



Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: Roles of aerosol water content and chemical composition

5 Yee Jun Tham^{1,2}, Zhe Wang¹, Qinyi Li¹, Weihao Wang¹, Xinfeng Wang³, Keding Lu⁴, Nan Ma⁵, Chao Yan², Simonas Kecorius⁵, Alfred Wiedensohler⁵, Yuanhang Zhang⁴, and Tao Wang¹

¹Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

²Institute for Atmospheric and Earth System Research/Physics, University of Helsinki, 00014, Helsinki, Finland

³Environment Research Institute, Shandong University, Jinan, Shandong, China

10 ⁴State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China

⁵Leibniz Institute for Tropospheric Research, Permoserstr. 15, 04318 Leipzig, Germany

Correspondence to: Z. Wang (z.wang@polyu.edu.hk) and T. Wang (cetwang@polyu.edu.hk)

15 **Abstract.** Heterogeneous uptake of dinitrogen pentoxide (N_2O_5) and production of nitryl chloride ($ClNO_2$) are important nocturnal atmospheric processes that have significant implications for the production of secondary pollutants. However, the understanding of N_2O_5 uptake processes and $ClNO_2$ production remains limited, especially in China. This study presents a field investigation of the N_2O_5 heterogeneous uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ production yield (ϕ) in a polluted area of northern China during the summer of 2014. The N_2O_5 uptake coefficient and $ClNO_2$ yield were estimated in 10 selected cases using simultaneously measured concentrations of $ClNO_2$ and particulate nitrate. The determined $\gamma(N_2O_5)$ and ϕ values varied greatly, with an average of 0.022 for $\gamma(N_2O_5)$ (in range of 0.006–0.034) and 0.34 for ϕ (range, 0.07–1.04). The variations in $\gamma(N_2O_5)$ could not be fully explained by the previously derived parameterizations of N_2O_5 uptake that consider nitrate, chloride, and the organic coating. Heterogeneous uptake of N_2O_5 was found to have a strong positive dependence on the relative humidity and aerosol water content. This result suggests that the heterogeneous uptake of N_2O_5 in Wangdu is governed mainly by the amount of water in the aerosol, a phenomenon that differs from other field observations in the United States and Europe. Laboratory-derived parameterization also overestimated the $ClNO_2$ yield. The observation-derived ϕ showed a decreasing trend with an increasing ratio of acetonitrile to carbon monoxide, an indicator of biomass burning emissions, which suggests a possible suppressive effect on the production yield of $ClNO_2$ in the plumes influenced by biomass burning in this region. The findings of this study illustrate the need to improve our understanding and to parameterize the key factors for $\gamma(N_2O_5)$ and ϕ to accurately assess the photochemical and haze pollution.

20

25

30

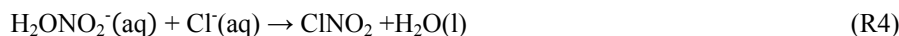
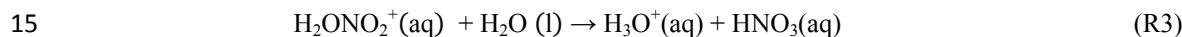


1 Introduction

The nocturnal heterogeneous reaction of dinitrogen pentoxide (N_2O_5) with aerosols is a loss pathway of NO_x and a source of aerosol nitrate and gas-phase nitryl chloride (ClNO_2) (Brown et al., 2006; Osthoff et al., 2008; Thornton et al., 2010; Sarwar et al., 2014) and thereby has important implications on air quality (e.g., Li et al., 2016). The process begins with the accumulation of gas-phase nitrate radical (NO_3) after sunset via the oxidation of nitrogen dioxide (NO_2) by O_3 and further reaction of NO_3 with another NO_2 , yielding a N_2O_5 . The accommodation of N_2O_5 on the aqueous surface of the aerosol (R1) and reaction with liquid water (H_2O) leads to the formation of a protonated nitric acid intermediate (H_2ONO_2^+) and a nitrate (NO_3^-) (R2; Thornton and Abbatt, 2005; Bertram and Thornton, 2009).



The H_2ONO_2^+ will proceed by reacting with another H_2O to form an aqueous nitric acid (HNO_3 ; R3). If chloride (Cl^-) is present in the aerosols, the H_2ONO_2^+ will undergo another pathway to produce a nitryl chloride (ClNO_2) through R4, which is a dominant source of highly reactive chlorine radicals in the troposphere (e.g., Riedel et al., 2012; 2014).



The heterogeneous loss rate of N_2O_5 ($k(\text{N}_2\text{O}_5)_{\text{het}}$) and the ClNO_2 production rate ($p(\text{ClNO}_2)$) are fundamentally governed by the probability of N_2O_5 lost upon collision with particle surface area in a volume of air (i.e., uptake coefficient, $\gamma(\text{N}_2\text{O}_5)$) and the ClNO_2 yield (ϕ), which is defined as the branching ratio between the formation of HNO_3 via R3 and ClNO_2 via R4. Assuming that the gas-phase diffusion to the aerosol surfaces is negligible, their relationship can be described by equations (1) and (2), in which $c_{\text{N}_2\text{O}_5}$ is the average molecular speed of N_2O_5 and S_a is the aerosol surface area.

$$20 \quad k(\text{N}_2\text{O}_5)_{\text{het}} = \frac{1}{4} c_{\text{N}_2\text{O}_5} \gamma(\text{N}_2\text{O}_5) S_a \quad (\text{Eq 1})$$

$$p(\text{ClNO}_2) = k(\text{N}_2\text{O}_5)_{\text{het}} [\text{N}_2\text{O}_5] \phi \quad (\text{Eq 2})$$

N_2O_5 uptake has been shown in the laboratory to be susceptible to changes in the water content, chloride, nitrate, and organic particle coatings in aerosols (e.g., Mentel et al., 1999; Bertram and Thornton, 2009). The presence of liquid water on the aerosols allows the accommodation of N_2O_5 (R1) and acts as a medium for the solvation process of N_2O_5 (R2). It has been found that N_2O_5 uptake is significantly enhanced in humid conditions than in dry conditions (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009; Gržinic et al., 2015). Higher loading of NO_3^- in the aerosol can dramatically decrease N_2O_5 uptake by reversing the solvation/ionization process of N_2O_5 , shifting the equilibrium in R2 to the left to reproduce N_2O_5 , which can be diffused out of the aerosol (known as the “nitrate suppression” effect). The rate of reversible reaction of R2 (i.e., H_2ONO_2^+ with NO_3^-) was documented to be 30 to 40 times faster than the reaction of H_2ONO_2^+ with liquid water in R3



(Bertram and Thornton, 2009; Griffiths et al., 2009). The presence of Cl⁻ in the aerosol, in contrast, can enhance the reactive uptake because Cl⁻ reacts effectively with H₂ONO₂⁺ (in R4), thus negating the “nitrate suppression” effect by shifting the equilibrium in R2 to the right (Finlayson-Pitts et al., 1989; Bertram and Thornton, 2009). The uptake of N₂O₅ can also be hindered by the presence of organics, because the organic coating layer on the aerosol could lower the liquid water content and/or limit the surface activity, thus suppressing the accommodation of N₂O₅ (e.g., Cosman et al., 2008; Gaston et al., 2014).

As for the ClNO₂ yield from N₂O₅ heterogeneous reactions, it was found to be dependent on the fate of H₂ONO₂⁺ and thus on the relative amount of Cl⁻ and water content (Benhke et al., 1997; Roberts et al., 2009; Bertram and Thornton, 2009). Therefore, ϕ can be expressed by the following equation (Eq.3).

$$\Phi_{\text{param.}} = \frac{1}{\frac{k_{R3}[\text{H}_2\text{O}]}{k_{R4}[\text{Cl}^-]} + 1} \quad (\text{Eq 3})$$

Roberts et al. (2009) reported that the coefficient rate of k_{R4} is about 450 times faster than that of k_{R3} , indicating that H₂ONO₂⁺ proceeds more favorably via R4, even with a small amount of Cl⁻. However, some laboratory experiments have suggested that the presence of halides (i.e., bromide), phenols, and humic acid may significantly reduce the ϕ (e.g., Schweitzer et al., 1998; Ryder et al., 2015).

The parameterization of $\gamma(\text{N}_2\text{O}_5)$ and ϕ as a function of the aerosol water content and aerosol chemical composition, derived based on the findings of the laboratory studies mentioned above (e.g., Antilla et al., 2006; Bertram and Thornton, 2009; Davis et al., 2008), has recently been compared with the ambient observations in different environments (Phillips et al., 2016; Chang et al., 2016; Wang Z. et al., 2017). Large discrepancies were observed between the $\gamma(\text{N}_2\text{O}_5)$ and ϕ values determined in the fields and the laboratory parameterizations derived with pure or mixed aerosol samples, where the laboratory parameterization values can be overestimated by up to an order of magnitude. Several reasons have been proposed for the discrepancies between the parameterization and observation values, including the failure of parameterization to account for 1) the complex mixture of organic composition (Bertram et al., 2009; Mielke et al., 2013); 2) the “real” nitrate suppression effect (Riedel et al., 2012; Morgan et al., 2015); and 3) the mixing states of the particles (Ryder et al., 2014; Wang X. et al., 2017). These results suggest the lack of comprehensive understanding of the N₂O₅ uptake and ClNO₂ production yield in various atmospheric environments around the world.

Most of the previous field studies of N₂O₅ uptake and ClNO₂ production have been conducted in the United States (US) and Europe regions (Brown et al., 2009; Chang et al., 2016). Direct field investigation of the N₂O₅ heterogeneous processes in China is very limited. Pathak et al. (2009, 2011) analyzed the aerosol composition and suggested that the accumulation of fine NO₃⁻ aerosol in downwind of Beijing and Shanghai was due to significant N₂O₅ heterogeneous



reactions. Wang et al. (2013) linked the observed NO_3^- with the precursors of N_2O_5 (i.e., NO_2 and O_3) in urban Shanghai and suggested that the N_2O_5 heterogeneous uptake dominated NO_3^- formation on polluted days. However, field measurements of N_2O_5 and ClNO_2 were not available until recently at several sites in southern and northern China (Tham et al., 2014; Wang Z. et al., 2017).

5

In the summer of 2014, a field campaign was carried out to investigate ClNO_2 and N_2O_5 at a semirural ground site at Wangdu in polluted northern China (Tham et al., 2016). Elevated levels of ClNO_2 up to 2070 pptv, but relatively low values of N_2O_5 (430 pptv), were observed on most nights at this site, and heterogeneous processes have been shown to have a significant effect on the following day's radical and ozone production at the site (Tham et al., 2016). Yet, the factors that drive the N_2O_5 heterogeneous uptake and ClNO_2 production yield remain unclear. In this study, we further analyze the dataset to investigate this topic. We first derive values for $\gamma(\text{N}_2\text{O}_5)$ and ϕ with the measurement data and then compare the values obtained in the field with various parameterizations derived from the laboratory studies. With the aid of the aerosol composition and meteorological measurements, we illustrate the factors that drive or influence the variations in $\gamma(\text{N}_2\text{O}_5)$ and ϕ at Wangdu. The values for $\gamma(\text{N}_2\text{O}_5)$ and ϕ obtained here are also compared with field results from the literature to provide an overview of the N_2O_5 - ClNO_2 heterogeneous process observed in various environments around the world.

15

2 Methods

The measurement site (38.66°N, 115.204°E) is located at a semirural area in Wangdu county of Hebei province, in the northern part of China. The Wangdu site is situated within the agricultural land but is bounded by villages and towns. Beijing (the national capital) is about 170 km to the northeast, Tianjin is about 180 km to the east, Shijiazhuang is about 90 km to the southwest, and Baoding is ~33 km to the northeast. Dozens of major coal-fired power stations are also located in the region. During the study period, frequent biomass burning activity was observed in the surrounding regions. Analysis of the air masses' back trajectories showed that the sampling site was frequently affected by these surrounding anthropogenic sources. Details on the sampling site and the meteorological conditions during the campaign can be found in Tham et al. (2016).

25

In this study, N_2O_5 and ClNO_2 were measured with an iodide chemical mass ionization mass spectrometer (CIMS), with which the N_2O_5 and ClNO_2 were detected as the iodide-cluster ions of $\text{I}(\text{ClNO}_2)^-$ and $\text{I}(\text{N}_2\text{O}_5)^-$, similar to those outlined by Kercher et al. (2009). The detection principles, calibration, and inlet maintenance were described in detail in our previous studies (Wang T. et al., 2016; Tham et al., 2016). The CIMS measurement at the Wangdu site was performed from 20 June to 9 July 2014. A corona discharge ion source setup (for generation of iodide primary ions) was used in the CIMS measurement from 20 to 26 June 2014 with a detection limit of 16 pptv for N_2O_5 and 14 pptv for ClNO_2 (3σ ; 1 min-averaged data) but was replaced by a radioactive ion source from 27 June 2014 until the end of the study with a detection limit of 7

30



pptv for N_2O_5 and 6 pptv for ClNO_2 (3σ ; 1 min-averaged data). The overall uncertainty of the CIMS measurement was estimated to be $\pm 25\%$, with a precision of 3%.

The present study was supported by other auxiliary measurements of aerosol and trace gases. Trace gases including
5 NO , NO_2 , O_3 , SO_2 , CO , and total odd nitrogen (NO_y) were measured with online gas analyzers (Tan et al., 2017). A gas
aerosol collector–ion chromatography system was used to measure the ionic compositions of $\text{PM}_{2.5}$, including NO_3^- , Cl^- , SO_4^{2-} ,
 NH_4^+ , and gas-phase HNO_3 (Dong et al., 2012). The particle surface area concentrations (S_a) were calculated based on the
wet ambient particle number size distribution predicted from the size-resolved kappa-Köhler function determined from
real-time measurement with a high humidity tandem differential mobility analyzer (Hennig et al., 2005; Liu et al., 2014).
10 Hydroxyl radical (OH) was measured with the laser-induced fluorescence technique (Tan et al., 2017). Volatile organic
compounds including methane, C_2 – C_{10} hydrocarbons, formaldehyde, and oxygenated hydrocarbons and acetonitrile (CH_3CN)
were measured with a cavity ring–down spectroscopy technique instrument, an online gas chromatograph equipped with a
mass spectrometer and a flame ionization detector, a Hantzsch fluorimetric monitor, and a proton-transfer-reaction mass
spectrometer, respectively (Yuan et al., 2010; Wang et al., 2014). Meteorological data including the wind profile, relative
15 humidity (RH), and temperature were measured with an ultrasonic anemometer and a weather station on a 20m tower.
Detailed descriptions of the instrumentation and observations of the aerosols, trace gases, and meteorological parameters at
Wangdu can be found in other publications (e.g., Wang Y. et al., 2016; Min et al., 2016; and Tham et al., 2016).

3 Results and Discussion

20 3.1 Nocturnal heterogeneous N_2O_5 reaction at Wangdu

Figure 1 illustrates the time series of NO_x , O_3 , N_2O_5 , ClNO_2 , particulate NO_3^- , S_a , the calculated production rate of NO_3 , and
the lifetime of N_2O_5 observed at Wangdu between 20 June and 9 July 2014. Abundance of NO_x and O_3 was observed at
night-time (20:00 to 05:00 local time); with average night-time mixing ratios of 21 and 30 ppbv, respectively. The elevated
25 night-time NO_x and O_3 levels led to the active production of NO_3 , with an average production rate of NO_3
($=k_{\text{O}_3+\text{NO}_2}[\text{NO}_2][\text{O}_3]$) of 1.7 ppb h^{-1} and a maximum level of 8.3 ppb h^{-1} for the entire campaign. Even with the rapid
production of NO_3 and the high NO_2 level at night, the observed N_2O_5 concentrations were typically low (i.e., average
nighttime concentration of $34 \pm 14 \text{ pptv}$). The low N_2O_5 value is consistent with the short steady-state lifetime of N_2O_5
($\tau(\text{N}_2\text{O}_5)$) for the study period, ranged from 0.1 to 10 min, suggesting that the direct loss of N_2O_5 via heterogeneous reaction
30 and/or indirect loss of N_2O_5 via decomposition to NO_3 (i.e., reactions of NO_3 with NO and volatile organic compounds
[VOCs]) were rapid in this region. The good correlation between the night-time levels of ClNO_2 and fine particulate NO_3^-
(the products of heterogeneous reactions of N_2O_5 via R3 and R4, respectively), with a coefficient of determination (r^2) of
greater than 0.6 on most nights, provides field evidence of active N_2O_5 heterogeneous uptake processes in this region.



3.2 Estimation of N₂O₅ uptake coefficient and ClNO₂ production yield

The consistent trends and clear correlation between ClNO₂ and fine particulate NO₃⁻ could be used to quantify N₂O₅ heterogeneous uptake following the method described by Phillips et al. (2016). The uptake coefficient of N₂O₅, γ (N₂O₅), was estimated based on the production rate of ClNO₂ ($p\text{ClNO}_2$) and the nitrate formation rate ($p\text{NO}_3^-$) from the following equation (4).

$$\gamma(\text{N}_2\text{O}_5) = \frac{2(p\text{ClNO}_2 + p\text{NO}_3^-)}{C_{\text{N}_2\text{O}_5} S_a[\text{N}_2\text{O}_5]} \quad (\text{Eq 4})$$

The yield of ClNO₂ was determined from the regression analysis of ClNO₂ versus particulate NO₃⁻ (Wagner et al., 2012; Riedel et al., 2013). The slope (m) from the regression plot was fitted into equation (5) to obtain the ϕ .

$$\phi = \frac{2m}{1+m} \quad (\text{Eq 5})$$

The concentrations of ClNO₂, N₂O₅, particulate NO₃⁻, and other related data used for this analysis were averaged or interpolated into 10 min. This analysis assumes 1) that the air mass is stable and losses of ClNO₂ and NO₃⁻ are insignificant within the duration of analysis; 2) that the NO₃⁻ produced via N₂O₅ heterogeneous uptake remains in the particle phase and does not significantly degas as HNO₃; and 3) that the night-time production of NO₃⁻ through the net HNO₃ uptake to aerosols is not important compared to that formed via N₂O₅ heterogeneous uptake.

The limitation of this method is that it cannot predict the $\gamma(\text{N}_2\text{O}_5)$ with negative changes in the concentrations of ClNO₂ or particulate NO₃⁻, which may be a result of differences in the origin or age of the air mass. In accordance with this limitation and with assumption (1) above, we carefully select plumes during the night-time that have meet the following criteria for the analysis: shorter periods of data, usually between 1.5 and 4 hours, with concurrent increases in ClNO₂ and NO₃⁻. The wind conditions and air mass age in the plume, represented by the ratios of NO_x to NO_y, were relatively stable, and no drastic changes were seen in other variables such as the particle surface area, RH, or temperature. In addition, the concentration of NO in the plume must be relatively constant as the presence of a transient NO plume may affect the concentration of N₂O₅, which can bias the estimation of $\gamma(\text{N}_2\text{O}_5)$. Figure 2 shows two examples of relatively constant conditions of relevant chemical composition and environmental variables, together with a plot of ClNO₂ versus particle NO₃⁻ for the night. It should also be noted that partitioning of NO₃⁻ to gas-phase HNO₃ and the contribution of particulate NO₃⁻ from other sources, like the reaction of OH with NO₂ and the oxidation of VOCs by NO₃, can bias the values predicted for $\gamma(\text{N}_2\text{O}_5)$ and ϕ .

To check the validity of assumptions (2) and (3) above, we also calculated the production rate of NO₃⁻/HNO₃ via reaction of OH+NO₂ ($=k_{\text{OH}+\text{NO}_2}[\text{OH}][\text{NO}_2]$) and NO₃+VOC ($=\sum_i k_i[\text{VOC}_i][\text{NO}_3]$), as shown in the average diurnal profiles of related species in Figure 3. It is clear that particulate NO₃⁻ was the dominant species during the night-time at Wangdu (Figure 3b). The strong correlation between ClNO₂ and particulate nitrate during the night indicates that the heterogeneous process



of N_2O_5 was the dominant source of particulate nitrate. Moreover, the production rate of HNO_3 , as calculated from the gas-phase reactions of $\text{OH}+\text{NO}_2$ and NO_3+VOC , shows a decreasing trend towards the night (Figure 3c), and the combination of these rates on average is only about one-third of the average $p\text{NO}_3^-$ during the night. The increase in night-time NO_3^- was also accompanied by an increase in ammonium (NH_4^+), which suggests that the repartition process to form ammonium nitrate was efficient, thus limiting the release of HNO_3 (Figure 3d). These results support the validity of the above assumptions and the determination of uptake and yield in this analysis.

With these methods and selection criteria, we can derive $\gamma(\text{N}_2\text{O}_5)$ and ϕ for 10 night-time plumes. Table 1 shows the estimated N_2O_5 uptake coefficients and ClNO_2 yields at Wangdu together with the errors that account for the scattering of data in the analysis and uncertainty from the measurement of N_2O_5 , ClNO_2 , aerosol surface area, and particulate NO_3^- . The estimated $\gamma(\text{N}_2\text{O}_5)$ values ranged from 0.006 to 0.034, with a median value of 0.023. A large variability was found in ϕ (range, 0.07 to 1.04). The relatively larger $\gamma(\text{N}_2\text{O}_5)$ and ϕ values observed on the night of 20–21 June are consistent with the observation of the highest ClNO_2 concentration, whereas the lower $\gamma(\text{N}_2\text{O}_5)$ and ϕ values on the night of 28–29 June explain the observation of the elevated N_2O_5 and small ClNO_2 mixing ratios (c.f. Figure 1). The observed $\gamma(\text{N}_2\text{O}_5)$ and ϕ values at Wangdu were compared with literature values derived from previous field observations in various locations in North America, Europe, and China, as summarized in Figure 4 and Table 2. The variable values of $\gamma(\text{N}_2\text{O}_5)$ in this study fall in the range of $\gamma(\text{N}_2\text{O}_5)$ (<0.001 to 0.11) and ϕ (0.01–1.38) reported around the world. The values are also within the range of N_2O_5 uptake coefficients and ClNO_2 yields determined in regions of China regions ($\gamma(\text{N}_2\text{O}_5) = 0.004\text{--}0.103$; $\phi = 0.01\text{--}0.98$), which are in the middle to upper end of the values reported around the world. The observed significant ClNO_2 concentrations and high yields of ϕ here, consistent with other studies at inland sites (c.f. Table 2), also point to the fact that ClNO_2 production can be efficient in regions far from the oceanic source of chloride and further highlight the important role of anthropogenic chloride emissions in the chlorine activation process and the next-day's photochemistry. The question arises here is what drive the large variability in the $\gamma(\text{N}_2\text{O}_5)$ and ϕ at Wangdu.

3.3 Factors that control the N_2O_5 uptake coefficient

Heterogeneous uptake of N_2O_5 is governed by various factors, including the amount of water and the physical and chemical characteristics of the aerosols (Chang et al., 2011; Brown and Stutz, 2012). To gain better insight into the factors that drive the N_2O_5 heterogeneous uptake, the determined $\gamma(\text{N}_2\text{O}_5)$ values were compared with those predicted from complex laboratory-derived parameterizations, and their relationships with the aerosol water content and aerosol compositions observed at Wangdu were examined.

The parameterization of N_2O_5 uptake coefficient derived from Bertram and Thornton (2009) ($\gamma_{\text{B\&T}}$) considers the amount of nitrate, chloride, and water in the aerosol as the controlling factors and can be calculated with equation (6):



$$\gamma_{B\&T} = Ak \left(1 - \frac{1}{\left(\frac{k_{R3}[\text{H}_2\text{O}](l)}{k_{R2b}[\text{NO}_3^-]} \right) + 1 + \left(\frac{k_{R4}[\text{Cl}^-]}{k_{R2b}[\text{NO}_3^-]} \right)} \right) \quad (\text{Eq 6})$$

where A is an empirical pre-factor calculated from the volume of aerosol (V), S_a , $c_{\text{N}_2\text{O}_5}$, and Henry's law coefficient of N_2O_5 ($A = 4/c_{\text{N}_2\text{O}_5} \times V/S_a \times H_{\text{aq}}$); $k = 1.15 \times 10^6 - (1.15 \times 10^6) \exp(-0.13[\text{H}_2\text{O}])$; $k_{R3}/k_{R2b} = 0.06$; and $k_{R4}/k_{R2b} = 29$. The concentration of aerosol liquid water ($[\text{H}_2\text{O}]$) used in this study was estimated from the E-AIM model IV with inputs of measured aerosol composition (<http://www.aim.env.uea.ac.uk/aim/model4/model4a.php>) (Wexler and Clegg, 2002), and the V/S_a was taken from the field measurement at Wangdu. This $\gamma_{B\&T}$, however, does not account for the suppression of $\gamma(\text{N}_2\text{O}_5)$ from the organics, but it is frequently used with the parameterization formulated by Anttila et al. (2006), who treated the organic fraction in the aerosols as a coating, as given in equation (7) (e.g., Morgan et al., 2015; Phillips et al., 2016; Chang et al., 2016). The net uptake of N_2O_5 onto an aqueous core and organic coating ($\gamma_{B\&T+\text{Org}}$) can be determined by equation (8).

$$\gamma_{\text{Org}} = \frac{4RH_{\text{org}}D_{\text{org}}R_c}{C_{\text{N}_2\text{O}_5}LR_p} \quad (\text{Eq 7})$$

$$\frac{1}{\gamma_{B\&T+\text{Org}}} = \frac{1}{\gamma_{B\&T}} + \frac{1}{\gamma_{\text{Org}}} \quad (\text{Eq 8})$$

Here, the H_{org} is the Henry's Law constant of N_2O_5 for organic coating; D_{org} is the solubility and diffusivity of N_2O_5 in the organic coating of thickness L ; and R_c and R_p are the radii of the aqueous core and particle, respectively. The L was calculated following the method in Reimer et al. (2009) with the assumption of hydrophobic organic coating (density, 1.27 g cm^{-3}) on the aqueous inorganic core (with a density of 1.77 g cm^{-3}). The $H_{\text{org}}D_{\text{org}}$ is equal to $0.03 \times H_{\text{aq}}D_{\text{aq}}$, where $H_{\text{aq}} = 5000 \text{ M atm}^{-1}$ and $D_{\text{aq}} = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Chang et al., 2011 and references therein). In addition, Evan and Jacob (2005) proposed a simpler parameterization of N_2O_5 uptake on sulfate aerosol ($\gamma_{E\&J}$) as a function of temperature and RH, as given by equation (9).

$$\gamma_{E\&J} = (2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times \text{RH} - 3.43 \times 10^{-6} \times \text{RH}^2 + 7.52 \times 10^{-8} \times \text{RH}^3) \times 10^{(4 \times 10^{-2} \times (T-294))} \quad (\text{Eq 9})$$

Figure 5 illustrates a comparison of field-derived N_2O_5 uptake coefficients with the values computed from the above parameterizations. The computed $\gamma_{B\&T}$ (red circle) ranged from 0.046 to 0.094 and was consistently higher than the field-derived $\gamma(\text{N}_2\text{O}_5)$ by up to a factor of 9. By accounting for the effects of organic coating on the N_2O_5 uptake coefficient via equations (7) and (8), the calculated N_2O_5 uptake coefficients (green circle in Figure 5) are significantly underestimated. Note that only six cases were available to compute the $\gamma_{B\&T+\text{Org}}$ due to the limited organic aerosols data for the study period. The N_2O_5 uptake coefficients computed from the parameterization suggested by Evan and Jacob (2005) are generally consistent with the field-derived $\gamma(\text{N}_2\text{O}_5)$ (as shown by blue circles). The different results from these parameterizations may suggest more complex aerosol composition or properties in the real ambient atmosphere than in the aerosol sample used in the laboratory study.

We then examine the relationships of the field-derived $\gamma(\text{N}_2\text{O}_5)$ with RH, water content, and aerosol compositions, as



illustrated in Figure 6. It can be seen in Figure 6a that the $\gamma(\text{N}_2\text{O}_5)$ has a clear correlation with the aerosol water content ($r^2 = 0.86$; $p < 0.01$, t -test). The strong dependence of $\gamma(\text{N}_2\text{O}_5)$ on the aerosol water content was observed at RH lower than 80% or $[\text{H}_2\text{O}]$ lower than 40 mol L^{-1} . The $\gamma(\text{N}_2\text{O}_5)$ then plateaus at about 0.032 when the RH exceeds 80%. This pattern is similar to the trends observed in laboratory studies for N_2O_5 uptake onto aqueous sulfate and malonic acid aerosols, in which the $\gamma(\text{N}_2\text{O}_5)$ strongly increases with humidity at RH below 40-50% but becomes insensitive above this threshold (e.g., Hallquist et al., 2003; Thornton et al., 2003). The $\gamma(\text{N}_2\text{O}_5)$ at Wangdu shows a trend of decreasing with the concentration of NO_3^- per volume of aerosol (see Figure 5b), which is similar to the results from the previous laboratory studies (Bertram and Thornton, 2009; Griffiths et al., 2009). However, we do not think that $[\text{NO}_3^-]$ is the dominant limiting factor for N_2O_5 uptake at this site, as seen in the consistency of the $\gamma(\text{N}_2\text{O}_5)$ data points with the change in RH (in the color code of Figure 6b), the increasing trend of $\gamma(\text{N}_2\text{O}_5)$ with the concentration of particulate nitrate in the air (c.f. Figure 6c), and the positive dependency of $\gamma(\text{N}_2\text{O}_5)$ on the molar ratio of $[\text{H}_2\text{O}]/[\text{NO}_3^-]$ (c.f. Figure 6d), which reflect that the N_2O_5 uptake is more sensitive to the aerosol water content than to the NO_3^- , at least up to $[\text{H}_2\text{O}]:[\text{NO}_3^-]$ of 20. The increase in ambient particulate nitrate is probably due to the faster N_2O_5 heterogeneous reaction. The N_2O_5 uptake does not show an increasing trend with the chloride-to-nitrate molar ratio, a pattern demonstrated in the laboratory result (Bertram and Thornton, 2009), but rather a decrease for high $[\text{Cl}^-]/[\text{NO}_3^-]$ ratios, and it also correlates with differences in RH (c.f. Figure 6e). There is a lack of correlation of $\gamma(\text{N}_2\text{O}_5)$ with the $[\text{Org}]:[\text{SO}_4^-]$ observed in the ratio range of 0.5–1.2, indicating that the suppression of organics on the N_2O_5 uptake may be insignificant at Wangdu. These results are in line with the parameterization comparison results shown in Figure 5, reveal that the variation in the N_2O_5 uptake at Wangdu is not driven by the chemical properties of aerosols like NO_3^- , Cl^- , and organics, but rather that the RH or the aerosol water content plays a defining role in the N_2O_5 heterogeneous uptake.

The response of N_2O_5 uptake on the changes in RH is consistent with the changes in the sulfate (SO_4^{2-}) concentrations (see Figure 6g), which mainly determine the hygroscopicity of the aerosols and were found to be responsible for the particle growth at Wangdu (Wu et al., 2017). The hygroscopic growth of aerosols inferred by the RH (water uptake) can affect the amount of water in the aerosol and the volume-to-surface area ratio ($[\text{H}_2\text{O}]/S_a$). The good positive correlation of $\gamma(\text{N}_2\text{O}_5)$ with $[\text{H}_2\text{O}]/S_a$ (see Figure 6h) suggests that the increased volume of aerosol, in particular the layer of aerosol water content, could allow efficient diffusion of N_2O_5 and solvation of N_2O_5 into H_2ONO_2^+ and NO_3^- for further aqueous reactions, whereas a smaller volume of aerosol (less water content) may be easily saturated by N_2O_5 and then diffuse the N_2O_5 out of the aerosol, limiting the solvation of the N_2O_5 process and restricting N_2O_5 uptake. Several laboratory studies have demonstrated that an increase in RH enhanced the particle aqueous volume and increased the bulk reactive N_2O_5 uptake on aqueous acids (i.e., malonic, succinic, and glutaric acid) and aqueous sulfate containing aerosols (Thornton et al., 2003; Hallquist et al., 2003). The increase in RH can also lower the viscosity of the aqueous layer in organic-containing aerosols, leading to greater diffusivity of N_2O_5 within the aerosol water layer, which ultimately increases the N_2O_5 uptake (Gržinic et al., 2015).



The strong dependency of N_2O_5 uptake upon the RH has not been clearly demonstrated in other field measurements. Field observations of $\gamma(\text{N}_2\text{O}_5)$ in North America and Europe show any significant direct dependence of $\gamma(\text{N}_2\text{O}_5)$ on RH but were strongly influenced by the aerosol composition (refer to the descriptions in Table 2). For instance, the flight measurements in Texas and London showed the independence of $\gamma(\text{N}_2\text{O}_5)$ at RH from 34% to 90%, but the $\gamma(\text{N}_2\text{O}_5)$ were generally controlled by the amount of NO_3^- and/or organic compounds (Brown et al., 2009; Morgan et al., 2015). A comparison of ground measurements in Seattle and Boulder showed variations in $\gamma(\text{N}_2\text{O}_5)$ at various $\text{H}_2\text{O}(l)$ levels in the two places, but the RH alone was insufficient to describe their observed $\gamma(\text{N}_2\text{O}_5)$ variability, and the organic composition of the aerosols was determined to have a dominant influences on $\gamma(\text{N}_2\text{O}_5)$ (Bertram et al., 2009). Another study from a mountainous site in Germany reported no significant correlation of $\gamma(\text{N}_2\text{O}_5)$ with aerosol compositions and only a weak dependence on humidity (Phillips et al., 2016). However, field measurements at Jinan and Mt. Tai in northern China during the same season also showed a positive relationship of $\gamma(\text{N}_2\text{O}_5)$ with an RH between 43% and 72% and aerosol water content of 31–65 mol L^{-1} , respectively (Wang X. et al., 2017; Wang Z. et al., 2017). The results of this study and previous reported results in the region may suggest that RH and aerosol water content are the important limiting factors for the N_2O_5 heterogeneous process in the polluted northern China. In summary, the more complex parameterizations considering nitrate, chloride, and the organic coating cannot fully represent the variation of $\gamma(\text{N}_2\text{O}_5)$ at Wangdu; instead, a simple parameterization that accounts only for temperature and RH appears to explain the variation in $\gamma(\text{N}_2\text{O}_5)$ at Wangdu. It would be of great interest to determine whether such a phenomenon can be found in other places.

3.4 Factors that affect the ClNO_2 production yield

In addition to the uptake coefficients, the factors that influence the branching yield of ClNO_2 from the N_2O_5 heterogeneous uptake were also assessed. Figure 7a shows the scatter plot of the ϕ calculated from equation (3) versus the ClNO_2 yield derived from the Wangdu field data from equation (5) in Section 3.2. Generally, the ϕ_{param} shows less variability but was obviously overestimated in relative to the field-determined ϕ . Such discrepancy has also been observed elsewhere (Thonton et al., 2010; Mielke et al., 2013; Riedel et al., 2013), including our recent observations in an urban site (Jinan) and a mountaintop site (Mt. Tai) in northern China, where the parameterized ϕ would be overestimated by up to two orders of magnitude (Wang X. et al., 2017; Wang Z. et al., 2017). Further analysis by linking the field-derived ClNO_2 yields with the aerosol water content (Figure 7b) and the Cl^- content (Figure 7c) show a weak positive correlation ($r^2 = 0.34$) and a weak negative trend ($r^2 = 0.25$), respectively (from quadratic fitting). The weak correlations reflect that the ClNO_2 yield is not solely controlled by the amount of water and chloride in the aerosol, as defined in the parameterization (see Eq. 3), and/or the existence of other nucleophiles that can compete with Cl^- in reactions R3 and R4.

An interesting observation from Wangdu is that the field-derived ϕ shows a good decreasing trend ($r^2 = 0.65$ from quadratic data fitting) with the ratio of acetonitrile to carbon monoxide ($\text{CH}_3\text{CN}/\text{CO}$), which is an indicator of biomass



burning emission (Christian et al., 2003; Akagi et al., 2011), as illustrated in Figure 7d. The ϕ decreased at larger $\text{CH}_3\text{CN}/\text{CO}$ ratios, which corresponds to higher $[\text{Cl}^-]$ concentrations per volume of aerosols (c.f. Figure 7c) because biomass burning emits a significant level of chloride particles. The observations here may suggest that the ϕ is likely “suppressed” in air masses influenced by biomass burning, which were frequently observed during the study period (Tham et al., 2016), and is
5 consistent with the recent field observation of much lower concentrations of ClNO_2 during the bonfire event in Manchester compared to that after the event (Reyes-Villegas et al., 2017) and with a laboratory experiment which demonstrated that only a small amount ($\sim 10\%$) of reacted N_2O_5 was converted to ClNO_2 on the biomass-burning aerosols (Ahern et al., 2017). Another laboratory study showed that the ClNO_2 yield can be reduced by as much as 80% in the presence of aromatic organic compounds like phenol and humic acid in the aerosol (Ryder et al., 2015), and previous studies in China reported
10 abundant humic-like substances (e.g., aromatic organic compounds) in aerosols with a large contribution from biomass burning (Fu et al., 2008). Therefore, the frequently observed influence of biomass burning at the Wangdu site during the campaign could in part explain the lower ϕ values and the discrepancy between observation and parameterization. Other factors, such as the nonuniform distribution of chloride within the aerosol, might also contribute to the overestimation of ϕ from the parameterization (Riedel et al., 2013). More studies are needed to investigate the effects of biomass burning
15 emissions on the heterogeneous process.

4 Summary and conclusions

We present an in-depth analysis of the N_2O_5 uptake coefficient and ClNO_2 yield in a polluted northern China environment during the summer of 2014. Large variations in the levels of $\gamma(\text{N}_2\text{O}_5)$ and ϕ were observed during the study, ranging from
20 0.006 to 0.034 and from 0.07 to 1.04, respectively. A comparison between the $\gamma(\text{N}_2\text{O}_5)$ values derived from the field and the parameterizations that considered the nitrate and chloride levels and the hydrophobic organic coating showed poor agreement, suggesting more complex influences of ambient aerosol properties at the site than with the pure or mixed samples used in the laboratory. The $\gamma(\text{N}_2\text{O}_5)$ values at Wangdu were found to have a clear dependence on the RH and the aerosol
25 water content, a phenomenon that has not been reported in previous field studies in the United States or Europe. The parameterization that explicitly considers the dependence on RH showed better agreement with the field-derived $\gamma(\text{N}_2\text{O}_5)$ compared to the more complex formulation that considers the aerosol composition. The ClNO_2 yield from the parameterization is generally overestimated when compared to the field derived values. The observed ϕ was found to be “suppressed” in the air masses influenced by biomass burning even though abundant aerosol chloride was present. The
30 results of this study point to the need for more field and laboratory studies to obtain realistic parameterization of the heterogeneous processes of N_2O_5 and ClNO_2 to better simulate the ozone and aerosol production in air quality models in regions of China with high NO_x emissions.



Acknowledgment. The authors thank Steven Poon, Qiaozhi Zha, Zheng Xu and Hao Wang for the logistics support, to Liming Cao and Lingyan He for providing the aerosol mass spectrometer data and to Li Zhang for scientific discussion. This work was funded by the National Natural Science Foundation of China (91544213, 41505103 and 41275123), National Key Research and Development Program of China (2016YFC0200500), PolyU Project of Strategic Importance (1-ZE13) and
5 Research Institute for Sustainable Urban Development (RISUD). The Peking University team acknowledges support from the National Natural Science Foundation of China (21190052) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05010500). The Leibniz Institute for Tropospheric Research team acknowledges funding from the Sino German Science Center (No. GZ663).

10

References

- Ahern, A., Goldberger, L., Jahl, L., Thornton, J., and Sullivan, R. C.: Production of N_2O_5 and ClNO_2 through nocturnal processing of biomass-burning aerosol, *Environ. Sci. Technol.*, 10.1021/acs.est.7b04386, 2017.
- 15 Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, *Atmos. Chem. Phys.*, 11, 4039-4072, 10.5194/acp-11-4039-2011, 2011.
- Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5 , *J. Phys. Chem. A*, 110, 10435-10443, 10.1021/jp062403c, 2006.
- 20 Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO_2 , from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, *J. Geophys. Res.-Atmos.*, 102, 3795-3804, Doi 10.1029/96jd03057, 1997.
- Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, *Atmos. Chem. Phys.*, 9, 8351-8363, 10.5194/acp-9-8351-2009, 2009.
- 25 Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N_2O_5 reactivity on ambient aerosol particles, *Geophys. Res. Lett.*, 36, L19803, 10.1029/2009gl040248, 2009.
- Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, *Chem. Soc. Rev.*, 41, 6405-6447, 2012.
- 30 Brown, S. S., Dube, W. P., Fuchs, H., Ryerson, T. B., Wollny, A. G., Brock, C. A., Bahreini, R., Middlebrook, A. M., Neuman, J. A., Atlas, E., Roberts, J. M., Osthoff, H. D., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Reactive uptake coefficients for N_2O_5 determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations, *J. Geophys. Res.-Atmos.*, 114, D00F10, 10.1029/2008jd011679, 2009.
- 35 Brown, S. S., Dube, W. P., Tham, Y. J., Zha, Q. Z., Xue, L. K., Poon, S., Wang, Z., Blake, D. R., Tsui, W., Parrish, D. D., and Wang, T.: Nighttime chemistry at a high altitude site above Hong Kong, *J. Geophys. Res.-Atmos.*, 121, 2457-2475, 10.1002/2015JD024566, 2016.
- Brown, S., Ryerson, T., Wollny, A., Brock, C., Peltier, R., Sullivan, A., Weber, R., Dube, W., Trainer, M., Meagher, J., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, 311, 67-70, 2006.
- 40 Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous atmospheric chemistry, ambient measurements, and model calculations of N_2O_5 : A review, *Aerosol Sci. Tech.*, 45, 665-695, 10.1080/02786826.2010.551672, 2011.



- Chang, W. L., Brown, S. S., Stutz, J., Middlebrook, A. M., Bahreini, R., Wagner, N. L., Dube, W. P., Pollack, I. B., Ryerson, T. B., and Riemer, N.: Evaluating N_2O_5 heterogeneous hydrolysis parameterizations for CalNex 2010, *J. Geophys. Res.-Atmos.*, 121, 5051-5070, 10.1002/2015JD024737, 2016.
- 5 Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Saharjo, B. H., and Ward, D. E.: Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, *J. Geophys. Res.-Atmos.*, 108, 10.1029/2003JD003704, 2003.
- Cosman, L. M., Knopf, D. A., and Bertram, A. K.: N_2O_5 reactive uptake on aqueous sulfuric acid solutions coated with branched and straight-chain insoluble organic surfactants, *J. Phys. Chem. A*, 112, 2386–2396, doi:10.1021/jp710685r, 2008.
- 10 Davis, J., Bhawe, P., and Foley, K.: Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, *Atmos. Chem. Phys.*, 8, 5295-5311, 2008.
- Dong, H. B., Zeng, L. M., Hu, M., Wu, Y. S., Zhang, Y. H., Slanina, J., Zheng, M., Wang, Z. F., and Jansen, R.: Technical Note: The application of an improved gas and aerosol collector for ambient air pollutants in China, *Atmos. Chem. Phys.*, 12, 10519-10533, 10.5194/acp-12-10519-2012, 2012.
- 15 Evans, M. J., and Jacob, D. J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophys. Res. Lett.*, 32, 10.1029/2005gl022469, 2005.
- Finlayson-Pitts, B., Ezell, M., and Pitts, J.: Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and ClONO₂, *Nature*, 337, 241-244, 1989.
- Folkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N_2O_5 , *Geophys. Res. Lett.*, 30, 2003.
- 20 Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y., and Wang, Z.: Organic molecular compositions and temporal variations of summertime mountain aerosols over Mt. Tai, North China Plain, *J. Geophys. Res.-Atmos.*, 113, 10.1029/2008JD009900, 2008.
- Fuchs, H., Tan, Z., Lu, K., Bohn, B., Broch, S., Brown, S. S., Dong, H., Gomm, S., Häsel, R., He, L., Hofzumahaus, A., 25 Holland, F., Li, X., Liu, Y., Lu, S., Min, K. E., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: OH reactivity at a rural site (Wangdu) in the North China Plain: contributions from OH reactants and experimental OH budget, *Atmos. Chem. Phys.*, 17, 645-661, 10.5194/acp-17-645-2017, 2017.
- Gaston, C. J., and Thornton, J. A.: Reacto-diffusive length of N_2O_5 in aqueous sulfate-and chloride-containing aerosol particles, *J. Phys. Chem. A*, 120, 1039-1045, 2016.
- 30 Gaston, C. J., Thornton, J. A., and Ng, N. L.: Reactive uptake of N_2O_5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations, *Atmos. Chem. Phys.*, 14, 5693-5707, 10.5194/acp-14-5693-2014, 2014.
- Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive uptake of N_2O_5 by aerosols 35 containing dicarboxylic acids. Effect of particle phase, composition, and nitrate content, *J. Phys. Chem. A*, 113, 5082-5090, 10.1021/jp8096814, 2009.
- Gržinić, G., Bartels-Rausch, T., Berkemeier, T., Türler, A., and Ammann, M.: Viscosity controls humidity dependence of N_2O_5 uptake to citric acid aerosol, *Atmos. Chem. Phys.*, 15, 13615-13625, 2015.
- Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N_2O_5 on sub-micron sulfate aerosols, *Phys. Chem. Chem. Phys.*, 5, 3453-3463, 2003.
- 40 Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity, *J. Aerosol Sci.*, 36, 1210-1223, 10.1016/j.jaerosci.2005.01.005, 2005.
- Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N_2O_5 : simultaneous, in situ detection of ClONO₂ and N_2O_5 by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 2, 193-204, 10.5194/amt-2-193-2009, 2009.



- Kuang, B. Y., Lin, P., Huang, X. H. H., and Yu, J. Z.: Sources of humic-like substances in the Pearl River Delta, China: positive matrix factorization analysis of PM_{2.5} major components and source markers, *Atmos. Chem. Phys.*, 15, 1995-2008, 10.5194/acp-15-1995-2015, 2015.
- 5 Kuang, Y., Zhao, C., Ma, N., Liu, H., Bian, Y., Tao, J., and Hu, M.: Deliquescent phenomena of ambient aerosols on the North China Plain, *Geophys. Res. Lett.*, 43, 8744-8750, 2016.
- Li, Q., Zhang, L., Wang, T., Tham, Y.J., Ahmadov, R., Xue, L., Zhang, Q., Zheng, J.: Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China. *Atmos. Chem. Phys.*, 16, 14875-14890, 2016.
- 10 Lin, P., Engling, G., and Yu, J. Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China, *Atmos. Chem. Phys.*, 10, 6487-6500, 10.5194/acp-10-6487-2010, 2010.
- Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Muller, K., and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain, *Atmos. Chem. Phys.*, 14, 2525-2539, 10.5194/acp-14-2525-2014, 2014.
- 15 Liu, X., Qu, H., Huey, L. G., Wang, Y., Sjostedt, S., Zeng, L., Lu, K., Wu, Y., Hu, M., Shao, M., Zhu, T., and Zhang, Y.: High levels of daytime molecular chlorine and nitryl chloride at a rural site on the North China Plain, *Environ. Sci. Technol.*, 51, 9588-9595, 10.1021/acs.est.7b03039, 2017.
- Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, 1, 5451-5457, Doi 10.1039/A905338g, 1999.
- 20 Mielke, L. H., Furgeson, A., and Osthoff, H. D.: Observation of ClNO₂ in a mid-continental urban environment, *Environ. Sci. Technol.*, 45, 8889-8896, 10.1021/es201955u, 2011.
- Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Washenfelder, R. A., Young, C. J., Gilman, J. B., de Gouw, J. A., Flynn, J. H., Grossberg, N., Lefter, B. L., Liu, J., Weber, R. J., and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NO_x reservoir species during CalNex-LA 2010, *J. Geophys. Res.-Atmos.*, 118, 10638-10652, 10.1002/jgrd.50783, 2013.
- 25 Min, K. E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor, *Atmos. Meas. Tech.*, 9, 423-440, 10.5194/amt-9-423-2016, 2016.
- 30 Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N₂O₅ uptake: airborne regional measurements in northwestern Europe, *Atmos. Chem. Phys.*, 15, 973-990, 10.5194/acp-15-973-2015, 2015.
- 35 Nie, W., Hong, J., Häme, S. A. K., Ding, A., Li, Y., Yan, C., Hao, L., Mikkilä, J., Zheng, L., Xie, Y., Zhu, C., Xu, Z., Chi, X., Huang, X., Zhou, Y., Lin, P., Virtanen, A., Worsnop, D. R., Kulmala, M., Ehn, M., Yu, J., Kerminen, V. M., and Petäjä, T.: Volatility of mixed atmospheric humic-like substances and ammonium sulfate particles, *Atmos. Chem. Phys.*, 17, 3659-3672, 10.5194/acp-17-3659-2017, 2017.
- Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nature Geosci.*, 1, 324-328, 2008.
- 40 Pathak, R. K., Wang, T., and Wu, W. S.: Nighttime enhancement of PM_{2.5} nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of N₂O₅ and HNO₃ partitioning, *Atmos. Environ.*, 45, 1183-1191, <https://doi.org/10.1016/j.atmosenv.2010.09.003>, 2011.
- Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, *Atmos. Chem. Phys.*, 9, 1711-1722, 10.5194/acp-9-1711-2009, 2009.



- Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S., Bingemer, H., Lelieveld, J., and Crowley, J. N.: Estimating N_2O_5 uptake coefficients using ambient measurements of NO_3 , N_2O_5 , ClNO_2 and particle-phase nitrate, *Atmos. Chem. Phys.*, 16, 13231-13249, 10.5194/acp-16-13231-2016, 2016.
- 5 Reyes-Villegas, E., Priestley, M., Ting, Y. C., Haslett, S., Bannan, T., Le breton, M., Williams, P. I., Bacak, A., Flynn, M. J., Coe, H., Percival, C., and Allan, J. D.: Simultaneous Aerosol Mass Spectrometry and Chemical Ionisation Mass Spectrometry measurements during a biomass burning event in the UK: Insights into nitrate chemistry, *Atmos. Chem. Phys. Discuss.*, 2017, 1-22, 10.5194/acp-2017-605, 2017.
- 10 Riedel, T. P., Bertram, T. H., Crisp, T. A., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S.-M., Gilman, J., de Gouw, J., Bon, D. M., Wagner, N. L., Brown, S. S., and Thornton, J. A.: Nitryl chloride and molecular chlorine in the coastal marine boundary layer, *Environ. Sci. Technol.*, 46, 10463-10470, 10.1021/es204632r, 2012.
- Riedel, T. P., Bertram, T. H., Ryder, O. S., Liu, S., Day, D. A., Russell, L. M., Gaston, C. J., Prather, K. A., and Thornton, J. A.: Direct N_2O_5 reactivity measurements at a polluted coastal site, *Atmos. Chem. Phys.*, 12, 2959-2968, 10.5194/acp-12-2959-2012, 2012.
- 15 Riedel, T. P., Wagner, N. L., Dube, W. P., Middlebrook, A. M., Young, C. J., Ozturk, F., Bahreini, R., VandenBoer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S., and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO_2 and Cl_2 measurements from a tall tower in a polluted continental setting, *J. Geophys. Res.-Atmos.*, 118, 8702-8715, 10.1002/jgrd.50637, 2013.
- Riedel, T. P., Wolfe, G. M., Danas, K. T., Gilman, J. B., Kuster, W. C., Bon, D. M., Vlasenko, A., Li, S. M., Williams, E. J., Lerner, B. M., Veres, P. R., Roberts, J. M., Holloway, J. S., Lefér, B., Brown, S. S., and Thornton, J. A.: An MCM modeling study of nitryl chloride (ClNO_2) impacts on oxidation, ozone production and nitrogen oxide partitioning in polluted continental outflow, *Atmos. Chem. Phys.*, 14, 3789-2014, 2014.
- 20 Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler - Scharr, A., and Mentel, T.: Relative importance of organic coatings for the heterogeneous hydrolysis of N_2O_5 during summer in Europe, *J. Geophys. Res.-Atmos.*, 114, 2009.
- Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A. R., Coffman, D., Quinn, P., and Bates, T.: Laboratory studies of products of N_2O_5 uptake on Cl^- containing substrates, *Geophys. Res. Lett.*, 36, L20808, 10.1029/2009GL040448, 2009.
- Ryder, O. S., Ault, A. P., Cahill, J. F., Guasco, T. L., Riedel, T. P., Cuadra-Rodriguez, L. A., Gaston, C. J., Fitzgerald, E., Lee, C., Prather, K. A., and Bertram, T. H.: On the role of particle inorganic mixing state in the reactive uptake of N_2O_5 to ambient aerosol particles, *Environ. Sci. Technol.*, 48, 1618-1627, 10.1021/es4042622, 2014.
- 30 Ryder, O. S., Campbell, N. R., Shalowski, M., Al-Mashat, H., Nathanson, G. M., and Bertram, T. H.: Role of Organics in Regulating ClNO_2 Production at the Air-Sea Interface, *J. Phys. Chem. A*, 119, 8519-8526, 10.1021/jp5129673, 2015.
- Sarwar, G., Simon, H., Xing, J., and Mathur, R.: Importance of tropospheric ClNO_2 chemistry across the Northern Hemisphere, *Geophys. Res. Lett.*, 41, 2014GL059962, 10.1002/2014GL059962, 2014.
- 35 Schweitzer, F., Mirabel, P., and George, C.: Multiphase chemistry of N_2O_5 , ClNO_2 , and BrNO_2 , *J. Phys. Chem. A*, 102, 3942-3952, Doi 10.1021/Jp980748s, 1998.
- Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häsel, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO_2 and RO_2 radicals, *Atmos. Chem. Phys.*, 17, 663-690, 10.5194/acp-17-663-2017, 2017.
- 40 Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Groß, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, *Atmos. Chem. Phys.*, 16, 14959-14977, 10.5194/acp-16-14959-2016, 2016.
- 45 Tham, Y. J., Yan, C., Xue, L., Zha, Q., Wang, X., and Wang, T.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, *Chin. Sci. Bull.*, 59, 356-359, 10.1007/s11434-013-0063-y, 2014.



- Thornton, J. A., and Abbatt, J. P. D.: N₂O₅ reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, *J. Phys. Chem. A*, 109, 10004-10012, [10.1021/jp054183t](https://doi.org/10.1021/jp054183t), 2005.
- Thornton, J. A., Braban, C. F., and Abbatt, J. P.: N₂O₅ hydrolysis on sub-micron organic aerosols: The effect of relative humidity, particle phase, and particle size, *Phys. Chem. Chem. Phys.*, 5, 4593-4603, 2003.
- 5 Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, 464, 271-274, 2010.
- Wagner, N. L., Riedel, T. P., Roberts, J. M., Thornton, J. A., Angevine, W. M., Williams, E. J., Lerner, B. M., Vlasenko, A., Li, S. M., Dube, W. P., Coffman, D. J., Bon, D. M., de Gouw, J. A., Kuster, W. C., Gilman, J. B., and Brown, S. S.: The sea breeze/land breeze circulation in Los Angeles and its influence on nitryl chloride production in this region, *J. Geophys. Res.-Atmos.*, 117, D00V24, [10.1029/2012jd017810](https://doi.org/10.1029/2012jd017810), 2012.
- 10 Wagner, N. L., Riedel, T. P., Young, C. J., Bahreini, R., Brock, C. A., Dubé, W. P., Kim, S., Middlebrook, A. M., Öztürk, F., Roberts, J. M., Russo, R., Sive, B., Swarthout, R., Thornton, J. A., VandenBoer, T. C., Zhou, Y., and Brown, S. S.: N₂O₅ uptake coefficients and nocturnal NO₂ removal rates determined from ambient wintertime measurements, *J. Geophys. Res.-Atmos.*, 118, 9331-9350, [10.1002/jgrd.50653](https://doi.org/10.1002/jgrd.50653), 2013.
- 15 Wang, H., Lu, K., Chen, X., Zhu, Q., Chen, Q., Guo, S., Jiang, M., Li, X., Shang, D., Tan, Z., Wu, Y., Wu, Z., Zou, Q., Zheng, Y., Zeng, L., Zhu, T., Hu, M., and Zhang, Y.: High N₂O₅ Concentrations Observed in Urban Beijing: Implications of a Large Nitrate Formation Pathway, *Environ. Sci. Technol. Lett.*, 4, 416-420, [10.1021/acs.estlett.7b00341](https://doi.org/10.1021/acs.estlett.7b00341), 2017.
- Wang, H., Lu, K., Guo, S., Wu, Z., Shang, D., Tan, Z., Wang, Y., Le Breton, M., Zhu, W., Lou, S., Tang, M., Wu, Y., Zheng, J., Zeng, L., Hallquist, M., Hu, M., and Zhang, Y.: Efficient N₂O₅ Uptake and NO₃ Oxidation in the Outflow of Urban Beijing, *Atmos. Chem. Phys. Discuss.*, 2018, 1-27, [10.5194/acp-2018-88](https://doi.org/10.5194/acp-2018-88), 2018.
- 20 Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., Hu, M., and Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, *Anal Methods*, 6, 9424-9434, [10.1039/C4AY01855A](https://doi.org/10.1039/C4AY01855A), 2014.
- 25 Wang, S., Shi, C., Zhou, B., Zhao, H., Wang, Z., Yang, S., and Chen, L.: Observation of NO₃ radicals over Shanghai, China, *Atmos. Environ.*, 70, 401-409, <https://doi.org/10.1016/j.atmosenv.2013.01.022>, 2013.
- Wang, T., Tham, Y. J., Xue, L. K., Li, Q. Y., Zha, Q. Z., Wang, Z., Poon, S. C. N., Dube, W. P., Blake, D. R., Louie, P. K. K., Luk, C. W. Y., Tsui, W., and Brown, S. S.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, *J. Geophys. Res.-Atmos.*, 121, 2476-2489, [10.1002/2015JD024556](https://doi.org/10.1002/2015JD024556), 2016.
- 30 Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., Wang, W., Tham, Y. J., Wang, Z., Yang, L., Chen, J., and Wang, W.: Observations of N₂O₅ and ClNO₂ at a polluted urban surface site in North China: High N₂O₅ uptake coefficients and low ClNO₂ product yields, *Atmos. Environ.*, 156, 125-134, <https://doi.org/10.1016/j.atmosenv.2017.02.035>, 2017.
- Wang, Y., Chen, Z., Wu, Q., Liang, H., Huang, L., Li, H., Lu, K., Wu, Y., Dong, H., Zeng, L., and Zhang, Y.: Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain, *Atmos. Chem. Phys.*, 16, 10985-11000, [10.5194/acp-16-10985-2016](https://doi.org/10.5194/acp-16-10985-2016), 2016.
- 35 Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., Wang, X., and Wang, T.: Fast heterogeneous N₂O₅ uptake and ClNO₂ production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain, *Atmos. Chem. Phys.*, 17, 12361-12378, [10.5194/acp-17-12361-2017](https://doi.org/10.5194/acp-17-12361-2017), 2017.
- 40 Wexler, A. S., and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H⁺, NH₄⁺, Na⁺, SO₄²⁻, NO₃⁻, Cl⁻, Br⁻, and H₂O, *J. Geophys. Res.-Atmos.*, 107, [10.1029/2001jd000451](https://doi.org/10.1029/2001jd000451), 2002.
- Wu, Z. J., Ma, N., Größ, J., Kecorius, S., Lu, K. D., Shang, D. J., Wang, Y., Wu, Y. S., Zeng, L. M., Hu, M., Wiedensohler, A., and Zhang, Y. H.: Thermodynamic properties of nanoparticles during new particle formation events in the atmosphere of North China Plain, *Atmos. Res.*, 188, 55-63, <https://doi.org/10.1016/j.atmosres.2017.01.007>, 2017.
- 45 Yuan, B., Liu, Y., Shao, M., Lu, S. H., and Streets, D. G.: Biomass burning contributions to ambient VOCs species at a receptor site in the Pearl River Delta (PRD), China, *Environ. Sci. Technol.*, 44, 4577-4582, [10.1021/es1003389](https://doi.org/10.1021/es1003389), 2010.



Yun, H., Wang, T., Wang, W., Tham, Y. J., Li, Q., Wang, Z., and Poon, S. C. N.: Nighttime NO_x loss and ClNO₂ formation in the residual layer of a polluted region: Insights from field measurements and an iterative box model, *Sci. Total Environ.*, 622-623, 727-734, [10.1016/j.scitotenv.2017.11.352](https://doi.org/10.1016/j.scitotenv.2017.11.352), 2017.



Table 1: N_2O_5 uptake coefficients and ClNO_2 production yields from 10 selected plumes at Wangdu during the summer of 2014. The uncertainty (\pm) of the $\gamma(\text{N}_2\text{O}_5)$ and ϕ was estimated by the geometric mean of uncertainty from the scattering of the data plots and uncertainty from measurement of N_2O_5 , ClNO_2 , aerosol surface area, and particulate NO_3^- .

Plume	Date (Time)	$\gamma(\text{N}_2\text{O}_5)$	$\phi(\text{ClNO}_2)$
1	20 June (23:00) – 21 June (01:20)	0.029 ± 0.011	0.54 ± 0.19
2	21 June (03:30 – 05:00)	0.032 ± 0.015	1.04 ± 0.35
3	24 June (20:30 – 22:10)	0.014 ± 0.008	0.10 ± 0.05
4	24 June (22:30) – 25 June (00:00)	0.027 ± 0.009	0.38 ± 0.12
5	27 June (20:40) – 28 June (00:00)	0.011 ± 0.007	0.15 ± 0.09
6	28 June (22:30) – 29 June (00:40)	0.006 ± 0.002	0.20 ± 0.06
7	29 June (22:00) – 30 June (01:20)	0.015 ± 0.005	0.28 ± 0.12
8	30 June (21:10) – 1 July (00:10)	0.019 ± 0.007	0.18 ± 0.06
9	5 July (00:30) – 5 July (02:30)	0.032 ± 0.019	0.45 ± 0.27
10	5 July (23:40) – 6 July (02:00)	0.034 ± 0.014	0.07 ± 0.03

**Table 2: Summary of field-observed N_2O_5 uptake coefficient and $ClNO_2$ yield from previous studies.**

Location	Environment	$\gamma(N_2O_5)$	ϕ	Descriptions	Reference
North America					
New England, US	Coastal + Inland	0.001–0.017	<i>n.a.</i>	Aircraft measurement (below 1500 m). $\gamma(N_2O_5)$ is higher in elevated sulfate region.	Brown et al., 2006
Coast of Texas, US	Coastal	<i>n.a.</i>	0.10–0.65	Shipborne measurement. Influenced by urban outflow.	Osthoff et al., 2008
Texas, US	Coastal + Inland	0.0005–0.006	<i>n.a.</i>	Aircraft measurement (below 1000 m). $\gamma(N_2O_5)$ was independent of humidity (RH, 34% to 85%) and aerosol compositions.	Brown et al., 2009
Seattle, US	Coastal	0.005–0.04	<i>n.a.</i>	Urban/suburban environment. $\gamma(N_2O_5)$ was enhanced with higher RH but has strong correlation with organic-to-sulfate ratio.	Bertram et al., 2009
Calgary, Canada	Inland	0.02	0.15	Ground urban area. Influenced by anthropogenic activities within the urban area.	Mielke et al., 2011
La Jolla, US	Coastal	0.001–0.029	<i>n.a.</i>	Polluted coastal site. $\gamma(N_2O_5)$ was suppressed by nitrate.	Riedel et al., 2012
Coast of Los Angeles, US	Coastal	<i>n.a.</i>	0.15–0.62	Shipborne measurement. Influenced by land-sea breeze.	Wagner et al., 2012
Pasadena, US	Coastal	$\gamma\phi = 0.008$ (average)		Ground measurement during the California Nexus 2010 campaign. $\gamma\phi$ was enhanced by submicron chloride, but suppressed by organic matter and liquid water content.	Mielke et al., 2013
Boulder, US	Inland	0.002–0.1	0.01–0.98	Tower measurement (0-300 m) downwind of urban city. $\gamma(N_2O_5)$ dependence on nitrate. Higher ϕ in coal combustion plume.	Wagner et al., 2013 Riedel et al., 2013
Europe					
London	Coastal + Inland	0.01–0.03	<i>n.a.</i>	Aircraft measurement (500-1000 m). $\gamma(N_2O_5)$ was independent of humidity (RH, 50% to 90%) but dependent on nitrate loading.	Morgan et al., 2015
Kleiner Feldberg	Inland	0.004–0.11	0.029–1.38	Semirural mountain-top site in SW Germany (825 m above sea level). $\gamma(N_2O_5)$ was independent of aerosol compositions but has a weak dependence on humidity.	Phillips et al., 2016
China					



Hong Kong	Coastal	0.004–0.021	0.02–0.98	Rural mountain-top site in southern China (957 m above sea level). Influenced by pollution from urban area.	Brown et al., 2016 Yun et al., 2018
Jinan	Inland	0.042–0.092	0.01–0.08	Urban-surface in polluted urban area of northern China. $\gamma(\text{N}_2\text{O}_5)$ showed positive dependence on RH.	Wang X. et al., 2017
Mt. Tai	Inland	0.021–0.103	0.17–0.90	Mountaintop site in northern China (1465 m above sea level). Elevated $\gamma(\text{N}_2\text{O}_5)$ for high humidity (>80%) condition. Higher ϕ in coal-fired power plant plumes.	Wang Z. et al., 2017
Beijing-urban	Inland	0.025–0.072	<i>n.a</i>	Polluted urban surface-site in northern China during early autumn. High $\gamma(\text{N}_2\text{O}_5)$ was related to high aerosol liquid water content.	Wang H. et al., 2017
Beijing-rural	Inland	0.012–0.055	0.50–1.00	Rural surface site in northern of Beijing. Influenced by the outflow of the urban Beijing.	Wang H. et al., 2018
Wangdu	Inland	0.006–0.034	0.07–1.04	Semirural and surface site in northern China. $\gamma(\text{N}_2\text{O}_5)$ has strong dependence on humidity and aerosol water content. Variable ϕ and lower values for cases influenced by biomass burning activities.	This study

n.a = no information available

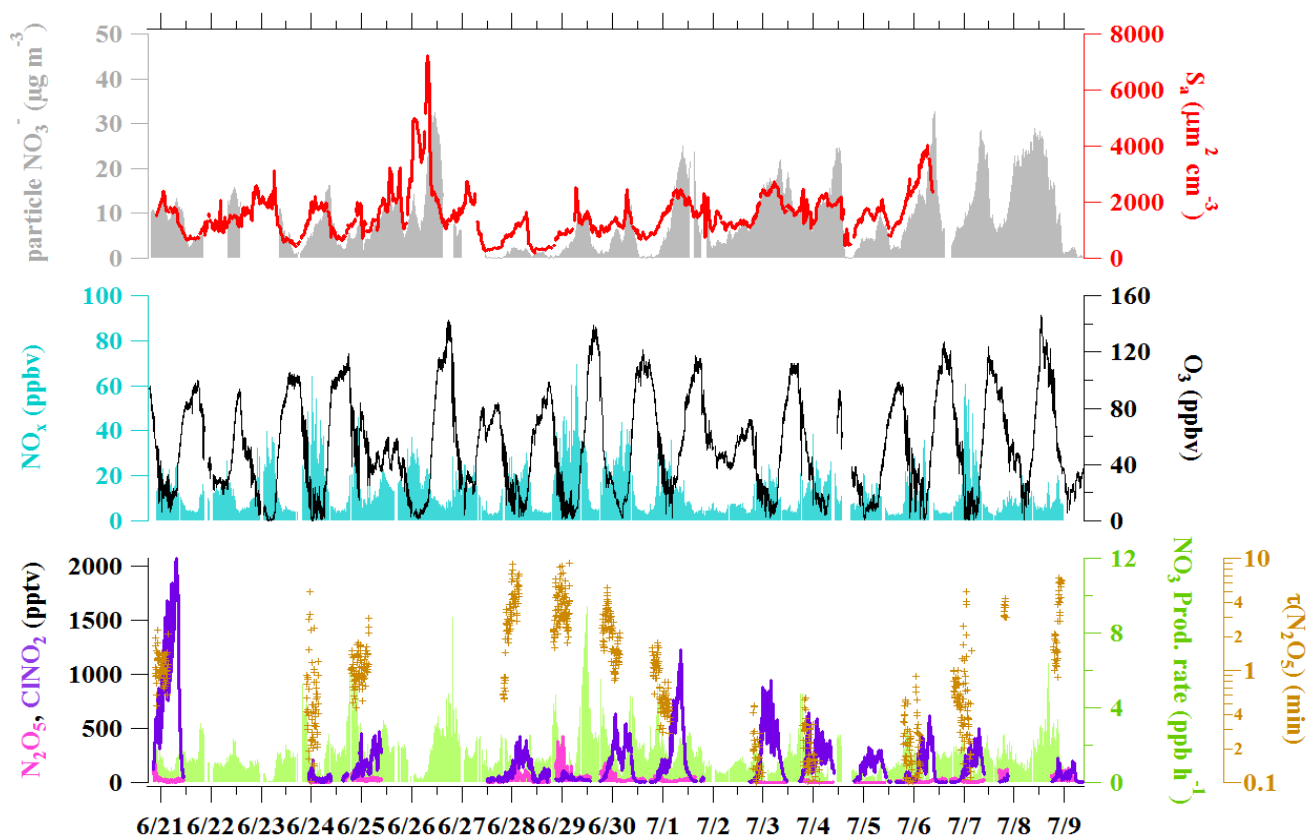


Figure 1: Time series of N_2O_5 , ClONO_2 , NO_3 production rate, the steady-state lifetime of N_2O_5 , O_3 , NO_x , fine particulate NO_3^- , and S_a data at Wangdu from 21 June to 9 July 2014. N_2O_5 and ClONO_2 are 1-min data, whereas the NO_x , O_3 , NO_3 production rate and $\tau(\text{N}_2\text{O}_5)$ are given as 5-min averages. The data for S_a and fine particulate NO_3^- are in 10-min and 30-min time resolutions, respectively. The data gaps were caused by technical problems, calibrations, or instrument maintenance.

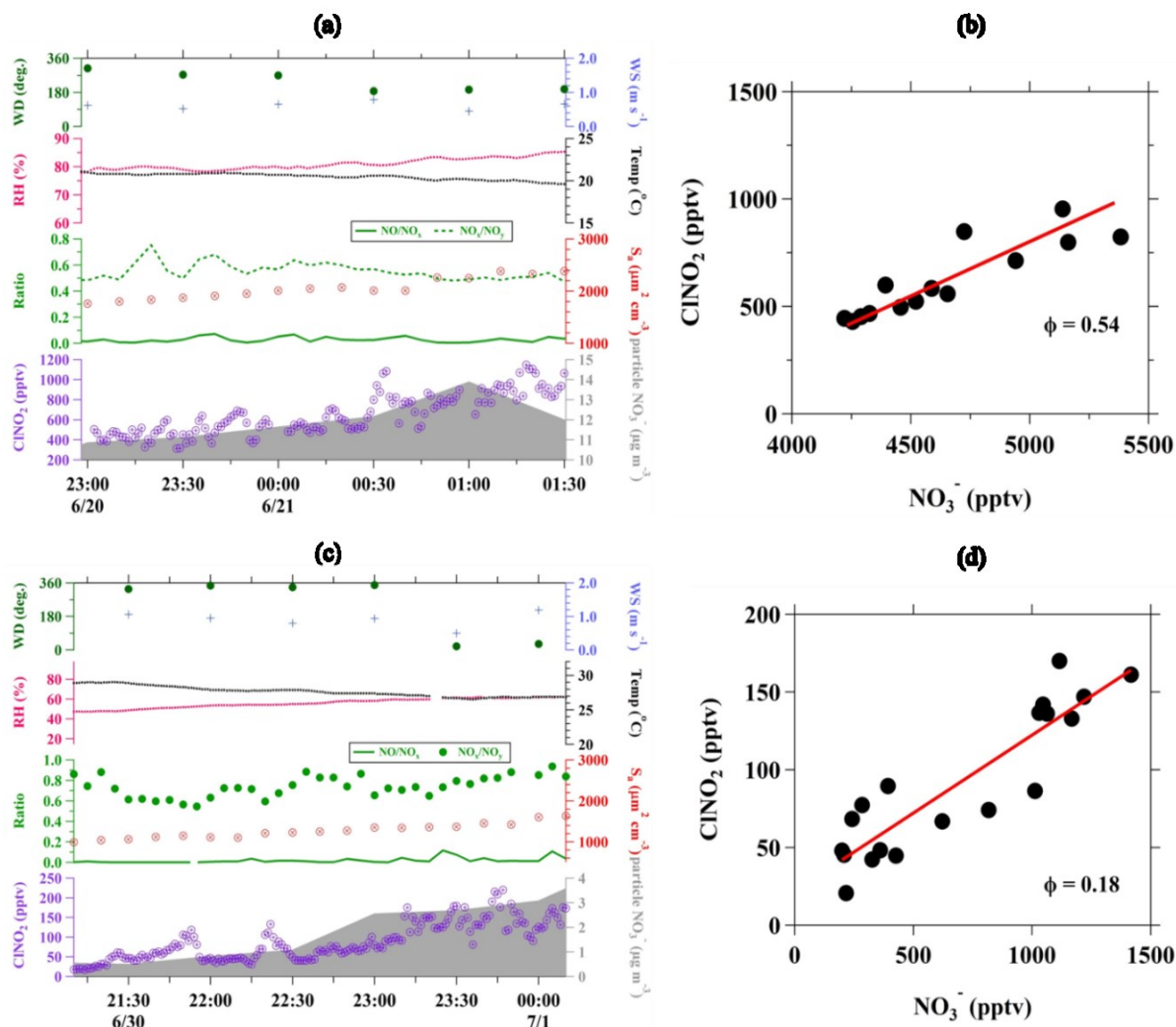


Figure 2: Example of the accumulation of CINO₂ and particulate NO₃⁻ concentrations during the relatively constant condition of relevant chemical compositions and environmental variables observed for (a) Plume 1 on 20-21 June 2014 and (c) Plume 7 on 29-30 June 2014. Scatter plots of CINO₂ versus particulate NO₃⁻ to estimate the CINO₂ yield (ϕ) for these two cases are shown in (b) and (d).

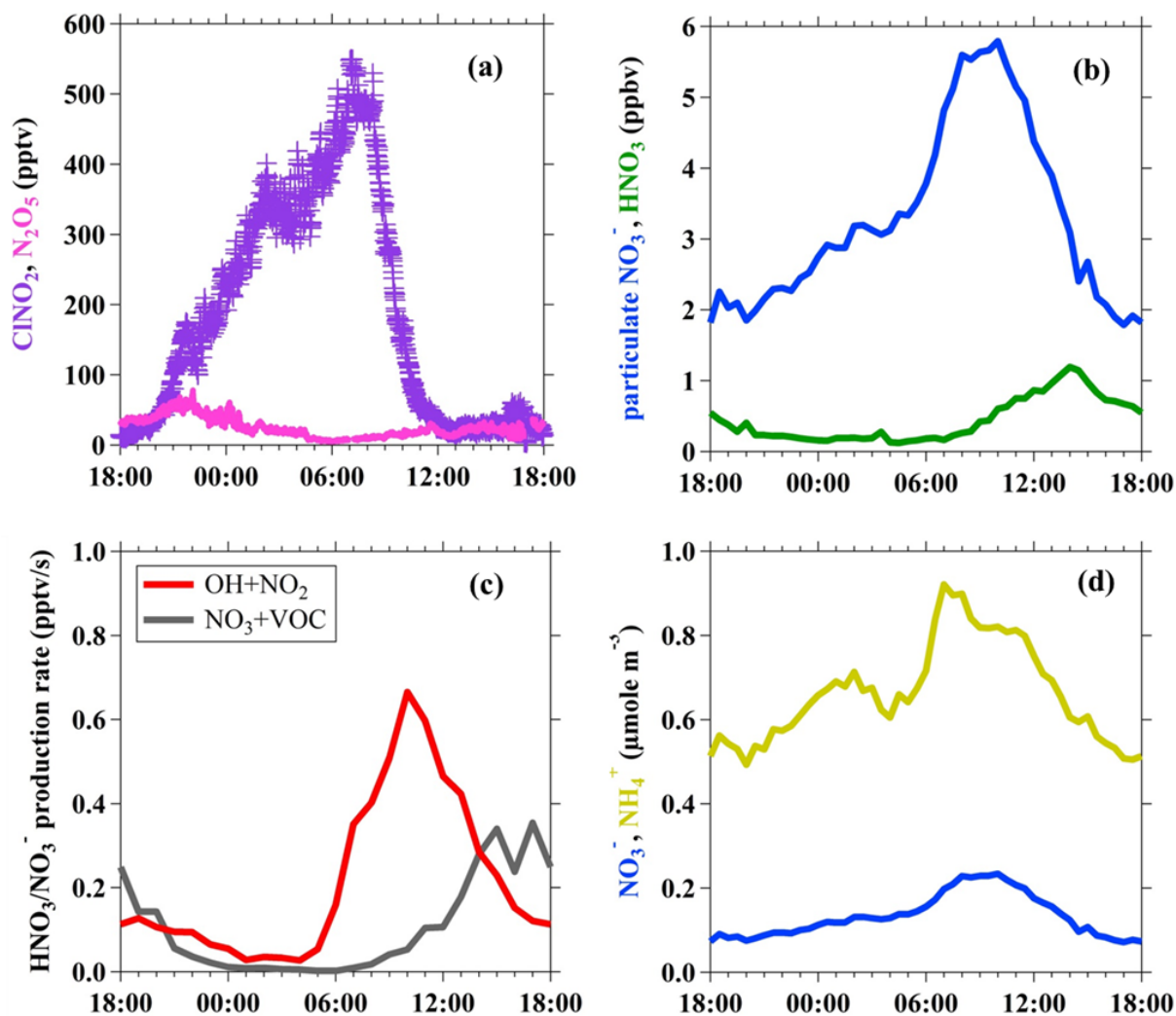


Figure 3: Diurnal variations of (a) N_2O_5 and ClNO_2 ; (b) particulate NO_3^- and gas-phase HNO_3 (c) gas-phase production rate of $\text{NO}_3^-/\text{HNO}_3$ via reaction of $\text{OH}+\text{NO}_2$ and NO_3+VOC ; and (d) concentrations of NH_4^+ in relation to particulate NO_3^- .

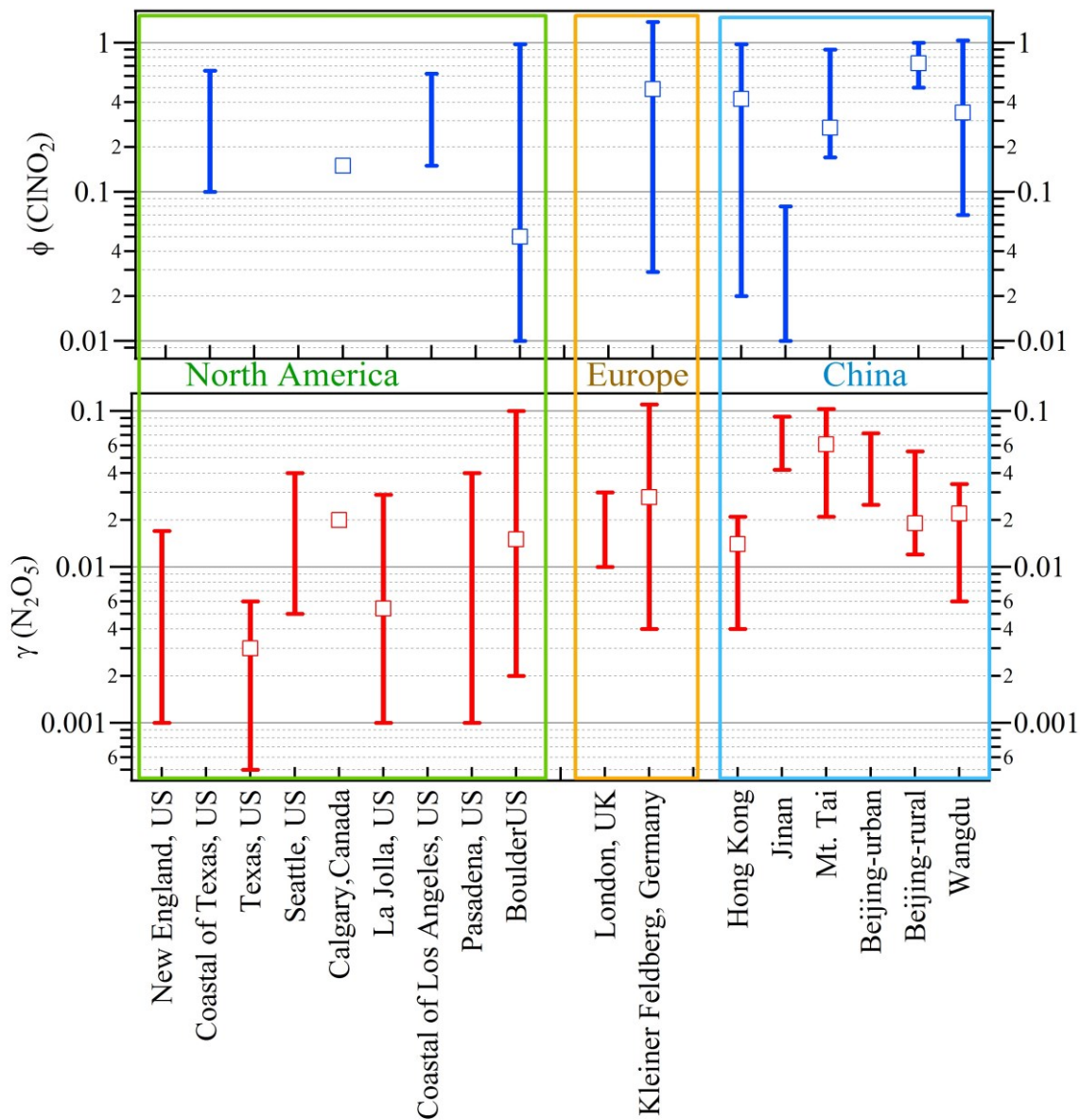


Figure 4: Comparison of field-observed N₂O₅ uptake coefficient and ClNO₂ yield from previous studies. Sticks represent the range of the reported values, and cubes represent the median or average values reported in these measurements. The corresponding references are listed in Table 2.

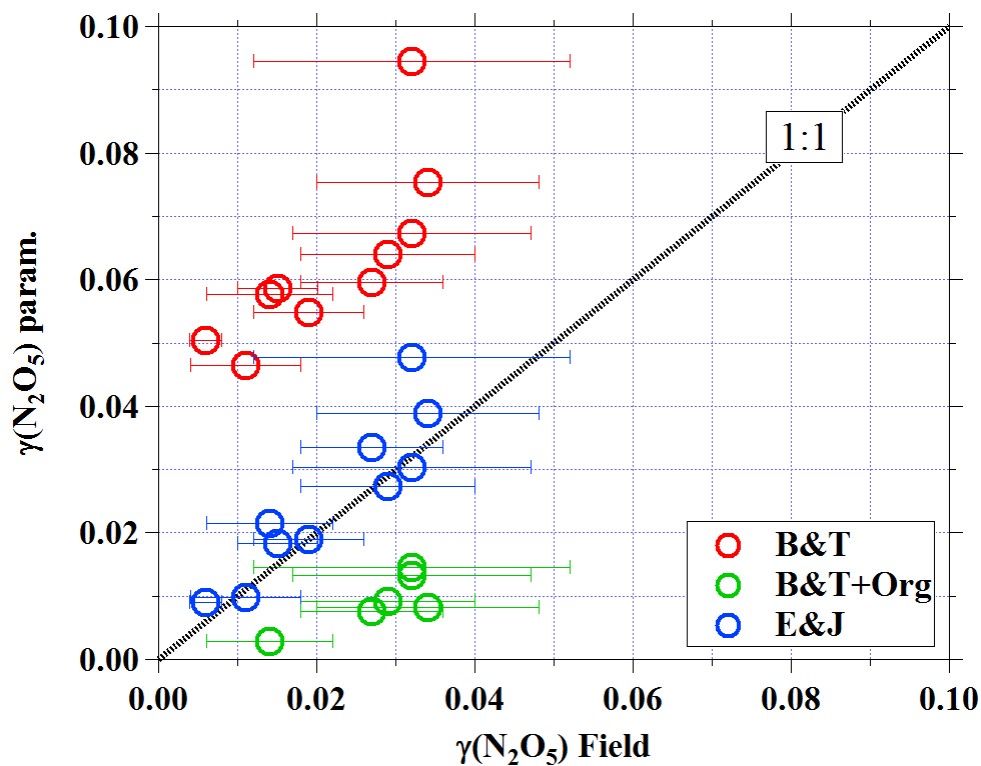


Figure 5: Comparison of field-derived N_2O_5 uptake coefficients with values computed from different parameterizations. The dashed line represents 1:1, and the error bars show the uncertainty of $\gamma(\text{N}_2\text{O}_5)$ derived from the field.

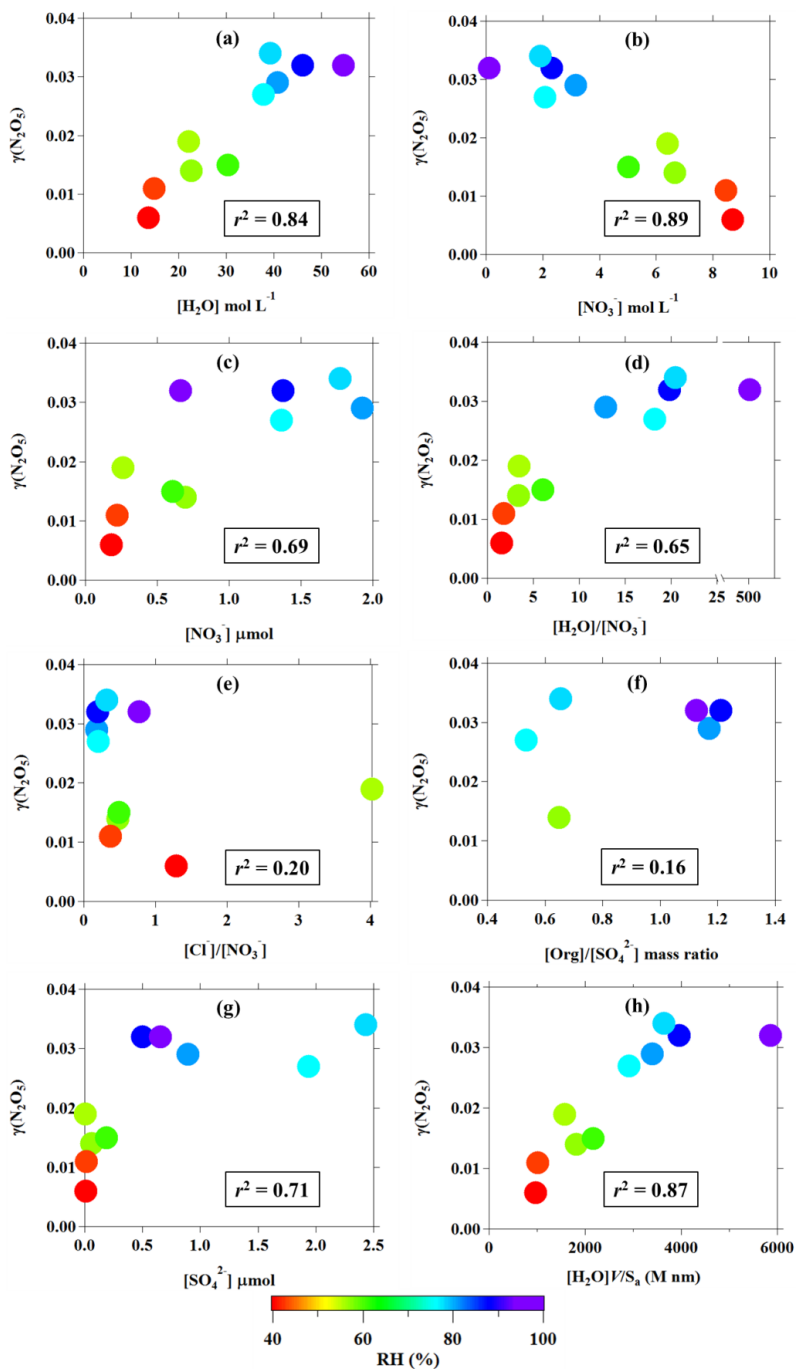


Figure 6: Relationship between field-derived $\gamma(\text{N}_2\text{O}_5)$ and a) aerosol water content (mol per volume of aerosol); b) nitrate concentration per volume of aerosol; c) particulate nitrate concentration ($\mu\text{mol m}^{-3}$ of air); d) H_2O to NO_3^- molar ratio; e) Cl^- to NO_3^- molar ratio; f) organic-to-sulfate mass ratio (data from aerosol mass spectrometer); g) concentration of SO_4^{2-} ($\mu\text{mol m}^{-3}$ of air); and h) amount of water in aerosol multiplied by the volume-to-surface area ratio. Color code represents the ambient RH, and the value in the box is the best correlation coefficient obtained from curve fittings.

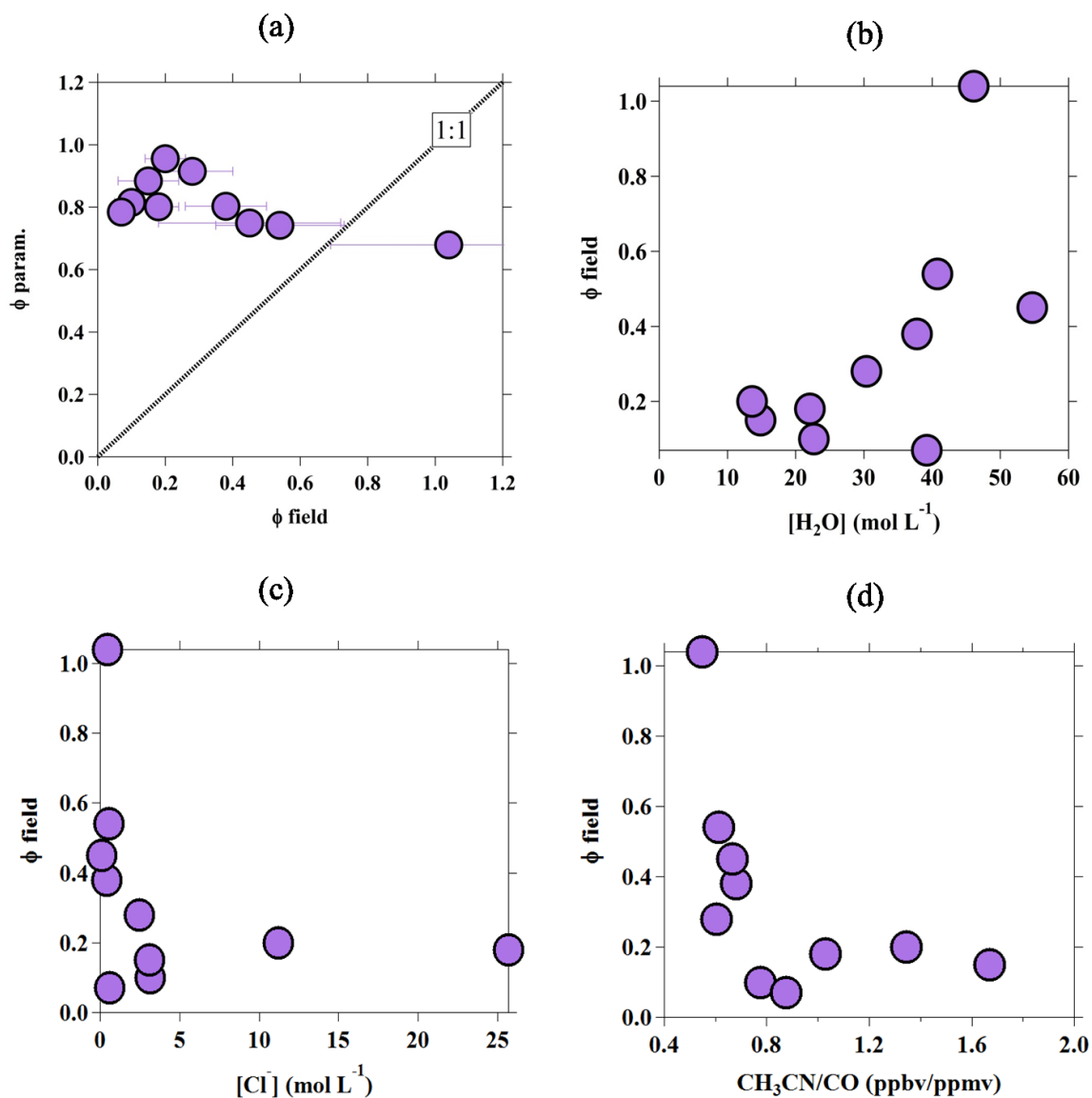


Figure 7: Scatter plots for (a) yield derived from the field versus yield calculated from the parameterization (error bars represent the uncertainty of field-derived ϕ , and black dotted line represents the 1:1 ratio); (b) field-derived yield versus aerosol water content; (c) field-derived yield versus chloride; and (d) field-derived yield versus $\text{CH}_3\text{CN}/\text{CO}$.