O$_3$ shows 2σ variation, and vertical bars in N$_2$O$_5$ and CINO$_2$ represent 10–90th percentile ranges.
Table 1. Chemical characteristics of coal-fired power plant and industrial plumes exhibiting high levels of ClNO₂ observed at Mt. Tai during the summer of 2014.

<table>
<thead>
<tr>
<th>Date</th>
<th>Duration</th>
<th>N₂O₅ (pptv)</th>
<th>Mean</th>
<th>Maximum</th>
<th>ClNO₂ (pptv)</th>
<th>Mean</th>
<th>Maximum</th>
<th>O₃</th>
<th>NO₃</th>
<th>NO₂/NO₃</th>
<th>ΔSO₂/NO₃</th>
<th>ΔCO/NOₓ</th>
<th>Ct⁻</th>
<th>τₚlumes</th>
<th>φₘ₈ClNO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>30–31 Jul</td>
<td>23:40–00:45</td>
<td>5.9</td>
<td>14.2</td>
<td></td>
<td>528</td>
<td>1265</td>
<td></td>
<td>70</td>
<td>6.5</td>
<td>0.49</td>
<td>0.57</td>
<td>83</td>
<td>2.34</td>
<td>3.2</td>
<td>0.57</td>
</tr>
<tr>
<td>3–4 Aug</td>
<td>23:30–00:00</td>
<td>20.1</td>
<td>23.8</td>
<td></td>
<td>506</td>
<td>833</td>
<td>106</td>
<td>2.8</td>
<td>0.22</td>
<td>2.43</td>
<td>108</td>
<td>NA</td>
<td>4.9</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>7 Aug</td>
<td>21:30–23:30</td>
<td>10.5</td>
<td>14.9</td>
<td></td>
<td>606</td>
<td>976</td>
<td>91</td>
<td>5.8</td>
<td>0.36</td>
<td>1.36</td>
<td>50</td>
<td>2.24</td>
<td>5.5</td>
<td>0.35d</td>
<td></td>
</tr>
<tr>
<td>8 Aug</td>
<td>22:00–23:10</td>
<td>11.0</td>
<td>15.1</td>
<td></td>
<td>841</td>
<td>2065</td>
<td>76</td>
<td>8.5</td>
<td>0.45</td>
<td>0.65</td>
<td>45</td>
<td>NA</td>
<td>2.1</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>8–9 Aug</td>
<td>23:40–01:15</td>
<td>6.8</td>
<td>12.6</td>
<td></td>
<td>315</td>
<td>599</td>
<td>77</td>
<td>4.3</td>
<td>0.41</td>
<td>0.54</td>
<td>85</td>
<td>NA</td>
<td>4.4</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>10 Aug</td>
<td>00:00–02:00</td>
<td>10.5</td>
<td>15.5</td>
<td></td>
<td>692</td>
<td>1684</td>
<td>72</td>
<td>6.2</td>
<td>0.43</td>
<td>1.67</td>
<td>50</td>
<td>1.10</td>
<td>4.6</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>17–18 Aug</td>
<td>22:00–01:30</td>
<td>3.5</td>
<td>7.7</td>
<td></td>
<td>409</td>
<td>802</td>
<td>60</td>
<td>9.5</td>
<td>0.55</td>
<td>0.48</td>
<td>33</td>
<td>1.01</td>
<td>4.6</td>
<td>0.26d</td>
<td></td>
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<tr>
<td>25–26 Aug</td>
<td>00:00–05:00</td>
<td>12.1</td>
<td>40.1</td>
<td></td>
<td>301</td>
<td>534</td>
<td>74</td>
<td>11.8</td>
<td>0.62</td>
<td>2.10</td>
<td>NA</td>
<td>1.88</td>
<td>3.0</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

* Slope of SO₂ vs. NO₂ in plumes; the overall slope for entire campaign was 0.31 with r² of 0.31. ** Same as previous note but with the campaign overall slope of 15.7 and r² of 0.23. *** Data not available in the case. **** For τₚlumes longer than the nocturnal processing period since sunset, the time since sunset was used in the ClNO₂ yield calculation.

Figure 4. (a) Time series for ClNO₂, N₂O₅, and related trace gases observed within the high-ClNO₂ plume from power plants and industry during the night of 30–31 July 2014. (b) Plot of O₃ vs. NO₂ concentrations for the plume; plume age was determined from the plot using Eq. (2). (c) 12 h HYSPLIT backward particle dispersion image depicting air masses arriving at the measurement site (blue triangle) at the time of the plume, and red dots indicating the location of major coal-fired facilities in cement and steel production and power plants in the region.

approximate measure of the plume age, with the assumption of pseudo-first-order kinetics and when the input of NOₓ is small compared to the excess O₃ (Brown et al., 2006). The estimated plume age can be determined as follows:

\[
τ_{\text{plumes}} \approx \frac{\ln(1 - S(m + 1))}{(SkO₃)},
\]

where \(m\) is the derived slope, \(k\) is the rate coefficient for the reaction of NOₓ with O₃, \(O₃\) is the average O₃ concentration in the plume, and \(S\) is a stoichiometric factor that varies between 1 for dominant NO₃ loss and 2 for dominant N₂O₅ loss (Brown et al., 2006). In the present study, heterogeneous N₂O₅ uptake dominated the reactive nitrogen loss; therefore, \(S = 2\) was used in the calculation. The plume ages for the 30–31 July and 8 August cases were calculated to be 3.2 and 2.1 h, respectively, which are consistent with the moderate NOₓ/NO₂ ratios of 0.4–0.5 and comparable to those observed in nocturnal power plant plumes in the eastern coast of the USA (Brown et al., 2006, 2007). The slopes of O₃ vs. NO₂ in Figs. 4b and 5b steeper than −1.0 also indicate the further reactions of NO₂ with O₃, which favor the formation of NO₃ and N₂O₅. However, the N₂O₅ concentrations only showed a slight increase (Fig. 4 case) or no apparent
change (Fig. 5 case), in contrast to the significant increases in ClNO$_2$ and high $p$(NO$_3$) values, which suggests rapid heterogeneous loss of N$_2$O$_5$ and significant ClNO$_2$ production during transport of these plumes from their sources.

The elevated ClNO$_2$ concentrations in the coal-fired power plant and industry plumes (here referred to collectively as coal-fired plumes) here are comparable to previous observations of power plant plumes via tower measurements in Colorado (Riedel et al., 2013) and at a mountain site in southern China (Wang et al., 2016), but the observed N$_2$O$_5$ within the plumes is significantly lower than those in other coal-fired plumes observed via aircraft, tower, and at mountain sites (Brown et al., 2007, 2016; Riedel et al., 2013). The previous measurement at a surface site in the NCP has observed sustained ClNO$_2$ peaks after sunrise, which was proposed to be the cause of the downward mixing of ClNO$_2$-rich air (estimated values of 1.7–4.0 ppbv) in the residual layer (Tham et al., 2016). In the present study, the frequent intercepts of coal-fired power plant and industrial plumes with elevated ClNO$_2$ concentrations at Mt. Tai, which was typically above the nocturnal boundary layer, affirm this hypothesis and provide direct evidence that significant ClNO$_2$ production occurred in the residual layer from the abundant nocturnal NO$_x$, chloride, and background O$_3$ over the NCP. The similar ClNO$_2$-laden air frequently observed at high-elevation sites in northern and southern China suggests ubiquitous ClNO$_2$ in the polluted residual layer and its importance in the daytime production of ozone in China (Tham et al., 2016; Wang et al., 2016). Moreover, the concurrent nitrate production from heterogeneous N$_2$O$_5$ reactions (cf. Reaction R3) may also contribute to the formation of haze pollution in these regions.

### 3.3 N$_2$O$_5$ reactivity and heterogeneous uptake coefficient

#### 3.3.1 Reactivity of N$_2$O$_5$ and NO$_3$

The mixing ratios of N$_2$O$_5$ depend on the nitrate radical production rate and on the reactivity of N$_2$O$_5$ and NO$_3$, including the individual loss rates for N$_2$O$_5$ or NO$_3$ that contribute to the removal of the pair. N$_2$O$_5$ reactivity can be assessed using the inverse N$_2$O$_5$ steady-state lifetime, which is the ratio of $p$(NO$_3$) to the observed N$_2$O$_5$ mixing ratios (e.g., Brown et al., 2006, 2009, 2016):

$$\tau(N_2O_5)^{-1} = \frac{p(NO_3)}{[N_2O_5]} \approx \frac{k(NO_3)}{Keq[NO_2]} + k(N_2O_5)^{het}. \tag{3}$$

The steady-state inverse lifetime of N$_2$O$_5$, $\tau(N_2O_5)^{-1}$, is the sum of the N$_2$O$_5$ loss rate via heterogeneous loss ($k(N_2O_5)^{het}$) and NO$_3$ reactions with volatile organic compounds (VOCs) ($k(NO_3)$) with a ratio of $Keq[NO_2]$. $Keq$ is the temperature-dependent N$_2$O$_5$–NO$_3$ equilibrium coefficient. High N$_2$O$_5$ reactivity was observed in the present study, with average nighttime $\tau(N_2O_5)$ of $1.41 \times 10^{-2}$ s$^{-1}$ before midnight and $1.30 \times 10^{-2}$ s$^{-1}$ after midnight, corresponding to a nighttime N$_2$O$_5$ lifetime of 1.2–1.5 min. This rapid N$_2$O$_5$ loss rate is comparable to the results from surface measurements in both urban and rural sites in the NCP (Tham et al., 2016; X. Wang et al., 2017). However, this loss rate is
significantly higher than those determined from a mountain site in southern China (Brown et al., 2016) and from tower and aircraft measurements in the USA (e.g., Brown et al., 2009; Wagner et al., 2013).

The NO$_3$ reactivity, or loss rate coefficient $k$(NO$_3$), can be estimated from the sum of the products of measured VOC concentrations and the bimolecular rate coefficients for the corresponding NO$_3$–VOC reactions (Atkinson and Arey, 2003):

$$k(\text{NO}_3) = k_{\text{NO+NO}_3[\text{NO}]} + \sum_i k_i [\text{VOC}_i].$$

Because of the lack of concurrent VOC measurements in the present study, we used the average VOC speciations measured before sunrise and in the evening at Mt. Tai during our previous study in 2007 (cf. Table S1 in the Supplement) to estimate $k$(NO$_3$). The determined nighttime $k$(NO$_3$) was 1.33 $\times$ 10$^{-2}$ s$^{-1}$ for the first half of the night and 1.07 $\times$ 10$^{-2}$ s$^{-1}$ for the period after midnight, which is equivalent to an NO$_3$ lifetime of approximately 1.5 min. The estimated $k$(NO$_3$) could be considered as an upper limit for coal-fired plumes because of potential lower biogenic VOC levels within the plumes. The estimation here does not account for the VOC changes between years and the night to night variability, which may result in uncertainties. The $k$(NO$_3$) derived by another approach, i.e., from the nighttime steady-state fits, provides a consistency check and evaluation of the errors, as described below.

The heterogeneous loss rate, $k$(NO$_2$)$_{\text{het}}$, can be obtained by subtracting the $k$(NO$_3$)/$K_{\text{eq}[\text{NO}_2]}$ from the determined $\tau$(NO$_2$)$_{-1}K_{\text{eq}[\text{NO}_2]}$ in Eq. (3). Figure 6a shows the averaged total N$_2$O$_5$ reactivity and fractions of N$_2$O$_5$ loss via NO$_3$ ($k$(NO$_3$)/$K_{\text{eq}[\text{NO}_2]}$) and heterogeneous N$_2$O$_5$ loss during the study period. As shown, the heterogeneous loss was dominant, accounting for 70–80% of total N$_2$O$_5$ reactivity, with a higher fraction before midnight. Figure 6b shows the contribution of different VOC categories to the average first-order NO$_3$ loss rate coefficients, $k$(NO$_3$). Biogenic monoter-

![Figure 6](image_url)

**Figure 6.** (a) Fractions of N$_2$O$_5$ loss rate coefficients through NO$_3$ loss and the heterogeneous reaction of N$_2$O$_5$ before (19:00–24:00 LT) and after midnight (01:00–05:00 LT); (b) pie chart showing the average nighttime contributions of different categories of VOCs to NO$_3$ reactivity during the study period.

![Figure 7](image_url)

**Figure 7.** Example fits of inverse N$_2$O$_5$ steady-state lifetimes according to Eq. (5) for two cases observed on the nights of 2 and 21 August 2014. The best fit values of $\gamma$ and $k_{\text{NO}_3}$ are shown.

Because the N$_2$O$_5$ uptake coefficient $\gamma$ is related to the first-order loss rate coefficient of N$_2$O$_5$, $k$(N$_2$O$_5$)$_{\text{het}}$ (Eq. 1), then Eq. (3) can be expressed as follows:

$$\tau(N_2O_5)^{-1}K_{eq}[NO_2] \approx k(\text{NO}_3) + \frac{1}{4}c_{N_2O_5}S_aK_{eq}[NO_2]N_2O_5.$$

The linear relationship between the left-hand side of Eq. (5) and $1/4c_{N_2O_5}S_aK_{eq}[NO_2]$ will give the N$_2$O$_5$ uptake coefficient $\gamma$ as the slope and the NO$_3$ loss rate coefficient $k$(NO$_3$) as the intercept (Brown et al., 2009). We selected data for periods in which $d[N_2O_5]/dt$ is close to zero and the lifetime is relatively stable, which best corresponds to steady-state conditions. Figure 7 shows two examples of $\tau$(N$_2$O$_5$)$^{-1}K_{eq}[NO_2]$ vs. $1/4c_{N_2O_5}S_aK_{eq}[NO_2]$ for cases observed on the nights of 2 and 21 August 2014. The $\gamma$ and $k$(NO$_3$) values derived from the linear fits are $\gamma = 0.040$ and
The large variability of \( \gamma \) is consistent with the observed low N\(_2\)O\(_3\) uptake and relatively high ClNO\(_2\) yields at Mt. Tai during the study period. Previous laboratory studies have investigated the dependence of \( \gamma \) on aerosol compositions and have developed mechanistic parameterizations of \( \gamma \) that can be employed in air quality models (Chang et al., 2011, and references therein). A commonly used parameterization was proposed by Bertram and Thornton (2009) and considered the aerosol volume-to-surface ratio (\( V/S \)), concentrations of nitrate, chloride, and water. For comparison, \( \gamma \) values were calculated using this parameterization based on the measured aerosol composition and molarity of water determined from the thermodynamic model with inputs of NH\(_4\)+, Na\(^+\), SO\(_4^{2-}\), NO\(_3^-\), and Cl\(^-\) (E-AIM model IV, http://www.aim.env.uea.ac.uk/aim/model4/model4a.php) (Wexler and Clegg, 2002). An error estimation showed that a 3 % change in RH implies an uncertainty in the particle liquid water content of \( \sim 5 \) %. In the calculation, mean values of \( V/S \) (64.8 - 77.2 nm) measured in the present study instead of empirical pre-factor \( A \) were used, and the reaction rate coefficients were employed as the empirical values suggested by Bertram and Thornton (2009).

Figure 8 shows a comparison of the \( \gamma \) values (with total uncertainty) determined from parameterization and measurements. Overall, the parameterized \( \gamma \) shows good correlation (\( r = 0.87 \)) with the observation-determined values and gives an average of 0.063 \( \pm \) 0.006, which is in good agreement with the average of 0.061 \( \pm \) 0.025 derived from steady-state analysis. However, the \( \gamma \) values from the parameterization are in the range of 0.052–0.070, with much lower variability than the measurement-determined values. Similar results with comparable averaged \( \gamma \) values between measurements and parameterization predictions but higher variability for measurement-derived \( \gamma \) have been reported at a mountain measurement in Germany (Phillips et al., 2016). A distinct difference of \( \gamma \) between the steady-state analysis and the parameterization has also been reported by Chang et al. (2016), who suggested that the uncertainty in determining aerosol water content would introduce errors in the parameterization. Bertram and Thornton (2009) suggested that predicted \( \gamma \) val-

\[ k(\text{NO}_3) = 0.025 \text{ s}^{-1} \] for the 2 August case and \( \gamma = 0.078 \) and \( k(\text{NO}_3) = 0.011 \text{ s}^{-1} \) for the 21 August case. Similar analyses were performed for 11 additional cases during the campaign, and the derived results are summarized in Table 2. The determined \( \gamma \) values range from 0.021 to 0.102, with a mean value of 0.061 \( \pm \) 0.025. The overall higher \( \gamma \) values were determined from parameterization and measurement-derived \( \gamma \) values (with total uncertainty) determined from parameterization and measurements. Overall, the parameterized \( \gamma \) shows good correlation (\( r = 0.87 \)) with the observation-determined values and gives an average of 0.063 \( \pm \) 0.006, which is in good agreement with the average of 0.061 \( \pm \) 0.025 derived from steady-state analysis. However, the \( \gamma \) values from the parameterization are in the range of 0.052–0.070, with much lower variability than the measurement-determined values. Similar results with comparable averaged \( \gamma \) values between measurements and parameterization predictions but higher variability for measurement-derived \( \gamma \) have been reported at a mountain measurement in Germany (Phillips et al., 2016). A distinct difference of \( \gamma \) between the steady-state analysis and the parameterization has also been reported by Chang et al. (2016), who suggested that the uncertainty in determining aerosol water content would introduce errors in the parameterization. Bertram and Thornton (2009) suggested that predicted \( \gamma \) val-

Table 2. Statistical summary of determined N\(_2\)O\(_3\) uptake coefficients \( \gamma \), ClNO\(_2\) yields \( \phi \), nitrate formation rates, and nocturnal NO\(_x\) removal rates at Mt. Tai during the study period.

<table>
<thead>
<tr>
<th>( \gamma \text{N}_2\text{O}_3 )</th>
<th>( k\text{NO}_3 )</th>
<th>( \phi \text{ClNO}_2 )</th>
<th>( \text{NO}_3^- ) formation rate (ppbv s(^{-1}))</th>
<th>( \text{NO}_3^- ) formation rate (µg m(^{-3}) h(^{-1}))</th>
<th>( \text{NO}_x ) removal rate (ppbv h(^{-1}))</th>
<th>( \text{NO}_x ) loss rate coefficient (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.061</td>
<td>0.015</td>
<td>0.28</td>
<td>0.29</td>
<td>2.2</td>
<td>1.12</td>
</tr>
<tr>
<td>SD</td>
<td>0.025</td>
<td>0.010</td>
<td>0.24</td>
<td>0.18</td>
<td>1.4</td>
<td>0.63</td>
</tr>
<tr>
<td>Median</td>
<td>0.070</td>
<td>0.011</td>
<td>0.20</td>
<td>0.26</td>
<td>2.0</td>
<td>0.98</td>
</tr>
<tr>
<td>Min</td>
<td>0.021</td>
<td>0.003</td>
<td>0.02</td>
<td>0.02</td>
<td>0.2</td>
<td>0.19</td>
</tr>
<tr>
<td>Max</td>
<td>0.102</td>
<td>0.034</td>
<td>0.90</td>
<td>0.62</td>
<td>4.8</td>
<td>2.34</td>
</tr>
</tbody>
</table>
ues would plateau and be independent of particulate chemical composition at particle water molarity above 15 M. In the present study, the particle water molarity in these cases was consistently above 25 M because of the high RH and frequent cloud cover at the mountain site, which may explain the lower variability of $\gamma$ values predicted by parameterization.

A moderate negative dependence ($r = 0.54$) of determined $\gamma$ on aerosol nitrate concentration can be inferred, with lower values of $\gamma$ associated with higher nitrate content (cf. Fig. S2a). This pattern is consistent with the nitrate suppress effect on $N_2O_5$ uptake identified in previous laboratory studies (Mentel et al., 1999) and is also similar to the anti-correlation of $\gamma$ and nitrate from tower measurements in the USA and aircraft measurements over the UK (Wagner et al., 2013; Morgan et al., 2015). The relationship between the $\gamma$ with the aerosol water to nitrate ratio also exhibits a consistent trend with the previous observations and parameterizations (e.g., Bertram and Thornton, 2009; Morgan et al., 2015), with increasing uptake as the ratio increases (Fig. S2b).

Furthermore, as suggested by Bertram and Thornton (2009), the presence of chloride can offset the suppression of $N_2O_5$ uptake by nitrate. The determined $\gamma$ values in the present study also show positive dependence on aerosol chloride concentration ($r = 0.59$), indicating the enhancement of $N_2O_5$ uptake by increased chloride contents in aerosols. This can be better described by the clear positive dependence ($r = 0.84$) of $\gamma$ on the molar ratio of particulate chloride to nitrate, as illustrated by the color-coded data in Figs. 8 and S3b. The variation in $\gamma$ values determined in the present study appears to be controlled largely by the particulate chloride-to-nitrate ratio, broadly following the competing effects of nitrate and chloride in the parameterization (Bertram and Thornton, 2009; Ryder et al., 2014). However, the discrepancy between the measurement- and parameterization-derived values may imply that some mechanisms and factors affecting $\gamma$ under conditions of high humid and pollution (e.g., reacto-diffusive length, salting effects) (Gaston and Thornton, 2016; Gržinić et al., 2017) should be further explicitly considered in the parameterization. The in situ $\gamma_{N_2O_5}$ measurement technique developed by Bertram et al. (2009a) may be useful in directly investigating the complex dependence of $\gamma$ on different factors in a range of environments.

### 3.4 CINO₂ production yield

To characterize the formation of CINO₂ from rapid heterogeneous $N_2O_5$ uptake and sufficient particulate chloride, the yields of CINO₂ ($\phi$) were examined for different plumes. For regional diffuse pollution cases, the $\phi$ defined in Reaction (R3) can be estimated from the ratio between CINO₂ production rate and $N_2O_5$ loss rate, as the first term in below equation.

$$\Phi = \frac{d\text{CINO}_2}{dt} \frac{k(N_2O_5)_{het}[N_2O_5]}{\int k(N_2O_5)_{het}[N_2O_5] \, dr}$$ (6)

The approach here assumes that the relevant properties of the nocturnal air mass are conserved and neglects other possible sources and sinks of CINO₂ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp CINO₂ peaks, the CINO₂ yield can be estimated from the ratio of the observed CINO₂ mixing ratio to the integrated $N_2O_5$ uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no CINO₂ was present at the point of plume emission from the combustion sources and no CINO₂ formation before sunset, and that the $\gamma$ and $\phi$ within the plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state $N_2O_5$ loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in $N_2O_5$ measurement and NO₃ reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the CINO₂ yield from the ratio of enhancements of CINO₂ and total nitrate (aerosol NO$_3^-$ + HNO$_3$) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach...
will only be used as a reference to validate the former analysis based on Eq. (6).

Two examples of the yield analysis are shown in Fig. 9, which indicate the time periods in which ClNO$_2$ concentration increased while other parameters (such as N$_2$O$_5$, NO$_y$, O$_3$, and SO$_2$ concentrations) were relatively stable. The $\phi$ values obtained for these two cases were 0.26 and 0.05 for 27 July and 6 August, respectively. Similar analyses were performed for all of other selected cases in which the ClNO$_2$ concentration increased and other relevant parameters were relatively constant for a short period, typically 2–3 h, and the obtained results were summarized in Table 2. The determined $\phi$ for the seven coal-fired plumes are also listed in Table 1. During the measurement period, $\phi$ varied from 0.02 to 0.90, with an average of 0.28 $\pm$ 0.24 and a median of 0.22. In comparison, the $\phi$ derived from the production ratio approach showed comparable results with an average of 0.25 $\pm$ 0.17, and the $\phi$ values from two different approaches match reasonably well with a reduced major axis regression (RMA) slope of 0.78 $\pm$ 0.08 and $r^2$ of 0.73 (cf. Fig. S4), which corroborates the yield analysis and indicates that the differences are within the overall uncertainty of 40%.

The large variability of $\phi$ is similar to field-derived values in most previous studies, and the mean value is comparable to that in the nocturnal residual layer over continental Colorado (0.18) (Thornton et al., 2010), but lower than that observed at a mountain site in Germany (0.49) (Phillips et al., 2016). The $\phi$ values for the coal-fired plumes (range of 0.20–0.90; average of 0.46 $\pm$ 0.24) are generally higher than the campaign average and those from regional diffuse pollution cases. The maximum $\phi$ (0.90) corresponds to the plume with the highest ClNO$_2$ mixing ratio observed during the campaign. This is consistent with a tower measurement in Colorado, in which higher ClNO$_2$ yields were also observed in inland power plant plumes (Riedel et al., 2013). Similar to that developed for $\gamma$, a parameterization of ClNO$_2$ yield as a function of aerosol water and chlorine composition has been proposed based on laboratory studies (Bertram and Thornton, 2009; Roberts et al., 2009):

$$\Phi = \frac{[\text{Cl}^-]}{k'[\text{H}_2\text{O}]+[\text{Cl}^-]}.$$  (7)

We compared the field-derived values to the parameterization for cases with available aerosol compositions, using an empirical $k'$ of 1/450, as recommended by Roberts et al. (2009). The particle liquid water content [H$_2$O] was calculated from the thermodynamic model (E-AIM model IV) based on measured aerosol composition, as described above. As shown in Fig. 10a, the $\phi$ values predicted by the parameterization are generally higher than those determined from observed ClNO$_2$ production rates, especially at low measurement-determined yields. For measured $\phi$ values higher than 0.4, smaller differences (< 20%) were observed between the two methods, which are within the aggregate uncertainty associated with measurement and derivation. The parameterized $\phi$ values exhibit positive dependence on the aerosol chloride concentration and the Cl$^-$/H$_2$O ratio, as shown by the color code in Fig. 10a. The measurement-determined values only exhibit such measurable dependence at low yields, implying the possible biased relationship due to higher aerosol water conditions in the present work. The discrepancy between the parameterization $\phi$ based upon aerosol composition and those derived from measured ClNO$_2$ concentrations has been found previously (e.g., Wagner et al., 2013), and the underlying causes have not been resolved.
By examining the relationships between the determined yield and other parameters, we found a slightly negative relationship between \( \phi \) and particulate nitrate concentration, as depicted in Fig. 10b. Although the data are scattered, the high-yield cases are mostly associated with lower nitrate concentrations, while the \( \phi \) values for the high nitrate cases (> 15 µg m\(^{-3}\)) are smaller. A similar trend was observed for the \( \text{NO}_x/\text{NO}_y \) ratio, which indicates the “age” of the air masses, suggesting that higher \( \phi \) values are usually associated with relatively “young” air masses exhibiting low nitrate concentrations. More secondary and dissolved organic matters in aged aerosols could be a possible factor contributing to the reduction of \( \text{CINO}_2 \) production efficiency (Mielke et al., 2013; Ryder et al., 2015; Phillips et al., 2016). Further studies are needed to characterize the combined effects of various parameters on \( \text{CINO}_2 \) yields, in particular the influences of the aerosol mixing state, chloride availability distribution among particle sizes, organic matter, acidity, other possible loss ways of \( \text{CINO}_2 \), and potential factors affecting in high humid and polluted conditions (Laskin et al., 2012; Mielke et al., 2013; Wagner et al., 2013; Ryder et al., 2015; Li et al., 2016; Phillips et al., 2016).

### 3.5 Effects of heterogeneous \( \text{N}_2\text{O}_5 \) reactions on nitrate formation and \( \text{NO}_x \) processing

In addition to abundant \( \text{CINO}_2 \) formation, rapid heterogeneous \( \text{N}_2\text{O}_5 \) uptake may also lead to the production of a large amount of nitrate, which is one of the main components of fine particles contributing to haze pollution in northern China (e.g., Huang et al., 2014). Based on the reactions described above, the formation rate of soluble nitrate from \( \text{N}_2\text{O}_5 \) reactions, \( p(\text{NO}_3^-) \), can be determined from the \( \text{CINO}_2 \) yield and \( \text{N}_2\text{O}_5 \) heterogeneous loss rate as follows:

\[
p(\text{NO}_3^-) = (2 - \phi)k_{\text{NO}_3}\text{[N}_2\text{O}_5].
\]

The \( p(\text{NO}_3^-) \) values obtained for the select cases during the study period ranged from 0.02 to 0.62 pptv s\(^{-1}\), with a mean value of 0.29 ± 0.18 pptv s\(^{-1}\), corresponding to 0.2–4.8 µg m\(^{-3}\) h\(^{-1}\) and 2.2 ± 1.4 µg m\(^{-3}\) h\(^{-1}\) (Table 2). The derived rates are comparable to the observed increases in nitrate concentrations (2–5 µg m\(^{-3}\) h\(^{-1}\)) during haze episodes in summer nights at a rural site in the NCP (Wen et al., 2015). By assuming that produced nitrate is conserved and neglecting the deposition and volatilization loss (e.g., via ammonium nitrate), the in situ \( \text{NO}_3^- \) formation could be predicted by integrating each derived formation rate over the corresponding analysis period. Similar to the \( \text{N}_2\text{O}_5 \) uptake coefficient and \( \text{CINO}_2 \) yield determination above, the nitrate formation estimation here assumes a conserved air mass with a constant formation rate over the study period. For coal-fired plumes, we equated the measured nitrate concentrations with the increases by assuming that no aerosol nitrate was directly emitted from the nocturnal point sources. As shown in Fig. 11, the predicted nitrate formation shows reasonable agreement with the measured increases in nitrate concentrations (∆\(\text{NO}_3^-\)) (RMA slope of 1.14 and \( r \) of 0.81). This consistency also can serve as a check to validate the reliability of the above-determined heterogeneous \( \text{N}_2\text{O}_5 \) reactivity and parameters of \( \gamma \) and \( \phi \). The in situ nitrate formation from heterogeneous \( \text{N}_2\text{O}_5 \) uptake was predicted to be as high as 17 µg m\(^{-3}\), with a mean value of 4.3 ± 4.5 µg m\(^{-3}\), accounting for 32 (±27)% of the observed average nitrate concentration during the cases. This is consistent with the maximum nitrate increase of 14.9 µg m\(^{-3}\) over south China (Li et al., 2016) and the 21% nitrate increase in polluted episodes in Beijing (Su et al., 2017) after considering the heterogeneous \( \text{N}_2\text{O}_5 \) uptake in the regional model simulation. As for a plume undergoing continuous chemical processing from dusk to sunrise, the heterogeneous \( \text{N}_2\text{O}_5 \) reactions would lead to substantial nitrate formation (e.g., 22 µg m\(^{-3}\) production for a 10 h night) and could contribute significantly to secondary fine aerosols as the main driver of the persistent haze pollution in northern China.

The formation of nitrate (including \( \text{HNO}_3 \)) and its subsequent removal by deposition is the predominant removal
mechanism of nitrogen oxides from the atmosphere (Chang et al., 2011). The nocturnal NO$_x$ removal rate depends on the NO$_x$ radical production rate, heterogeneous N$_2$O$_5$ loss rate, NO$_3$ reaction rate with VOCs, the partitioning between N$_2$O$_5$ and NO$_3$ concentrations, and ClNO$_2$ yield. ClNO$_2$ mainly functions as a reservoir of NO$_3$, rather than as a sink, because the formation of ClNO$_2$ throughout the night with subsequent morning photolysis recycles NO$_2$ (Behnke et al., 1997). The reactions of NO$_3$ with VOCs would predominantly produce organic nitrate products (Brown and Stutz, 2012, and references therein), but some fraction of NO$_2$ can be regenerated in the NO$_3$ reactions, i.e., with terpenes (e.g., Wängberg et al., 1997), or released from the decomposition of organic nitrate during the transport (e.g., Francisco and Krylowski, 2005). For simplicity, we neglect the recycling of NO$_2$ from NO$_3$–VOC reactions by assuming the complete removal of reactive nitrogen (Wagner et al., 2013). This would overestimate the NO$_3$ loss since the monoterpenes contribute to around half of NO$_3$ reactivity in the present study, but this assumption does not significantly affect the conclusion because the NO$_3$ loss with VOCs was the minor path compared to N$_2$O$_5$ heterogeneous loss. Thus, the nocturnal NO$_3$ loss rate can be quantified by the following equation:

$$L(\text{NO}_3) = (2 - \phi)k_{\text{N}_2\text{O}_5}\text{[N}_2\text{O}_5] + k_{\text{NO}_3}\text{[NO}_3]$$

$$= (1 - \phi)k_{\text{N}_2\text{O}_5}\text{[N}_2\text{O}_5] + p[\text{NO}_3].$$

(9)

Using the coefficients described above, we calculated the nocturnal loss rate of NO$_3$ for each case, as summarized in Table 2. The NO$_x$ removal rate varied from 0.19 to 2.34 ppbv h$^{-1}$, with a mean of 1.12 ± 0.63 ppbv h$^{-1}$, which corresponds to a pseudo-first-order loss rate coefficient of 0.24 ± 0.08 h$^{-1}$ on average for the studied cases. This loss rate is higher than that determined from a mountain site measurement in Taunus, Germany (~0.2 ppbv h$^{-1}$ with typical NO$_2$ level of 1–2 ppbv) (Crowley et al., 2010), and the results from aircraft measurements in the USA over Ohio, Pennsylvania, and the downwind region of New York (90 and 50% NO$_x$ loss in a 10 h night, respectively) (Brown et al., 2006). For reference, this nocturnal average loss rate is approximately equivalent to NO$_2$ loss via reaction with OH in afternoon condition assuming an OH concentration of around $2 \times 10^6$ molecules cm$^{-3}$, indicating the importance of nocturnal heterogeneous reactions on NO$_x$ processing and budget. Figure 12 shows the relationship between determined NO$_x$ loss rate and observed ambient NO$_x$ concentration at the measurement site. NO$_x$ loss rate appears to be strongly dependent upon NO$_x$ concentrations below 6 ppbv (slope = 0.32 h$^{-1}$; $r = 0.93$); the loss rate became more scattered at higher NO$_x$ conditions, which were typically observed in the coal-fired power plant and industrial plumes. This result implies that for low-NO$_x$ conditions (< 6 ppbv), 96% of NO$_x$ would be removed after 3 h of nocturnal processing, if no additional NO$_x$ emissions affect the plume during this period.

Comparing NO$_x$ loss to the nitrate formation rates, it can be inferred that the nitrate formation from heterogeneous N$_2$O$_5$ uptake is predominant in reactive NO$_x$ loss and accounts for an average of 87% of the NO$_x$ loss, although this fraction of individual cases varied between 35 and 100%. A box model simulation based on tower measurements at Colorado also reported that the largest proportion of the nitrate radical chemistry is N$_2$O$_5$ hydrolysis, which typically accounted for 80% of nitrate radical production, whereas the losses to NO$_3$–VOC reactions are less than 10% (Wagner et al., 2013). A recent model simulation for southern China also suggested that considering the N$_2$O$_5$ uptake and subsequent Cl activation could decrease regional NO$_x$ by more than 16% (Li et al., 2016). The results obtained in the present study demonstrate the significance of fast heterogeneous N$_2$O$_5$ chemistry on nocturnal NO$_x$ removal and fine nitrate formation in the polluted residual layer over the NCP.
4 Summary and conclusions

An intensive field study was conducted at a high-altitude site to characterize the reactive nitrogen chemistry in the polluted nocturnal residual layer over the NCP. The results revealed the frequently elevated CINO₂ mixing ratios (maximum of 2065 pptv) and efficient CINO₂ yields (0.46 ± 0.24) resulting from power plant and industrial plumes in the residual layer. The presence of CINO₂-laden air in the nocturnal residual layer confirms our previous hypothesis, based on a measurement in a rural site in the NCP, that the downward mixing of CINO₂-rich air into the surface in the next morning would have large impacts on early morning photochemistry and ozone production. Rapid heterogeneous N₂O₅ uptake and efficient CINO₂ and nitrate formation were observed during the study period. The γ values determined in the present study (average of 0.061 ± 0.025) exhibited a clear dependence on the particulate chloride-to-nitrate ratio and are higher than those observed in other locations, but consistent with those obtained at a surface site in the same region of the NCP. Laboratory-derived parameterizations predicted comparable mean γ values, but did not represent the high variability of the measured values, and tended to overestimate φ in the low yields. These discrepancies suggest that various aerosol physicochemical parameters have complicated effects on N₂O₅ uptake and CINO₂ yield, in particular in a high-humidity and polluted residual layer, which requires further investigation.

Fast heterogeneous N₂O₅ uptake dominated and accounted for a mean of 87% of the regional nocturnal NOₓ loss during the study periods in the NCP. The estimated nocturnal loss rate of NOₓ is higher than that previously observed in the USA and Europe, with an averaged loss rate and rate coefficient of 1.12 ± 0.63 ppbv h⁻¹ and 0.24 ± 0.08 h⁻¹, respectively. Moreover, heterogeneous reactions contributed to substantial nitrate production of up to 17 µg m⁻³h⁻¹, with a mean nocturnal formation rate of 2.2 ± 1.4 µg m⁻³h⁻¹, and in situ production could account for 32 ± 27% of the observed nitrate concentrations in the studied cases. The results may help explain the previously observed rapid nighttime growth of fine nitrate aerosols in the NCP and demonstrate the importance of heterogeneous N₂O₅–CINO₂ chemistry on NOₓ and aerosol budgets in the polluted residual layer over the NCP, which underpins the need for further studies regarding their roles in the formation of complex haze pollution in northern China.

Data availability. The data used in this study are available upon request from the corresponding author (z.wang@polyu.edu.hk).

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