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Fast heterogeneous loss of N_2O_5 leads to significant nighttime NO_x removal and nitrate aerosol formation at a coastal background environment of southern China

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Abstract: Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) play crucial roles in the nocturnal atmosphere. To quantify their impacts, we deployed a thermal-dissociation chemical ionization mass spectrometry (TD-CIMS), to measure their concentration, as well as $ClNO_2$ at a coastal background site in the southern of China during the late autumn of 2012. Moderate levels of NO_3, N_2O_5 and high concentration of $ClNO_2$ were observed during the study period, indicating active NO_x-O_3 chemistry in the region. Distinct features of NO_3, N_2O_5 and $ClNO_2$ mixing ratios were observed in different airmasses. Further analysis revealed that the N_2O_5 heterogeneous reaction was the dominant loss of N_2O_5 and NO_3, which showed higher loss rate compared to that in other coastal sites. Especially, the N_2O_5 loss rates could reach up to 0.0139 s^{-1} when airmasses went across the sea. The fast heterogeneous loss of N_2O_5 led to rapid NO_x loss which could be comparable to the daytime process through NO_2 oxidization by OH, and on the other hand, to rapid nitrate aerosol formation. In summary, our results revealed that the N_2O_5 hydrolysis could play significant roles in regulating the air quality by reducing NO_x but forming nitrate aerosols.

Keywords: dinitrogen pentoxide, TD-CIMS, N_2O_5 heterogeneous reaction, NO_x removal, nitrate aerosols

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Highlights:

1. N_2O_5 and NO_3 were observed with distinct features in different airmasses.
2. The fast hydrolysis of N_2O_5 dominated the loss of N_2O_5 and NO_3, particularly when continental air went across the sea before reaching the station.
3. The fast loss of N_2O_5 can contribute to a significant fraction of NO_x removal and nitrate aerosol formation.

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1. Introduction

Nitrogen oxides (NO_x = NO + NO_2), largely emitted by human activities, are key species in a number of atmospheric processes and therefore have crucial impact on climate and human health. In the daytime, NO_x play key roles in regulating ozone formation (Wang et al., 2006;Wang et al., 2010), participating in the formation of highly oxygenated molecules (Yan et al., 2016;Lee et al., 2016) and subsequent formation secondary organic aerosol (Hoyle et al., 2011), as well as leading to direct formation of inorganic nitrate aerosol (NO_3^-) by reacting with hydroxyl radical (OH) to form water soluble nitric acid (HNO_3, R1), and the R1 has been recognized as the termination of NO_x cycle in the atmosphere (*e.g.* (Ramanathan et al., 2001))

$$\mathrm{NO_2 + OH \rightarrow HNO_3} \qquad \text{(R1)}$$

At night, NO_x can participate in a different set of atmospheric processes. Oxidation of NO_2 by O_3 produces nitrate radical (NO_3, R2), a major oxidation in the nocturnal boundary layer. It can oxidize various volatile organic compounds (VOC, R3), producing oxygenate products, which can contribute to the formation of organic aerosols (Lucas and Prinn, 2005;Rollins et al., 2009;Ng et al., 2017). Another competing reaction is that NO_3 further reacts with NO_2 to form N_2O_5, after which NO_3 and N_2O_5 can establish a fast thermal equilibrium (R4, R4′). N_2O_5 either deposits on aerosol surface through heterogeneous reaction to form inorganic nitrate aerosol (R5) or serves as the reservoir of NO_3 and NO_2 (R4′). If aerosols contain chloride (Cl^-), heterogeneous reaction of N_2O_5 may lead to the formation of $ClNO_2$ (R6), which can further photolyze to release the chloride radical (Cl·) after sunrise (R7) and affect the atmospheric oxidation capacity (Tham et al., 2014).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R2}$$

$$\mathrm{NO_3 + VOC \rightarrow Products} \tag{R3}$$

$$\mathrm{NO_2 + NO_3 + M \rightarrow N_2O_5 + M} \tag{R4}$$

$$\mathrm{N_2O_5 + M \rightarrow NO_2 + NO_3 + M} \tag{R4′}$$

$$\mathrm{N_2O_5 + H_2O(s) \rightarrow 2HNO_3} \tag{R5}$$

$$\mathrm{N_2O_5 + Cl^- \rightarrow ClNO_2 + NO_3^-} \tag{R6}$$

$$\mathrm{ClNO_2} + hv \rightarrow \mathrm{Cl\cdot + NO_2} \tag{R7}$$

These nocturnal processes essentially convert NO_x into nitrate constituents in aerosols, causing a reduction in NO_x and an augment secondary aerosol mass concentration, which however, remain poorly quantified.

A major challenge in estimating the importance of these reactions is the large uncertainty of the N_2O_5 heterogeneous uptake coefficient of N_2O_5 ($\gamma_{N_2O_5}$), an important parameter for estimating the N_2O_5 heterogeneous loss rate (k_{N2O5}; see Eq 1):

$$k_{N_2O_5} = 0.25 \times S_a \times c \times \gamma_{N_2O_5} \qquad \text{(Eq.1)}$$

Here, S_a is the surface area of aerosol and c is the molecular velocity of N_2O_5. Both field and laboratory studies have shown that the $\gamma_{N_2O_5}$ values fall between *ca.* 0.001 – 0.2. However, the $\gamma_{N_2O_5}$ may significantly vary depending on the chemical composition of particles (Brown et al., 2006;Ammann et al., 2013;Brown and Stutz, 2012;Tang et al., 2017). For instance, chloride and water content in the aerosol promote N_2O_5 heterogeneous uptake while, nitrate and organic coating inhibit the heterogeneous uptake of N_2O_5 (Riedel et al., 2012;Tham et al., 2018;Bertram and Thornton, 2009). The mixing status and the diffusive length of the chemical compounds in the aerosol may also play crucial role in affecting the N_2O_5 heterogeneous uptake (Gaston and Thornton, 2016;Gaston et al., 2014;Ryder et al., 2014). Despite of these new insights, most chemical transfer models derived from the laboratory studies failed to reproduce the field determined $\gamma_{N_2O_5}$ (McDuffie et al., 2018), indicating that the complexity of heterogeneous uptake of N_2O_5 remains incompletely understood.

Measurements of N_2O_5 and its loss process either through N_2O_5 heterogeneous reaction or NO_3 loss reactions (term as N_2O_5 reactivity) have been the interest of many field studies in different places around the world over the past decade. For examples, Brown et al. (2003) reported the first simultaneous in situ measurement of a suite of nocturnal nitrogen oxide compounds in Boulder, Colorado, and N_2O_5 reached a peak concentration of nearly 3 ppbv under polluted conditions (Brown et al., 2003a;Brown et al., 2003b). Brown and co-workers then tracked the N_2O_5 reactivity through a flight measurement in New England and found that the N_2O_5 heterogeneous loss dominated the N_2O_5 sink and its lifetime in the polluted airmasses with high sulfate aerosol loading was two orders of magnitude shorter than in relatively cleaner airmasses from eastern Pennsylvania and New Jersey (Brown et al., 2006). A cruise measurement along the United States east coast showed more variation in the N_2O_5 reactivity where N_2O_5 heterogeneous loss dominated the N_2O_5 sink in the outflow airmasses during the night but N_2O_5 loss through the NO_3 sink become more important in airmasses characterized with higher level of terrestrially emitted biogenic VOC (Aldener et al., 2006). Another nighttime aircraft measurement downwind of urban, industrial and rural areas of Texas revealed that the N_2O_5 heterogeneous loss was of less importance (14 – 28% of the total reactivity) compared to the NO_3 reaction with VOC (Brown et al., 2011). Similar studies were also conducted in Europe, where Crowley et al. (2011) observed at a coastal site in southern Spain that the NO_3 loss reaction was prevailing in the marine airmasses, in contrast to the N_2O_5-dominated losses in the continental originated airmasses. An airborne N_2O_5 measurement in UK also showed that the N_2O_5 heterogeneous loss was faster than NO_3 loss rate aloft the Southern North Sea, while, the NO_3 loss was dominating in the air above the motorway, Greater London and English Channel (Morgan et al., 2015). As in Asia, Matsumoto et al. (2006) reported that the NO_3 loss accounted for 65 – 74 % of the total loss rate of N_2O_5 in Japan. Recent studies reported intense N_2O_5 heterogeneous uptake and dominating the N_2O_5 loss in the northern polluted regions of China (Tham et al., 2016;Wang et al., 2017a;Wang et al., 2017b;Wang et al., 2017c). These measurements have revealed the spatial variations in the N_2O_5/NO_3 reactivity around the world, indicating that the role of N_2O_5 can vary significantly over different environment and airmasses.

Hong Kong, one of the most urbanized coastal cities in Pearl River Delta (PRD), has been suffering from severe photochemical pollutions that are characterized by high mixing ratios of NO_x and O_3 (Wang et al., 2009a). Under such circumstances, the importance of N_2O_5 and NO_3 may be amplified in this environment, where pollution is typically distinctive in the airmasses from the inland of China compared to the inflows of marine air (Wang et al., 2003;Wang et al., 2005). Indeed, very high levels of N_2O_5 and $ClNO_2$, up to 7.7 and 4.7 ppbv, respectively, were observed at a mountain-top site in Hong Kong (Brown et al., 2016;Wang et al., 2016), and the NO_3/N_2O_5 chemistry removed 70% of the NO_x in the nocturnal residual layer and ultimately (Yun et al., 2017), perturbing the NO_x and O_3 level in the next day (Wang et al., 1998). Elevated levels (~ 2 ppbv) of $ClNO_2$ were also observed at a coastal and ground-level site (Hok Tsui) in Hong Kong, and the photolysis of $ClNO_2$ in the early morning led to fast production of Cl atoms, whose oxidative power was several times of that from ozone photolysis (Tham et al., 2014). Continuing that work, this paper analyzes nighttime reactivity N_2O_5 and NO_3 in different airmasses arriving at the coastal site, and discusses the role of N_2O_5 heterogeneous uptake in the NO_x reduction and nitrate aerosol formation.

2. Methods

2.1. Site descriptions

The measurement took place at Hok Tsui atmospheric monitoring station which is located at the southeast tip of Hong Kong Island (22.22° N, 114.25° E). Figure 1 shows the location of the study site in relation to Hong Kong urban areas and major cities in Pearl River Delta (*i.e.* Shenzhen, Guangzhou and Macau). The site sits on a 60 m high cliff (above sea level), facing the South China Sea from northeast to the west (~270° view). Hok Tsui is typically in the upwind of the urban cores of Hong Kong and PRD and there are no strong emission sources within the surrounding area (the nearest Hong Kong's urban center is approximately 15 km away), but can be occasionally influenced by urban plumes (*e.g.* (Wang et al., 1998;Xue et al., 2016)). Therefore, measurements at Hok Tsui station are expected to have a mixture of background characteristics from the ocean and airmasses transported from the urban areas, which is a suitable for investigating the reactivity of NO_3 and N_2O_5 in the different air masses. More detail descriptions of the site can be found elsewhere (Cheng et al., 2000; Wang et al., 2009b;).

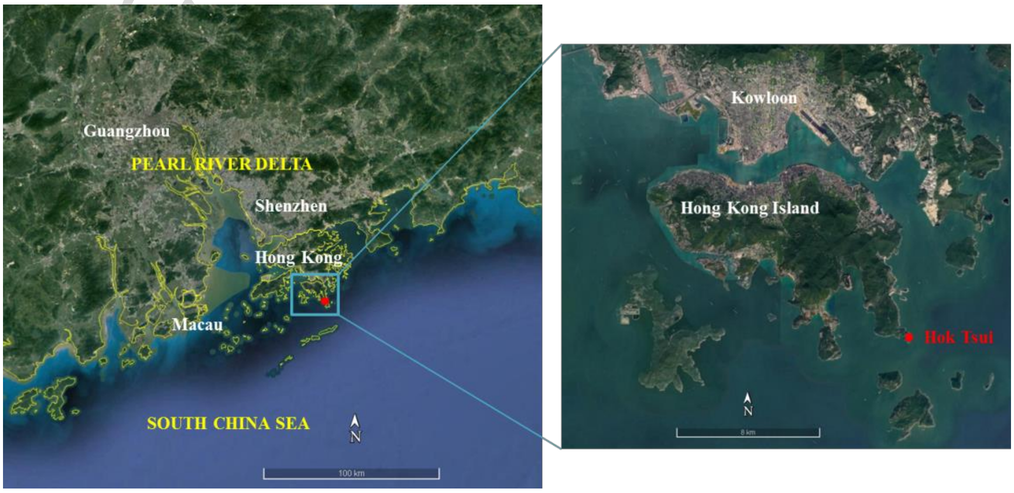

Figure 1. The location of Hok Tsui site in relative to the urbanization areas in Pearl River Delta, China.

2.2. Measurements

2.2.1. Measurement of NO_3+N_2O_5 and $ClNO_2$

A thermal dissociation-chemical ionization mass spectrometer (TD-CIMS) was used to measure the NO_3+N_2O_5 and $ClNO_2$. A 3 m length of perfluoroalkoxy (PFA) tubing (inner diameter of 9.5 mm; outer diameter of 12.7 mm) was used to draw down the ambient air at a total flow-rate of 6 standard liters per minute (SLPM), leading to a residence time of less than a second. Only 1.55 SLPM out of the total flow was sampled through a 14.8 cm length of heating region (heated at 180˚C) before entering the CIMS while the remaining flow was dumped. The N_2O_5 was thermal-dissociated into NO_3 by the high inlet temperature, while the $ClNO_2$ would be able to pass through the heating region (Thaler et al., 2011), and subsequently ionized by the reagent ions (iodide, I^-) to produce NO_3^- ions (detected at 62 *m*/*z*), and $I(ClNO_2)^-$ ions, detected at 208 *m*/*z* (Kercher et al., 2009;Slusher et al., 2004). During the campaign, the instrument background was determined hourly by adding a small flow of high concentration of NO (~1000 ppm) into the top of the sampling inlet, in order to 'titrate' the NO_3 and N_2O_5, ultimately. The TD-CIMS was calibrated weekly and the average sensitivity during the campaign was determined to be 1.9 ± 0.1 Hz/pptv 0.44±0.05 Hz/ppt (mean ± standard deviation) for NO_3+N_2O_5 and $ClNO_2$, respectively. The detection limit (1 minute average, 3σ) was estimated to be 10 pptv and 2 pptv for NO_3+N_2O_5 and $ClNO_2$, respectively. The detail sampling, detection, calibration procedures can be found in elsewhere (Wang et al., 2014; Tham et al. 2014).

It has been found that the co-existence of peroxy acetyl nitrate (PAN) and NO_x caused an overestimation of NO_3+N_2O_5 signals (62 *m*/*z*) in the daytime [45], but such interference was insignificant during the nighttime at Hok Tsui due to relatively low level of PAN and NO_x. Therefore, only nighttime data (19:00-06:00, local time) were extracted for the analysis and the correction of such interference at the nighttime 62 *m*/*z* data was estimated to be smaller than 15%. Another uncertainty of this measurement is that the potential loss of N_2O_5 on the inlet surface (i.e., conversion to $ClNO_2$) might be enhanced when particles deposited on the wall of inlet tube over time. To avoid the large uncertainty from inlet chemistry, only the data from 23 August to 19 September 2012 were used in this study. Upon checking on the ambient data during the instrument background measurements (flooding the inlet with high NO concentration), there is no significant reduction in the $ClNO_2$ signal, whereas the NO_3+N_2O_5 signal immediately dropped to zero level. This observation suggests that the inlet chemistry (conversion of N_2O_5 to $ClNO_2$ on inlet surface) was insignificant, at least in this selected study period.

2.2.2. *Auxiliary measurements*

In addition to TD-CIMS, other ancillary measurement included the routine gases and meteorological parameters. O_3 was measured with a commercial UV photometric analyzer (Model 49i, Thermo Environmental Instruments TEI, USA). NO_x (NO and NO_2) was measured with a chemiluminescence instrument (Model 42i, TEI) equipped with a photolytic NO_2-converter (Air Quality Design, USA), which is more suitable for measurement in rural site (Xu et al., 2012). The ambient temperature and relative humidity (RH) were monitored with a temperature/RH probe (Model 41382VC/VF, M.R. YOUNG, USA). Wind speed and direction were monitored using a wind monitor (Gill, UK). Photolysis rate of NO_2 was obtained using a filter radiometer (Meteorologie consult gmbh). All of the inlets and meteorological probes/sensors were installed close to each other to reduce inhomogeneity of the sample air.

2.3. *Estimating the steady-state NO_3 and N_2O_5 loss rates*

N_2O_5 can achieve fast thermal equilibrium with NO_3 and NO_2 in ambient condition and can be described by using Eq. 2 and Eq. 3.

$$[N_2O_5]= K_{eq}[NO_2][NO_3] \quad \text{(Eq.2)}$$

$$K_{eq}=k_4/k_4^{'} \quad \text{(Eq.3)}$$

Here, K_{eq} is the thermal equilibrium, k_4 and k_4' are the rate constant from R_4 and R_4', respectively; $k_4 = 1.9 \times 10^{-12}$ $(T/300)^{0.2}$ cm^3 molecule^{-1} s^{-1} (Viggiano et al., 1981) and $k_{4'} = 9.7 \times 10^{14}$ $(T/300)^{0.1}$ exp$^{(-11080/T)}$ s^{-1} (Hahn et al., 2000). With the known $K_{eq}[NO_2]$, we can then calculate the N_2O_5 to NO_3 ratio and separate the measured total NO_3+N_2O_5 into individual concentrations of NO_3 and N_2O_5 for further analysis.

Brown et al. (2003) proposed a statistical method to derive the steady-state loss rates of NO_3 and N_2O_5, based on the field measured NO_2, O_3, NO_3 and N_2O_5. Briefly, the production starts in R1, production of $NO_3 = k_1[NO_2][O_3]$. If the NO_3 and N_2O_5 are both in steady-state condition, where their total formation rate and total loss rate are in equivalent, the equation can be shown as in Eq. 4.

$$k_1[NO_2][O_3] = k_{NO_3}[NO_3] + k_{N_2O_5}[N_2O_5] \quad \text{(Eq.4)}$$

where, the k_{NO3} and k_{N2O5} denote the first-order loss rates for NO_3 and N_2O_5, respectively. It should be note that Eq.4 only holds when NO_3 and N_2O_5 are pseudo steady state, *i.e.*, the production and loss of NO_3 and N_2O_5 are much faster than their net changes.

The steady-state lifetime of NO_3, $\tau(NO_3)$, can be calculated from Eq. 5, and the inverse lifetime of NO_3 ($\tau(NO_3)^{-1}$), also known as the total loss rate, can be redefined as in Eq.6.

$$\tau(NO_3) = \frac{[NO_3]}{k_1[NO_2][O_3]} = \frac{[NO_3]}{k_{NO_3}[NO_3]+ k_{N_2O_5}[N_2O_5]} \quad \text{(Eq.5)}$$

$$\tau(NO_3)^{-1} = k_{NO_3} + K_{eq}[NO_2]\, k_{N_2O_5} \quad \text{(Eq.6)}$$

From Eq. 6, the inverse of NO_3 lifetime can be described as a linear function of $K_{eq}[NO_2]$. The $\tau(NO_3)^{-1}$ and $K_{eq}[NO_2]$ were obtained from the measurement and the k_{NO3} and k_{N2O5} were determined by fitting the slope and intercept of the function.

As has been mentioned, this analysis assumes the steady-state of NO_3 and N_2O_5, which however, may not hold under some circumstances. For example, if the measurement location is too close to the emission source, the equilibrium may not be established and/or there is insufficient time to achieve steady-state. Here, we used a simple box model to test the validity of steady-state assumption for our measurement. In this model, R2, R4, and R4’ were used as the production of NO_3 and N_2O_5, whereas k_{NO3} and k_{N2O5} determined from the field measurement were used to describe the total first-order loss rates of NO_3 and N_2O_5, respectively, regardless of detailed loss pathways. According to the selected case studies in Section 3.2 below, four sets of initial input parameters were tested. The initial concentrations of NO_3 and N_2O_5 were set to zero, and a nighttime mean temperature of 300 K was used in these runs. The model results of these four cases are presented in Figure 2. In all of the four cases, after fast accumulations at the beginning, the NO_3 and N_2O_5 slowly decrease, indicating a relatively small net changing rate. Also showed in the bottom two panels of the sub-figures that the net variations of NO_3 and N_2O_5 become much smaller than their production and loss rates after a short period (*c.a.* 15 min), suggesting that both of them are in pseudo steady-state. As the distance from the nearest major NO_x emission source was approximately 15 km away and with a maximum wind speed of 5 m s^{-1}, a minimum of 50 min was required for the air plume to reach the measurement site, which is probably enough for NO_3 and N_2O_5 to achieve steady-state for all of our selected cases.

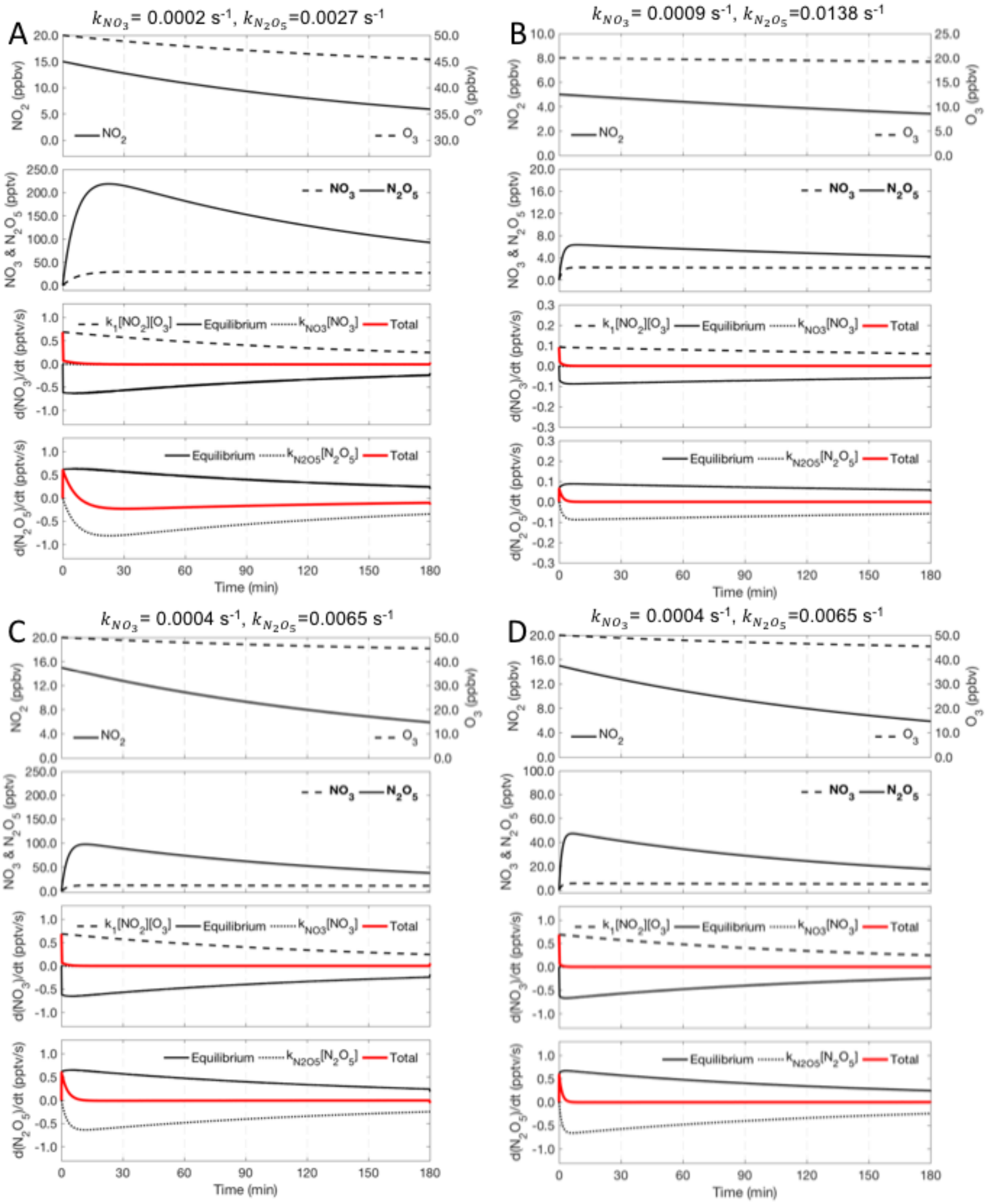

Figure 2. Verifying the steady-state of NO_3 and N_2O_5. Model input parameters in **A-D** are obtained from the four cases shown in Section 3.2.

2.4. Calculation of OH concentration

The OH concentration was calculated according to the Ehhalt and Rohrer (2000) parameterization, which based on the function of NO_2 mixing ratio, and the photolysis rates of O_3 and NO_2.

$$[OH]= 4.1\times10^{9} \times (J_{O^1D})^{0.83}(J_{NO_2})0^{.19}\frac{140[NO_2] + 1}{0.41[NO_2]^2 + 1.7[NO_2] + 1} \quad \text{(Eq.7)}$$

The J_{NO2} is the photolysis rate of NO_2 (from filter radiometer measurement), while J_{O1D}, photolysis rate of O_3, was estimated from the Tropospheric Ultraviolet and Visible (TUV) Radiation Model and then scaled by the measured J_{NO2}. This parameterization was developed for the summertime conditions (in Germany) with high solar intensity, relative humidity, and biogenic VOC emissions, which are quite similar to the conditions in Hong Kong, but, uncertainty may arise if photolysis of nitrous acid (HONO) is the predominant OH source. The calculated values were consistent with those measured in PRD region and modeled OH concentrations at this site (Li et al., 2018;Hofzumahaus et al., 2009), therefore, may serve as the simplified reference of OH levels in this study.

3. Results & Discussion

3.1. Observation of NO_3, N_2O_5 and $ClNO_2$

Figure 3 shows the time-series of NO_3, N_2O_5, and $ClNO_2$ together with related trace gases and meteorological parameters for period between 23 August and 19 September 2012. Similar to the previous observations at this location (*e.g.* Wang et al., 2003; Wang et al., 1998), abundant of NO_x (up to 51 ppbv) and O_3 (up to 152 ppbv) were observed during the measurement period. These high levels of NO_x and O_3 lead to the active NO_x-O_3 oxidation, thus, significant of NO_3 was observed starting from sunset and decrease at sunrise, with an average nighttime concentration of 7±12 pptv (mean±standard deviation). Concurrently, N_2O_5 was observed to have a mean nighttime concentration of 17±33 pptv, with a maximum of 336 pptv observed on the night of 23–24 August 2012. $ClNO_2$, a product from the N_2O_5 heterogeneous reaction, was observed with an average night-time concentration of 112±218 pptv and can reach up to 2000 pptv during the measurement period, suggesting that there are active N_2O_5 heterogeneous processes in the region. The detail observations of $ClNO_2$ at this site have been reported in our previous study (Tham et al., 2014).

The higher mixing ratios of NO_3, N_2O_5 and $ClNO_2$ observed at the site are typically corresponding to the northerly wind (see wind direction in Figure 3), which suggest that the polluted airmasses are coming from the urban-cores of Hong Kong and PRD regions. Detailed analysis of 24-h back trajectories calculated by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998) for the measurement period reveal that the airmasses arriving at the measurement site alternately originated from the continent regions (urban areas of Hong Kong and PRD) and the sea (South China Sea). For instance, airmasses were originated from the continent regions in between 23 and 26 Aug 2012 (refer as Type Ia), and then shifted to marine origins from 29 August to 14 September 2012 (Type II) before turning into the continent origins from 15 to 20 September 2012 (Type Ib). There are specific days on 27–28 August 2012 and 18–19 September 2012 that have a mixture of continent and marine airmass, where the continental air moved onto the sea (staying on the sea for more than 12 hours) before arriving at our measurement site (Type III).

Table 1 summarizes the mean concentration for N_2O_5, NO_3, $ClNO_2$, O_3 and NO_2 and the lifetime of NO_3 and N_2O_5 in different type of airmasses. Owing to the high concentrations of precursors (i.e. NO_2 and O_3), highest mixing ratios of NO_3, N_2O_5 and $ClNO_2$ were measured in the continental airmasses, in contrast to their lowest concentrations observed in the pristine marine airmasses (typically close to detection limits). The mixture of continent and marine airmass, on the other hand, has moderate concentrations of NO_3, N_2O_5 and $ClNO_2$, although NO_2 and O_3 were similar to the continental airmasses. The lifetime of N_2O_5 (and NO_3 due to their internal equilibrium) in all types of masses were notably shorter than those in the earlier studies in US and Europe (*e.g.* Brown et al., 2006; Crowley et al., 2011; Morgan et al., 2015; Brown et al., 2009), especially in Type III airmasses, which suggested fast losses of

N_2O_5 and NO_3 at this location. In addition, higher ratios between $ClNO_2$ and N_2O_5 were found in marine-involved airmasses, indicating more active N_2O_5 heterogeneous chemical processes, probably on the chloride-rich marine aerosols.

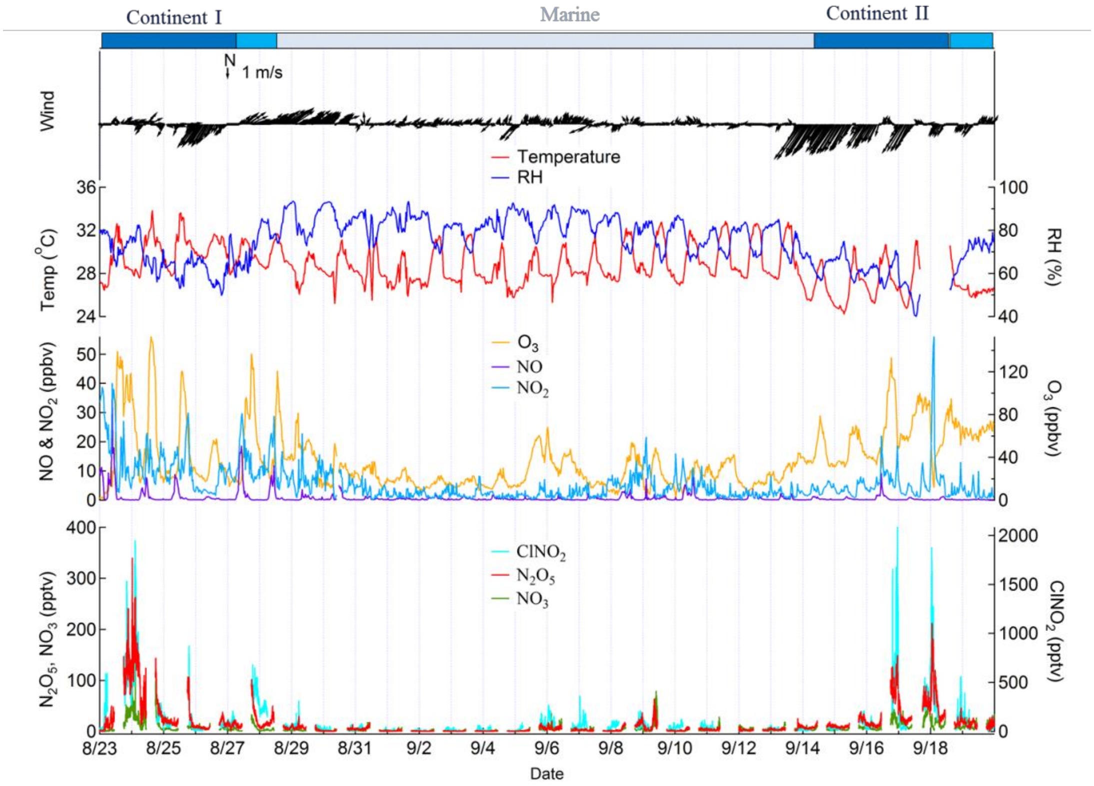

Figure 3. Temporal variations of meteorological parameters (wind, temperature, and RH), trace gases (CO, O_3, NO, and NO_2), as well as the sum of NO_3 and N_2O_5 and $ClNO_2$. Since this technique detects the sum of NO_3+N_2O_5, the airmasses origins were determined from the 48 hours back trajectories derived from HYSPLIT.

Table 1. Mean nighttime values (± standard deviation, 1σ) for the concentration of N_2O_5, NO_3, $ClNO_2$, O_3, and NO_2, together with N_2O_5 steady-state lifetime and $ClNO_2$ to N_2O_5 ratio in different type of airmasses.

Airmass	**Period**	**N_2O_5 (pptv)**	**NO_3 (pptv)**	**$ClNO_2$ (pptv)**	**NO_2 (ppbv)**	**O_3 (ppbv)**	**$\tau(N_2O_5)^1$ (s)**	**$ClNO_2/N_2O_5{}^2$**
Whole period	23 Aug – 19 Sept	17±33	7±12	112±218	6±7	33±24	76±61	6.9
Continental	23 - 26Aug	49±58	14±22	264±348	12±9	40±31	119±76	5.3

(Type Ia)								
Marine (Type II)	29 Aug - 14 Sept	4±4	2±3	33±36	4±4	22±13	51±43	9.1
Continental (Type Ib)	15 - 17Sept	44±39	15±13	269±355	7±10	56±25	138±47	6.1
Continental+ Marine (Type III)	27/28 Aug and 18/19 Sept	15±10	8±6	154±135	6±4	52±24	79±53	10.1

[1] similar to Eq.5, $\tau(N_2O_5) = \frac{[N_2O_5]}{k_1[NO_2][O_3]}$.

[2] mean ratio.

3.2. N_2O_5 and NO_3 reactivity

With the observations of short N_2O_5 lifetimes, it is crucial to assess the dominant loss pathway of N_2O_5, either through NO_3 loss reactions or N_2O_5 heterogeneous uptake, in order to further determine its importance in the atmospheric processes. We distinguished the N_2O_5 reactivity by evaluating the loss rate of NO_3 and N_2O_5 predicted by the steady-state method described in Section 2.3. As aforementioned, this method may not be valid if the N_2O_5 is not in steady-state or the plume changes throughout the night, which may result in a negative intercept value. Therefore, we carefully selected the valid time period of N_2O_5 data for four different nights to represent the determined types of airmasses, namely on 24 August, representing continent airmass (Type Ia); on 9 September, representing airmass origin from marine (Type II); 16 September, representing another continent airmass (Type Ib); and the night of 18 September represents the mixture of continent and marine airmass (Type III).

Figure 4 depicts the 24-h airmass back trajectories for the selected four cases, and the loss rates of NO_3 and N_2O_5 in these airmasses. The results revealed that the N_2O_5 heterogeneous loss was overwhelming the loss through the NO_3 reactions. The $k_{N_2O_5}$ were determined to be 0.0027 s^{-1}, 0.0138 s^-

^{1}, 0.0065 s^{-1}, and 0.0139 s^{-1} in the Type Ia, Type II, Type Ib and Type III airmasses, respectively. The determined k_{NO3} were more than one order of magnitude smaller, derived to be 0.0002 s^{-1} for Type Ia, 0.0009 s^{-1} for Type II, and 0.0004 s^{-1} for both Type Ib and Type III. The predominant loss pathway for N_2O_5 heterogeneous reaction has been observed in other marine or coastal environment (*e.g.* [24,27,54–56], but the absolute N_2O_5 heterogeneous loss rates in at our site are considerably faster than most of the rates reported in those studies. For example, measurement in San Francisco bay observed the k_{N2O5} in the range of 5.6×10^{-5} to 9.8×10^{-4} s^{-1} (Wood et al., 2005), while cruise measurements along the United States east coast and Los Angeles basin reported N_2O_5 heterogeneous loss rate in between 10^{-4} and 10^{-3} s^{-1} (Osthoff et al., 2008;Wagner et al., 2012). Morgan et al. (2015) observed a largest k_{N2O5} of 1×10^{-3} s^{-1} in a plume during the aircraft measurement near London and English Channel.

Among the airmasses, the marine-influenced airmasses (*i.e.* Type II and Type III) were determined to have faster N_2O_5 loss rates (see Figure 4) and larger $ClNO_2$ to N_2O_5 ratios (see Table 1). In other words, the N_2O_5 heterogeneous loss and production of $ClNO_2$ were higher when the air parcel interacted with the sea than in those the airmasses originated from the continent urban areas. This implied that the marine environment was more efficient in processing the N_2O_5. It can be seen that the calculated back trajectories height for the Marine and Continent + Marine airmasses were lower than 500 m at least 6 hours before arriving at the site (see Figure 4), suggesting that the airmass containing N_2O_5 and $ClNO_2$ had been processed along the surface of the ocean after the sunset. During the transport along the ocean, the N_2O_5 can either being uptake onto the sea-spray to produce $ClNO_2$, and/or deposit onto the sea surface microlayer leading to the terminal loss of N_2O_5 (Finlayson-Pitts et al., 1989). Previous studies at this site have shown that high chloride concentrations were frequently observed in total suspended particles, PM_{10} and $PM_{2.5}$ (Cheng et al., 2000; Lai et al., 2007). Given the observation of considerable $ClNO_2$ concentrations (up to 680 pptv), and higher RH in these types of airmasses, which can promote heterogeneous uptake (Ammann et al., 2013; Brown et al., 2012), we believe that the heterogeneous reaction of N_2O_5 was enhanced by the sea-spray/chloride-rich aerosols. However, the importance of N_2O_5 deposition and loss mechanism on the sea surface microlayer is unknown in this region, thereby, more future studies are needed to quantify the roles of air-sea interactions in affecting the N_2O_5 lifetime.

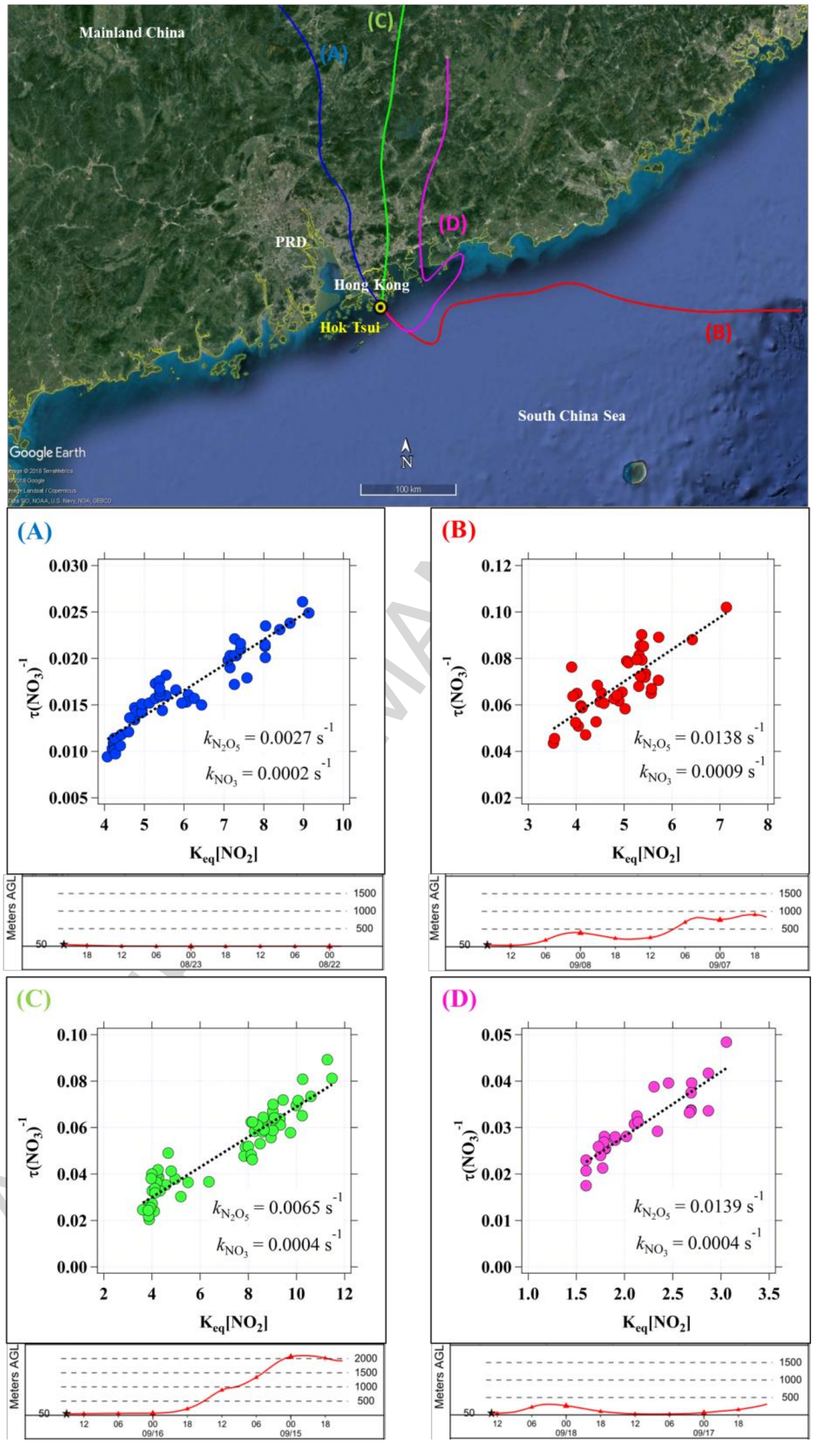

Figure 4. 48-h back-trajectories calculated from HYSPLIT for four specific nights: **(A)** 23 – 24 August, **(B)**; 8 – 9 September **(C)**; 16 – 17 September; and **(D)** 18 – 19 September. Scatter plots showing the determined loss rates of

NO_3 and N_2O_5 using the method described in Section 2.3. Lower panel of each plot shows the height of the airmass before arriving at the sampling site.

3.3. Nighttime NO_x loss rate

Heterogeneous uptake of N_2O_5 can lead to production of nitrate aerosols and $ClNO_2$ as a cost of NO_x. In this section, we evaluated the potential nighttime NO_x loss from the N_2O_5 heterogeneous uptake. The potential nighttime NO_x removal rate can be calculated by Eq.8, where the ϕ is the production yield of $ClNO_2$, which will recycle a NO_2 when photolyzed at sunrise. Setting the ϕ to 0 and 1 gives the upper (high) and the lower (low) limit of the NO_x removal rate ($L(NO_x)$) and nitrate aerosol production rate ($P(NO_3^-)$), respectively.

$$L(\mathrm{NO_x}) = P(\mathrm{NO_3^-}) = (2-\phi)k_{\mathrm{N_2O_5}}[N_2O_5] \quad \text{(Eq.8)}$$

By using the k_{N2O5} determined above and assume that the rate is constant throughout the night, the potential nighttime NO_x removal rates for the 4 examples of airmass types were shown in Table 2.

Since significant levels of $ClNO_2$ has been observed concurrently, the actually NO_x removal rate might be more close to the lower limits, which were 0.38±0.11 and 0.36±0.22 pptv s^{-1} for Type Ia and Ib, 0.15±0.11 pptv s^{-1} for Type II, and 0.23±0.10 pptv s^{-1} for Type III. Although k_{N2O5} was lower in continental airmasses than in the marine one, the $L(NO_x)$ and $P(NO_3^-)$ were higher owing to the more abundant N_2O_5, suggesting that N_2O_5 pathway play a more crucial role in continental airmasses. It is also important to note that, despite the moderate $L(NO_x)$ and $P(NO_3^-)$ in the Type III airmass, the actually influence of such airmass type might be more significant. It is possible that NO_2, O_3, and N_2O_5 had experienced efficient losses before reaching our observation station.

We further compared the lower limit of NO_x removal rates via N_2O_5 hydrolysis with the upper limit of main daytime NO_x loss rates assuming that all nitric acid produced via OH oxidation (R1) eventually deposit on surfaces. The OH was calculated using the method described in Section 2.4. Figure 5 shows the time series of the NO_x removal rates and nitrate aerosol formation rates in the four cases. In the Type Ia and Ib airmasses, N_2O_5 heterogeneous reaction contributed about 20–25 % of the NO_x removal and nitrate aerosol formation; this value dropped to 15 % in the Type II airmass and increased almost to half in the Type III case. These results are consistent with the study of Yun et al. (2018) that has modeled up to 79% of NO_2 loss in the nocturnal residual layer of Hong Kong was caused by the N_2O_5 heterogeneous reaction. Therefore, we conclude that the N_2O_5 heterogeneous reaction can play a significant role in affecting the NO_x lifetime in this coastal region, especially in the airmasses with continental origins.

Table 2. Mean NO_x removal rates and nitrate aerosol formation rates via N_2O_5 heterogeneous reaction during the four cases (± standard deviation, 1σ), as well as their comparison with the adjacent daytime via HNO_3 deposition pathway. The lower and higher limits of N_2O_5 pathway are calculated by assuming a unit or zero production of $ClNO_2$, respectively; The NO_2 + OH values are higher limit, assuming all gas-phase HNO_3 will deposit on particle surfaces.

Airmass	**via N_2O_5 heterogeneous reaction**				**via HNO_3 deposition**	
	$L(NO_x)_{low}$ (pptv s^{-1})	$P(NO_3^-)_{low}$ (μg m^{-3} h^{-1})	$L(NO_x)_{high}$ (pptv s^{-1})	$P(NO_3^-)_{high}$ (μg m^{-3} h^{-1})	$L(NO_x)_{high}$ (pptv s^{-1})	$P(NO_3^-)_{high}$ (μg m^{-3} h^{-1})
Type 1a	0.38±0.11	3.79±1.09	0.76±0.22	7.58±2.19	1.33±0.58	13.30±5.80
Type II	0.15±0.11	1.52±1.07	0.29±0.22	2.90±2.20	0.87±0.55	8.63±5.48
Type 1b	0.36±0.22	3.62±2.20	0.72±0.44	7.24±4.41	1.14±0.56	11.39±5.62
Type III	0.23±0.10	2.30±0.96	0.46±0.20	4.61±1.98	0.25±0.20	2.54±2.02

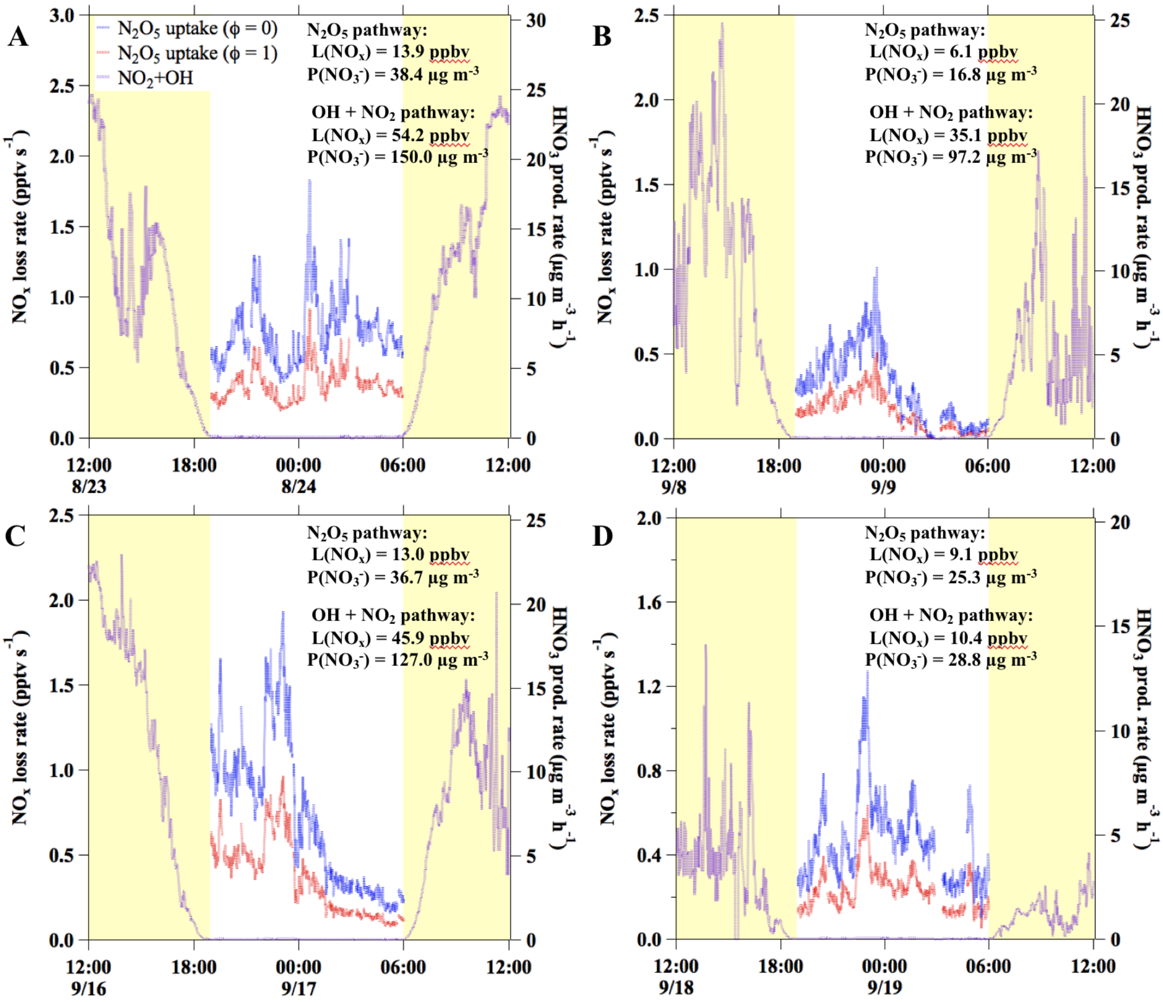

Figure 5. The NO_x removal rate in pptv s^{-1} (left axis) and corresponding inorganic nitrate aerosol production rate in μg m^{-3} h^{-1} (right axis) for a) 23-24 August 2012 (Continent I); b) 8-9 September 2012 (Marine); c) 16-17 September 2012 (Continent II); and d) 18-19 September 2012 (Continent + Marine).

4. Summary and conclusions

This study presents a simultaneous measurement of NO_3, N_2O_5 and $ClNO_2$ using a TD-CIMS at a ground-level coastal site of southern China during the autumn of 2012. During the measurement period, three types of airmasses were determined based on their back trajectories: purely continental air, purely marine air, and marine air with continental origin. Steady-state analysis of N_2O_5 revealed that the overall loss rate of NO_3 and N_2O_5 was high in all four example types of airmasses arriving at the location. In contrast to the finding in the nocturnal residual layer that NO_3 and N_2O_5 have overall similar loss rates (Brown et al., 2016), N_2O_5 loss dominated (>95 %) the overall loss and exhibited higher rates in marine air or when the air went across the sea. In such airmasses, faster loss rate of N_2O_5 and higher ratios of $ClNO_2$ to N_2O_5 were also observed compared to continental airmasses, suggesting stronger heterogeneous reaction of N_2O_5 on chlorine-rich aerosols. Although we did not have the concurrent aerosol measurement, the higher N_2O_5 loss rate might be attributed to several reasons: 1) the chorine-rich and organic-poor marine aerosols; 2) the higher RH; 3) net deposition on sea surface. The fast loss of N_2O_5 contributed to a significant fraction of NO_x removal and nitrate aerosol formation in this coastal ground-level site. Together with previous studies [Brown et al., 2016; Wang et al., 2016; Yun et al., 2018], the NO_x removal via NO_3 and N_2O_5 pathways can influence the NOx budget and nitrate formation in a large portion of the planetary boundary layer in the coastal regions of southern China.

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