



## Article

# Heterogeneous Uptake of $\text{N}_2\text{O}_5$ in Sand Dust and Urban Aerosols Observed during the Dry Season in Beijing

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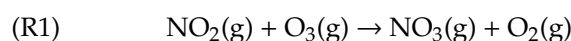


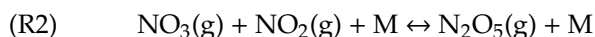
**Abstract:** The uptake of dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) on aerosols affects the nocturnal removal of  $\text{NO}_x$  and particulate nitrate formation in the atmosphere. This study investigates  $\text{N}_2\text{O}_5$  uptake processes using field observations from an urban site in Beijing during April–May 2017, a period characterized by dry weather conditions. For the first time, a very large  $\text{N}_2\text{O}_5$  uptake rate ( $k(\text{N}_2\text{O}_5)$  up to  $\sim 0.01 \text{ s}^{-1}$ ) was observed during a sand storm event, and the uptake coefficient ( $\gamma(\text{N}_2\text{O}_5)$ ) was estimated to be 0.044. The  $\gamma(\text{N}_2\text{O}_5)$  in urban air masses was also determined and exhibited moderate correlation ( $r = 0.68$ ) with aerosol volume to surface ratio ( $V_a/S_a$ ), but little relation to aerosol water, nitrate, and chloride, a finding that contrasts with previous results. Several commonly used parameterizations of  $\gamma(\text{N}_2\text{O}_5)$  underestimated the field-derived  $\gamma(\text{N}_2\text{O}_5)$ . A new parameterization is suggested for dry conditions, which considers the effect of  $V_a/S_a$ , temperature, and relative humidity.

**Keywords:**  $\text{N}_2\text{O}_5$  uptake; sand dust; particle size; aerosol compositions

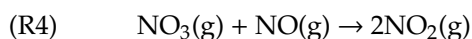
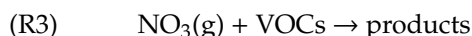
## 1. Introduction

Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) is an important nighttime reservoir of  $\text{NO}_x$  which is a key precursor to photochemical production of ozone [1]. The loss of  $\text{N}_2\text{O}_5$  on aerosol surface, therefore, affects the lifetime of  $\text{NO}_x$  and produces nitrate aerosol, contributing to particulate pollution (e.g., [2]). The formation of  $\text{N}_2\text{O}_5$  is initiated by the gas phase production of nitrate radical ( $\text{NO}_3$ ), which is in rapid equilibrium with  $\text{N}_2\text{O}_5$  (R2) [3,4]. As (R2) is a second-order reaction, M in (R2) denotes the third body, i.e., ambient air.

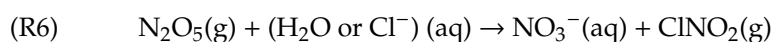
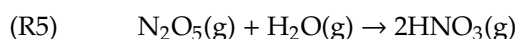




$\text{NO}_3$  and  $\text{N}_2\text{O}_5$  are partially removed via gas phase reactions of  $\text{NO}_3$  with volatile organic compounds (VOCs) and  $\text{NO}$  [5]:



$\text{N}_2\text{O}_5$  can undergo homogeneous hydrolysis with water vapor in the gas phase [6], producing nitric acid (R5) or heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on the aerosol surface forming nitryl chloride ( $\text{ClNO}_2$ ) and particulate nitrate ( $\text{NO}_3^-$ ) (R6) [7,8].  $\text{ClNO}_2$  yield ( $\varphi(\text{ClNO}_2)$ ) is used to describe the amount of  $\text{ClNO}_2$  production from unit loss of  $\text{N}_2\text{O}_5$  on aerosols [9].



The rate of  $\text{N}_2\text{O}_5$  uptake on aerosols ( $k(\text{N}_2\text{O}_5)$ ,  $\text{s}^{-1}$ ) can be expressed as (Equation (1)), where  $c(\text{N}_2\text{O}_5)$  (m/s) is the mean molecular speed of  $\text{N}_2\text{O}_5$ ,  $S_a$  ( $\mu\text{m}^2/\text{cm}^3$ ) is the aerosol surface area density, and  $\gamma(\text{N}_2\text{O}_5)$  is the uptake probability of  $\text{N}_2\text{O}_5$  on the aerosol surface.

$$k(\text{N}_2\text{O}_5) = \frac{1}{4} c(\text{N}_2\text{O}_5) S_a \gamma(\text{N}_2\text{O}_5) \quad (1)$$

$\gamma(\text{N}_2\text{O}_5)$  is highly variable ( $10^{-4}$  to 0.2) and has complicated dependences on the chemical composition and physical properties of aerosols according to field studies (e.g., [2,10,11]). Laboratory studies have found that  $\text{N}_2\text{O}_5$  uptake is enhanced by chloride and aerosol water content ( $[\text{H}_2\text{O}]$ ) but suppressed by inorganic nitrate [12–15] and aerosol organic coating [16,17]. Sand dust has also been found to be an important interface for  $\text{N}_2\text{O}_5$  uptake [18,19], but differing results have been obtained even for the same dust type [19–22]. For example, different laboratory studies of Saharan dust reported  $\gamma(\text{N}_2\text{O}_5)$  in the range 0.013–0.2 [20,21,23,24]. Although laboratory studies have suggested large  $\gamma(\text{N}_2\text{O}_5)$  on mineral dust, there have been no reports on direct observations of  $\text{N}_2\text{O}_5$  uptake on ambient mineral dust.

Several parameterizations of  $\gamma(\text{N}_2\text{O}_5)$  have been proposed to predict  $\gamma(\text{N}_2\text{O}_5)$  based on laboratory results on the relation of  $\gamma(\text{N}_2\text{O}_5)$  to temperature, relative humidity (RH), aerosol size, and aerosol inorganic and organic content (e.g., [14,16,25,26]). To evaluate the validity of these parameterizations in the real atmosphere,  $\gamma(\text{N}_2\text{O}_5)$  was derived using field observations or direct measurements of  $\text{N}_2\text{O}_5$  reactivity [10,27–29]. The enhancement effect of chloride and  $[\text{H}_2\text{O}]$  and the inhibition effect of nitrate on  $\gamma(\text{N}_2\text{O}_5)$  have been observed in the field [11,30–32]. However, the parameterized  $\gamma(\text{N}_2\text{O}_5)$  based on the observed physiochemical properties of aerosols has been found to be inconsistent with observed  $\gamma(\text{N}_2\text{O}_5)$  [10,31]. For example, the widely adopted parameterization proposed by Bertram and Thornton (denoted  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$ ) has often yielded higher values than the observed or directly measured  $\gamma(\text{N}_2\text{O}_5)$  when the observed  $\gamma(\text{N}_2\text{O}_5)$  is small ( $<0.02$ ) [11,28,32,33]. The discrepancy may be due to overestimation of the enhancement effect of chloride, presence of organic aerosols, and unknown suppression effects on  $\text{N}_2\text{O}_5$  uptake [33]. More investigation of  $\gamma(\text{N}_2\text{O}_5)$  in the real atmosphere is needed to improve the parametrization, while observation of  $\text{N}_2\text{O}_5$  uptake on ambient sand dust is also desirable.

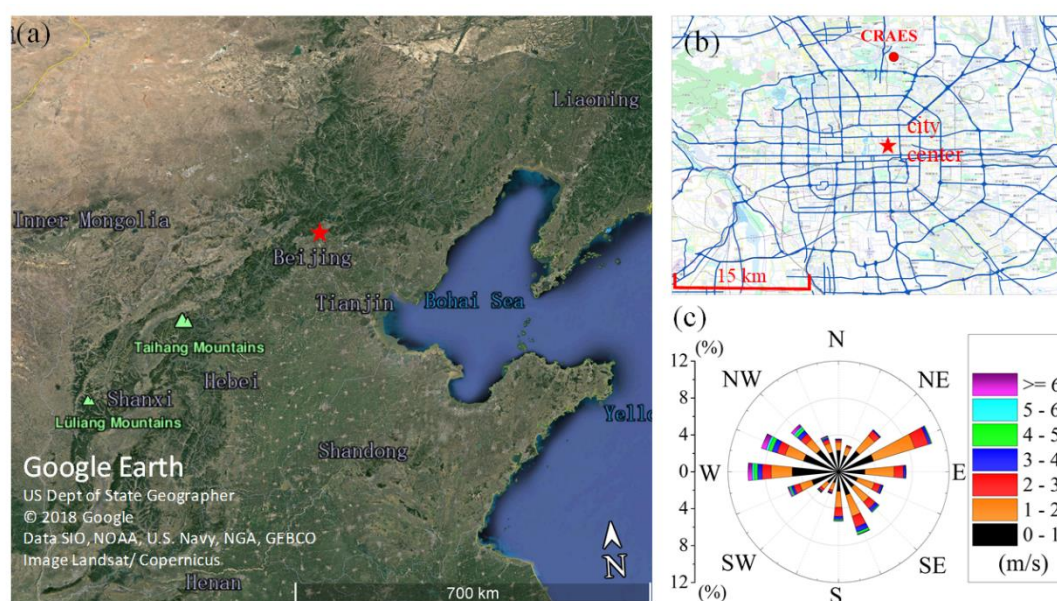
The present study examines the heterogeneous uptake of  $\text{N}_2\text{O}_5$  based on field measurements in urban Beijing during April and May 2017, when RH was low ( $27 \pm 18\%$ , average  $\pm$  standard deviation) and dust storms took place. We first introduce the meteorological conditions, chemical characteristics, and diurnal patterns of  $\text{N}_2\text{O}_5$  and related chemical species at the sampling site. The loss rate coefficients of  $\text{N}_2\text{O}_5$  are calculated to reveal the dominant removal pathways of  $\text{N}_2\text{O}_5$ .  $\gamma(\text{N}_2\text{O}_5)$  is then estimated

from the field measurements and compared to parameterized values. Meteorological and chemical factors that influence  $\gamma(\text{N}_2\text{O}_5)$  are examined. A modified parameterization is proposed for relatively dry conditions.

## 2. Methods

### 2.1. Measurement Site and Period

Field measurements were conducted in spring 2017 (April 24th to May 31st) at the Chinese Research Academy of Environmental Science (CRAES) ( $40.04^\circ \text{ N}$ ,  $116.42^\circ \text{ E}$ ), which is situated in the northern part of the Beijing urban area (Figure 1). The surrounding areas are mainly residential, with some commercial buildings. For more information on the measurement site, the reader is referred to [34,35]. The Gobi Desert and Inner Mongolia lie to the northwest of Beijing, and sand dust from these regions can impact Beijing during the spring (e.g., [36]).



**Figure 1.** (a) A regional view of the position of Beijing on the North China Plain. (b) Location of the sampling site, CRAES, in Beijing, and major roads (blue line). The red star denotes the center of Beijing. (c) Wind rose plot during the observation period. (The map is from Google Earth).

### 2.2. Instruments

#### 2.2.1. Chemical Ionization Mass Spectrometry (CIMS) Setup

$\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  were simultaneously measured using a quadrupole CIMS. The same instrument was used in several previous field studies [32,37–39]. The reader is referred to the earlier publications for detailed information on the principles, configuration, and calibration methods. Briefly,  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  molecules are combined with the reagent  $\text{I}^-(\text{H}_2\text{O})$  to generate  $\text{I}(\text{ClNO}_2)^-$  and  $\text{I}(\text{N}_2\text{O}_5)^-$  in CIMS, which are detected at  $m/z$  208 and  $m/z$  235, respectively. In the present study, the detection limits were 3 pptv and 4 pptv ( $3\sigma$ , 1 min average) for  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ , respectively. The sensitivities of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  were determined to be  $0.78 \pm 0.05 \text{ Hz/pptv}$  and  $0.58 \pm 0.04 \text{ Hz/pptv}$ , respectively, based on daily calibrations. The dependency of  $\text{N}_2\text{O}_5$  sensitivity on RH was measured on-site and used to correct ambient  $\text{N}_2\text{O}_5$  data (Figure S2). The indoor temperature was kept constant at  $\sim 296 \text{ K}$  by air conditioners.

The sampling inlet of the CIMS system was installed  $\sim 1.5 \text{ m}$  above the roof of a four-story building ( $\sim 15 \text{ m a.s.l.}$ ). The sampling line was 3.5 m PFA tubing (1/4-inch O.D.), which was replaced daily with

a new one that was washed to reduce the loss of  $N_2O_5$  in the sample line. The total flow through the sample line was ~10 liters per minute (LPM), with 1.5 LPM being distributed to CIMS and 4.0 LPM to other instruments, while the remaining flow was discarded by a bypass pump. The loss of  $N_2O_5$  in the sampling line was checked every two days, which was <10% after one day of use. Overall uncertainty was 25% for  $N_2O_5$  and  $ClNO_2$  [38]. The measurements were conducted at a time resolution of ~10 s, and the data were later averaged to 1 min for further analysis.

### 2.2.2. Other Measurements

Trace gases, aerosol, and VOC composition related to  $N_2O_5$  and  $ClNO_2$  were concurrently measured.  $NO$  and  $NO_2$  were measured using a chemiluminescence analyzer equipped with a blue-light converter (model 42i-TL, Thermo Scientific Company, Waltham, MA, USA).  $NO_y$  was measured using a total reactive nitrogen oxides analyzer with a  $MoO$  converter heated to 350 °C (model EC9843, Ecotech Company, Melbourne, Australia).  $O_3$  and  $SO_2$  were detected using UV photometry (model 49i, Thermo Scientific Company, Waltham, MA, USA) and pulsed-UV fluorescence (model 43C, Thermo Scientific Company, Waltham, MA, USA), respectively. All of the instruments were calibrated every two weeks.  $PM_{2.5}$  mass concentration was measured using a beta attenuation monitor (model BAM 1020, Met One Instrument Inc., Grants Pass, WA, USA). Ionic compositions of  $PM_{2.5}$  ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) were measured on an hourly basis utilizing the Monitor for Aerosols and Gases in ambient air (MARGA, Metrohm Company, Herisau, Switzerland) [40,41]. An internal standard, bromide lithium, was used for regular calibration. VOCs were measured by an online gas chromatograph equipped with a flame ionization detector (GC-FID) (Chromatotec Group, Bordeaux, France) [42]. A list of measured species and reaction rate constants with  $NO_3$  radical at 298K are shown in Table S1 [5]. Organic carbon (OC) and elemental carbon (EC) were measured by an OC-EC field analyzer (model-4, Sunset Laboratory Inc., Tigard, OR, USA).

The dry-state particle size distribution was measured by a wide-range particle spectrometer (WPS Model 1000XP, MSP Corporation, Shoreview, MN, USA) covering the 10 nm~10  $\mu m$  size ranges [43]. Aerosol surface area density ( $S_a$ ) was estimated by assuming that particles were spherical. Hygroscopic growth of aerosols was estimated following the method in [44], and a growth factor for the diameter of particles,  $GF = 0.582 \left( 8.46 + \frac{1}{1-RH} \right)^{1/3}$  was adopted for all the size ranges [45,46]. The growth factor for  $S_a$  is the square of GF. Particles larger than 10  $\mu m$  were significant in the heavy sand storm event, but they cannot be captured by the WPS instrument. Thus, the  $S_a$  in such cases was estimated based on its relationship to  $PM_{2.5}$  during the observation period (Figure S6). For the same reason, the calculation of  $V_a/S_a$  is not applicable during heavy storm events. In other cases, it is assumed that particles larger than 10  $\mu m$  contribute little to the total aerosol surface area.

### 2.3. Estimation of $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$

A modified steady state method was applied to estimate  $\gamma(N_2O_5)$  and  $\varphi(ClNO_2)$  [3,39,42,47]. Due to rapid equilibrium between  $NO_3$  and  $N_2O_5$ , these two species are regarded as a pair. The changing rate of the  $NO_3$  and  $N_2O_5$  pair equals the production rate of  $NO_3$  radical minus the total loss rate of  $NO_3$  and  $N_2O_5$  (Equation (2)), assuming that transportation effect can be ignored.

$$\begin{aligned} d([N_2O_5] + [NO_3])/dt &= d[NO_3]/dt + d[N_2O_5]/dt \\ &= k_1[NO_2][O_3] - k(NO_3)[NO_3] - k(N_2O_5)[N_2O_5] \end{aligned} \quad (2)$$

where  $k_1$  is the rate constant of (R1).  $k(NO_3)$ , known as  $NO_3$  reactivity, is expressed as follows:

$$k(NO_3) = k_{NO+NO_3}[NO] + \sum k_i[VOC_i] \quad (3)$$



where  $k_1$  is the rate constant of  $\text{NO}_3 + \text{VOC}$  reactions. The  $\text{NO}_3$  radical concentration is estimated from the  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  equilibrium:

$$[\text{NO}_3] = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2]K_{\text{eq}}} \quad (4)$$

where  $K_{\text{eq}}$  is the temperature-dependent equilibrium coefficient of the  $\text{NO}_3$ – $\text{N}_2\text{O}_5$  pair. Substitution of (Equation (3)) and (Equation (4)) into (Equation (2)) and rearrangement yields (Equation (5)) as follows, where  $k(\text{N}_2\text{O}_5)$  is extracted.

$$k(\text{N}_2\text{O}_5) = (k_1[\text{NO}_2][\text{O}_3] - k(\text{NO}_3)[\text{N}_2\text{O}_5]/([\text{NO}_2]K_{\text{eq}}) - d[\text{N}_2\text{O}_5]/dt - d[\text{NO}_3]/dt)/[\text{N}_2\text{O}_5]. \quad (5)$$

$d[\text{N}_2\text{O}_5]/dt$  and  $d[\text{NO}_3]/dt$  are approximated as the rate of increase of  $[\text{N}_2\text{O}_5]$  and  $[\text{NO}_3]$  over 5 min, and thus can be replaced by  $\delta[\text{N}_2\text{O}_5]/\delta t$  and  $\delta[\text{NO}_3]/\delta t$  with  $\delta t = 5$  min. Then, the time series of  $k(\text{N}_2\text{O}_5)$  can be derived. The heterogeneous loss rate coefficient of  $\text{N}_2\text{O}_5$  ( $k(\text{N}_2\text{O}_5)_{\text{het}}$ ) is obtained when the homogeneous loss rate coefficient of  $\text{N}_2\text{O}_5$  is subtracted [6,48].

$$k(\text{N}_2\text{O}_5)_{\text{het}} = k(\text{N}_2\text{O}_5) - k(\text{N}_2\text{O}_5)_{\text{homo}} \quad (6)$$

$$k(\text{N}_2\text{O}_5)_{\text{homo}} = k_a \times [\text{H}_2\text{O}] + k_b \times [\text{H}_2\text{O}]^2. \quad (7)$$

When the surface area density ( $S_a$ ) of aerosols and velocity of  $\text{N}_2\text{O}_5$  molecules ( $c(\text{N}_2\text{O}_5)$ ) are available,  $\gamma(\text{N}_2\text{O}_5)$  can be obtained following (Equation (1)). Then  $\varphi(\text{ClNO}_2)$  can be calculated using the below formula by integrating over the whole period of the selected case.

$$\varphi(\text{ClNO}_2) = \frac{\Delta[\text{ClNO}_2]}{\int k(\text{N}_2\text{O}_5)_{\text{het}} [\text{N}_2\text{O}_5] dt} \quad (8)$$

#### 2.4. Parameterizations of $\gamma(\text{N}_2\text{O}_5)$ and $\varphi(\text{ClNO}_2)$

We evaluated three parameterizations of  $\gamma(\text{N}_2\text{O}_5)$ . The first relates  $\gamma(\text{N}_2\text{O}_5)$  to RH and temperature (T) (denoted  $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}}$ ) [25] in which the dependences of  $\gamma(\text{N}_2\text{O}_5)$  on RH and T were separately derived on ammonium sulfate aerosol [12,13].

$$\gamma(\text{N}_2\text{O}_5)_{\text{EJ}} = (2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times \text{RH} - 3.43 \times 10^{-6} \times \text{RH}^2 + 7.52 \times 10^{-8} \times \text{RH}^3) \times 10^{(0.04 \times (T - 294))} \quad (9)$$

The second parameterization of  $\gamma(\text{N}_2\text{O}_5)$  (denoted  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$ ) considers the bulk concentration of chloride  $[\text{Cl}^-]$ , nitrate  $[\text{NO}_3^-]$ , and aerosol water content ( $[\text{H}_2\text{O}]$ ) [14]. Three important assumptions are adopted to establish this parameterization: (1) the whole particle is in an aqueous phase; (2) aerosols can be supersaturated; and (3) the accommodated  $\text{N}_2\text{O}_5$  can react within the whole particle volume. Then  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$  is expressed as (Equation (10)).

$$\gamma(\text{N}_2\text{O}_5)_{\text{BT}} = Ak \left( 1 - \frac{1}{1 + \frac{k_{\text{R3}}[\text{H}_2\text{O}]}{k_{\text{R2b}}[\text{NO}_3^-]} + \frac{k_{\text{R4}}[\text{Cl}^-]}{k_{\text{R2b}}[\text{NO}_3^-]}} \right) \quad (10)$$

where  $[\text{H}_2\text{O}]$ ,  $[\text{Cl}^-]$ , and  $[\text{NO}_3^-]$  are derived from the extended aerosol inorganics model (E-AIM) (Text S1) [49]. Organic aerosols were not considered in the E-AIM model.  $k_{\text{R2b}}$ ,  $k_{\text{R3}}$ , and  $k_{\text{R4}}$  are reaction rate constants:  $k_{\text{R4}}/k_{\text{R2b}} = 29 \pm 6$ ;  $k_{\text{R3}}/k_{\text{R2b}} = 0.06 \pm 0.01$  [14].  $A$  is proportional to  $V_a/S_a$ .  $k$  is an empirical pre-factor in which  $k = \beta(1 - \exp(-\delta[\text{H}_2\text{O}]))$  with  $\beta = (11.5 \pm 3) \times 10^5$  and  $\delta = 0.13 \pm 0.05$ .

The third parameterization (denoted  $\gamma(\text{N}_2\text{O}_5)_A$ ) adds the inhibition effect of the organic coating on  $\gamma(\text{N}_2\text{O}_5)$  [16].

$$\frac{1}{\gamma(\text{N}_2\text{O}_5)_A} = \frac{1}{\gamma_{\text{core}}} + \frac{1}{\gamma_{\text{Org}}} \quad (11)$$

$$\gamma_{\text{Org}} = \frac{4RT H_{\text{org}} D_{\text{org}} R_c}{c(\text{N}_2\text{O}_5) L R_p} \quad (12)$$

(Equation (11)) treats the  $\text{N}_2\text{O}_5$  uptake process as a net effect through the aqueous core ( $\gamma_{\text{core}}$ ) and the organic coating ( $\gamma_{\text{Org}}$ ). In this study,  $\gamma_{\text{core}}$  adopts Bertram and Thornton's parameterization for easy comparison with previous studies [29,31].  $\gamma_{\text{Org}}$  is calculated using (Equation (12)), in which  $R_c$  is the radius of the aqueous core,  $R_p$  denotes the radius of the particle, and  $L$  means the depth of the organic coating. And  $R_c$ ,  $R_p$ , and  $L$  are calculated following a previous study [50].  $H_{\text{org}}$  and  $D_{\text{org}}$  are the Henry's law constant and the diffusion coefficient of  $\text{N}_2\text{O}_5$  in organic coating, which are calculated by assuming  $H_{\text{org}} D_{\text{org}} = 0.03 H_{\text{aq}} D_{\text{aq}}$  [2,11].  $H_{\text{aq}}$  (5000 M/atm) and  $D_{\text{aq}}$  ( $10^{-9} \text{ m}^2/\text{s}$ ) are the corresponding parameters of  $\text{N}_2\text{O}_5$  in the aqueous core [2].

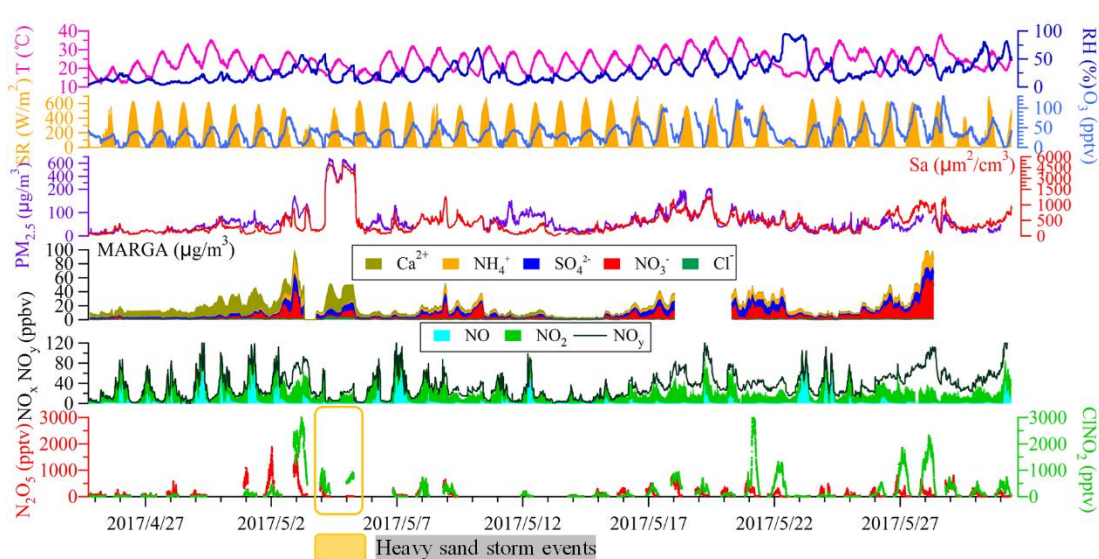
The parameterized  $\text{ClNO}_2$  yield is also calculated using the following equation [14].

$$\varphi(\text{ClNO}_2)_{\text{BT}} = \left(1 + \frac{[\text{H}_2\text{O}]}{483[\text{Cl}^-]}\right)^{-1} \quad (13)$$

### 3. Results and Discussion

#### 3.1. Overall Observations

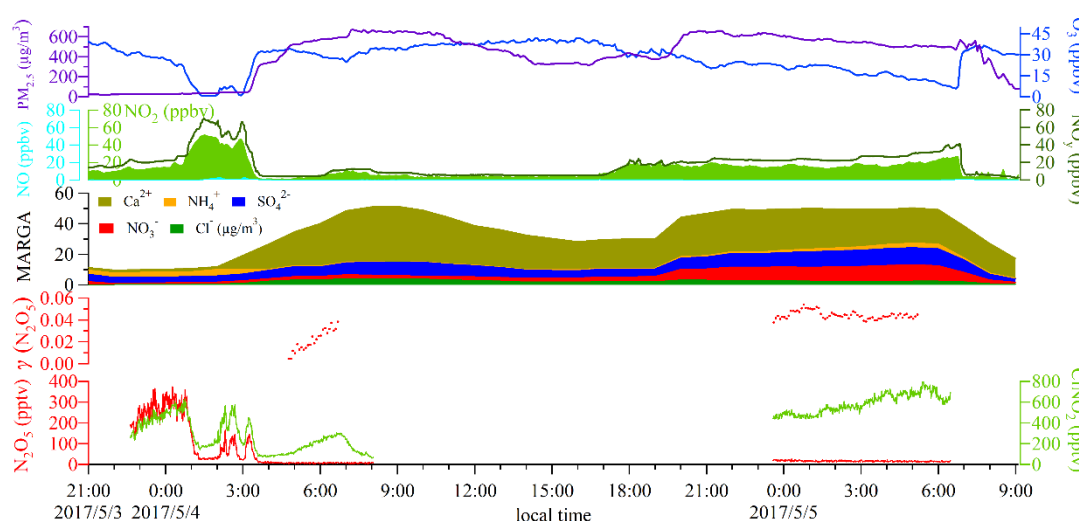
Measurement results for  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , and related chemical and meteorological parameters are shown in Figure 2 for the period from 24th April to 31st May. The weather conditions were mainly sunny, except for a little rain on 23rd May. Wind speeds were mostly below 3 m/s (Figure 1c). A prominent feature of the field study was dry weather, with an average relative humidity (RH) of  $27 \pm 18\%$  during the whole campaign. Both  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  exhibited typical diurnal variations, increasing during the night and decreasing during the day (Figure S3).



**Figure 2.** Time series of  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , related species, and meteorological parameters from 24th April to 31st May 2017. The sampling period in orange denotes a heavy sand storm event. Data gaps are caused by technical issues with the instruments or calibration.

The early part of the study (24th April to 2nd May) was influenced by dry air masses mainly from the northwest, as indicated by the backward trajectories (Figure S1) calculated using the online hybrid single-particle lagrangian integrated trajectory (HYSPLIT) model [51].  $\text{N}_2\text{O}_5$  levels were higher than those of  $\text{ClNO}_2$  from 24th April to 1st May with low aerosol loadings, suggesting low  $\text{N}_2\text{O}_5$  uptake or  $\text{ClNO}_2$  yield. This period was influenced by light dust, as indicated by abundant  $\text{Ca}^{2+}$  ( $10\text{--}40\text{ }\mu\text{g}/\text{m}^3$ ) and moderate  $\text{PM}_{2.5}$  ( $20\text{--}100\text{ }\mu\text{g}/\text{m}^3$ ) mixed with fresh urban emissions. The night of May 2nd was an exception as the air mass originated from the southeast, bringing humid air and higher  $\text{ClNO}_2$  to  $\text{N}_2\text{O}_5$  ratios. Overall, this period is referred to as “light dust” in the subsequent discussion.

A heavy sand storm impacted Beijing on the night of 3rd and 4th May, with  $\text{PM}_{2.5}$  reaching  $\sim 700\text{ }\mu\text{g}/\text{m}^3$  (Figure 2). The sand storm event is displayed separately for clarity (Figure 3).  $\text{ClNO}_2$  mixing ratios of up to  $0.82\text{ ppbv}$  and much lower  $\text{N}_2\text{O}_5$  levels ( $10\text{--}20\text{ pptv}$ ) were observed, indicating rapid  $\text{N}_2\text{O}_5$  loss on sand dust. To our knowledge, this is the first observation of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  during a heavy dust event. This period is denoted as a “sand storm.”



**Figure 3.** Time series of  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , and related species in a heavy sand storm event on the night of 3rd and 4th May. Also shown is the 5-min average  $\gamma(\text{N}_2\text{O}_5)$  (see Section 3.3).

In the later period of observation (14th May to 31st May, Figure S3), air masses arrived from the south or east (Figure S1), with a mean RH in the range  $20\text{--}60\%$ . Daytime ozone levels were  $80\text{--}120\text{ ppbv}$ , indicating moderately high photochemical pollution. This period is named “urban air.” During this period,  $\text{ClNO}_2$  levels were generally higher than those of  $\text{N}_2\text{O}_5$ . The levels of  $\text{N}_2\text{O}_5$  (up to  $0.7\text{ ppbv}$ ) and  $\text{ClNO}_2$  (up to  $3.0\text{ ppbv}$ ) were slightly higher than or comparable to values previously reported in polluted North China and urban/industrial regions of the US and EU [32,38,52–58], but lower than our previous observations in southern China [37,39].

### 3.2. $\text{N}_2\text{O}_5$ Reactivity and Loss Pathways

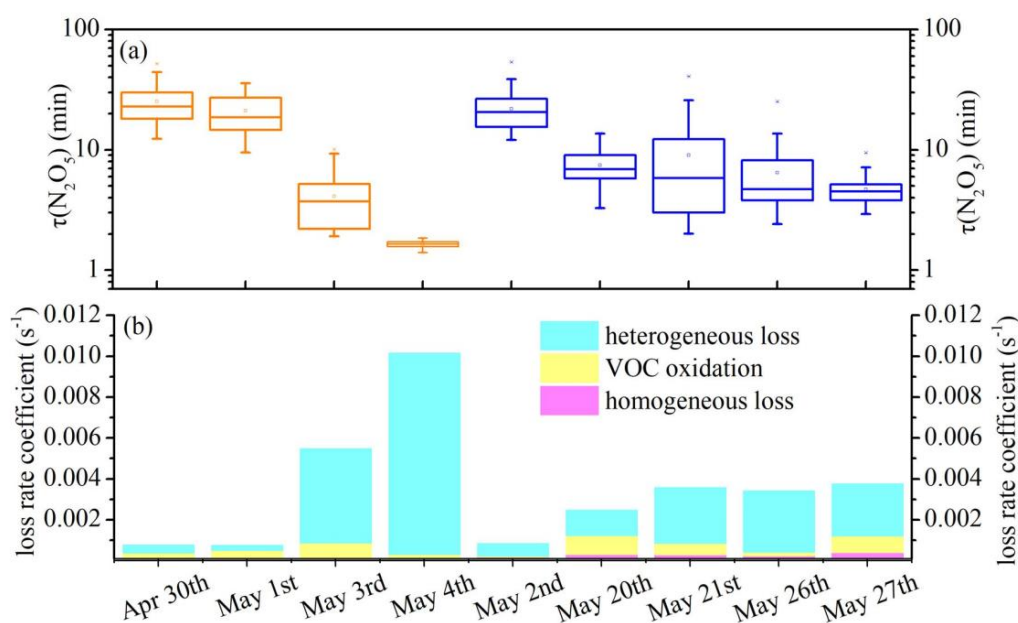
This section examines the relative importance of the three  $\text{N}_2\text{O}_5$  loss reactions, i.e., VOC oxidation, homogeneous loss, and heterogeneous loss. The lifetime of  $\text{N}_2\text{O}_5$  ( $\tau(\text{N}_2\text{O}_5)$ ) is a measure of its total reactivity and was estimated using (Equation (14)).  $P(\text{NO}_3)$  is the production rate of  $\text{NO}_3$  radical from the  $\text{NO}_2$  and  $\text{O}_3$  reaction. We selected nighttime periods with abundant  $\text{N}_2\text{O}_5$  or  $\text{ClNO}_2$  and low  $\text{NO}$  levels ( $\text{NO} < 0.1\text{ ppbv}$ ). A total of nine cases were selected (see Figure 4), including two “light dust” (30th April and 1st May), two “sand storm” (3rd May and 4th May), and five “urban air.” Results show that the  $\tau(\text{N}_2\text{O}_5)$  ranged from 1 min to 45 min (Figure 4a). The shortest  $\tau(\text{N}_2\text{O}_5)$  was found in the sand

storm on May 4th night, which is attributable to the rapid heterogeneous loss rate coefficient of  $\text{N}_2\text{O}_5$  (up to  $0.01 \text{ s}^{-1}$ , Figure 4b).

$$\tau(\text{N}_2\text{O}_5) = \frac{\text{N}_2\text{O}_5 \text{ concentration}}{\text{N}_2\text{O}_5 \text{ loss rate}} = \frac{[\text{N}_2\text{O}_5]}{\text{P}(\text{NO}_3) - \delta[\text{N}_2\text{O}_5]/\delta t - \delta[\text{NO}_3]/\delta t} \quad (14)$$

The loss rate coefficients of  $\text{N}_2\text{O}_5$  uptake were calculated and compared with other loss pathways (Figure 4b). The indirect loss through gas-phase reactions of  $\text{NO}_3$  radical with VOCs contributed 1.9%–30.2% of total  $\text{N}_2\text{O}_5$  loss. Biogenic VOCs dominated the nocturnal  $\text{NO}_3 + \text{VOCs}$  reaction (67.2% of  $\text{NO}_3$  loss), while aromatic hydrocarbons (20.1%) and alkenes (12.5%) also made significant contributions. The homogeneous loss of  $\text{N}_2\text{O}_5$  by  $\text{H}_2\text{O}(\text{g})$  contributed 1.2%–20.6% of  $\text{N}_2\text{O}_5$  loss. These values may be the upper limit if the rate constant of the homogeneous  $\text{N}_2\text{O}_5$  hydrolysis adopted from [6] is overestimated as suggested by [10,59]. The most important removal pathway of  $\text{N}_2\text{O}_5$  was heterogeneous uptake on aerosols, contributing 58.1%–96.9% of total  $\text{N}_2\text{O}_5$  loss. The heterogeneous loss rate coefficient of  $\text{N}_2\text{O}_5$  ( $k(\text{N}_2\text{O}_5)_{\text{het}}$ ) was most prominent in the sand storm on the nights of 3rd May and 4th May.

It is worth noting that other potential  $\text{NO}_3$  loss pathways which were not considered in our analysis may give rise to uncertainties in our result. For example,  $\text{NO}_3 + \text{VOCs}$  reactions can produce  $\text{HO}_x$  and  $\text{RO}_x$  radicals, which consume  $\text{NO}_3$  radical [60]. In addition,  $\text{NO}_3$  is subject to heterogeneous loss [61]. Due to a lack of measurements of  $\text{RO}_x$ , and  $\text{HO}_x$ , and limited knowledge on the  $\text{NO}_3$  uptake coefficient, these  $\text{NO}_3$  loss pathways are not included here.



**Figure 4.** (a)  $\text{N}_2\text{O}_5$  lifetime and (b)  $\text{N}_2\text{O}_5$  loss rate coefficients in selected  $\text{N}_2\text{O}_5$ -rich or  $\text{ClNO}_2$ -rich air masses. The upper and bottom whiskers show the 10% and 90% percentiles. The upper, middle, and bottom lines in the boxes denote the 75%, median, and 25% percentiles, respectively. The squares show the average values. Orange denotes light dust cases and heavy sand storm events, while blue represents urban air masses. The selected time periods were 20:00–04:00 local time (LT) for each night. For example, 30th Apr denoted 30th Apr 20:00 LT–1st May 04:00 LT. Exceptions were the night of 3rd May where 04:30–06:30 LT on 4th May was selected, and 4th May where 01:00–05:30 LT on 5th May was selected.

### 3.3. Derivation of $\gamma(\text{N}_2\text{O}_5)$ and Evaluation of Parameterizations

To estimate  $\gamma(\text{N}_2\text{O}_5)$  from the measurement data, the following selection criteria were adopted; the procedures were similar to those used in previous studies with minor modifications [11,47].



1. The air mass should be stable without dramatic changes in temperature, RH, and wind direction. Wind speed should be less than 3 m/s to minimize the effect of air mass transport.
2. Ambient NO should be below 0.1 ppbv. Otherwise, little production of N<sub>2</sub>O<sub>5</sub> would occur.
3. ClNO<sub>2</sub> should exhibit an increasing trend, indicating considerable uptake of N<sub>2</sub>O<sub>5</sub>. In cases with decreasing or fluctuating ClNO<sub>2</sub>, physical processes or changes of air mass may invalidate the method for the estimation of  $\gamma(\text{N}_2\text{O}_5)$ .
4. S<sub>a</sub> should be above 200  $\mu\text{m}^2/\text{cm}^3$  to facilitate significant N<sub>2</sub>O<sub>5</sub> uptake. In cases with S<sub>a</sub> below 200  $\mu\text{m}^2/\text{cm}^3$ , we found that the derived  $\gamma(\text{N}_2\text{O}_5)$  was either abnormally high (for example, above 0.1), or even negative. This phenomenon indicates that the method we adopted may be invalid in low aerosol loadings.

Two examples that satisfy the criteria are shown in Figure S4. In total, nine cases were selected, with durations of 2 to 7 h, and  $\gamma(\text{N}_2\text{O}_5)$  and  $\phi(\text{ClNO}_2)$  were calculated following the method in Section 2.3, as summarized in Table 1.  $\gamma(\text{N}_2\text{O}_5)$  ranged from 0.013 to 0.042 in urban air masses. The  $\gamma(\text{N}_2\text{O}_5)$  range is comparable to the results of one previous study in urban Beijing (0.012–0.055) [57] and higher than those obtained in some places in the US and Europe [27,59], but lower than other results obtained over the North China Plain [32,44]. The field-derived  $\phi(\text{ClNO}_2)$  ( $0.218 \pm 0.247$ ) was much lower than parameterized values using (Equation (13)) ( $0.796 \pm 0.056$ ) in all cases, which is consistent with the findings in previous studies, suggesting an overestimation of ClNO<sub>2</sub> yield in the current parameterization or an unknown suppression effect on ClNO<sub>2</sub> yield [32,62].

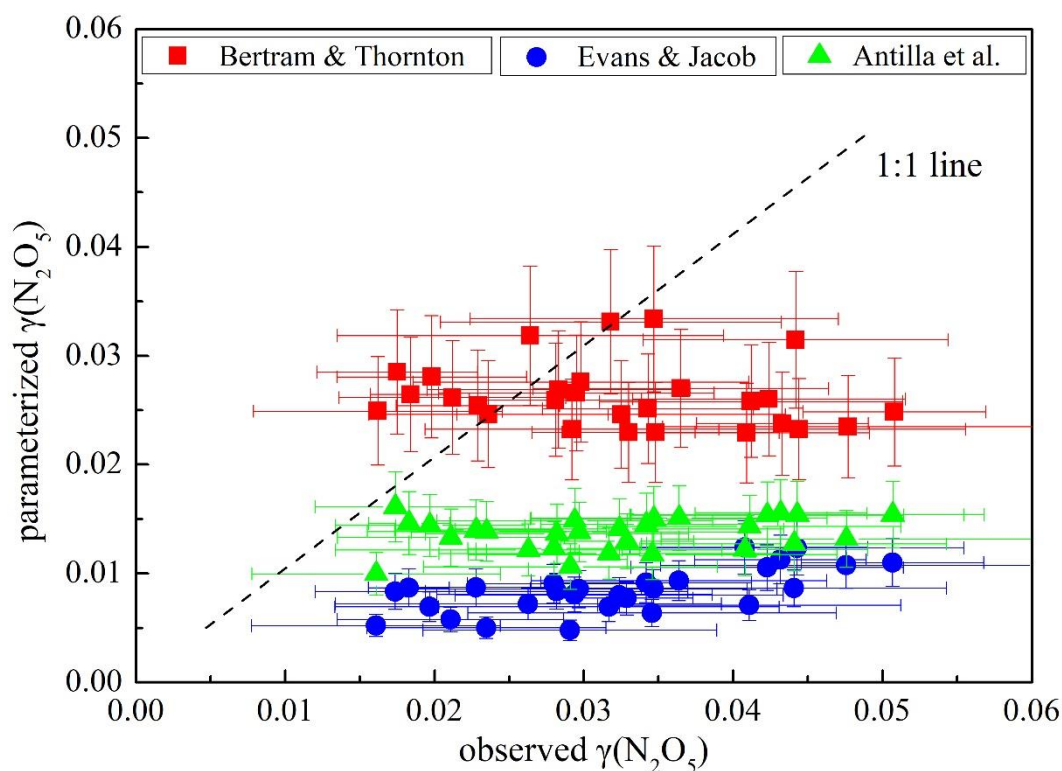
**Table 1.** Field-derived N<sub>2</sub>O<sub>5</sub> uptake coefficient (average  $\pm$  standard deviation) and ClNO<sub>2</sub> production yield estimated for the selected periods. The time periods are all local time (LT). Since only one  $\phi(\text{ClNO}_2)$  value was derived for each time period, no standard deviation was obtained for  $\phi(\text{ClNO}_2)$ .

Category	Periods		$\gamma(\text{N}_2\text{O}_5)$	$\phi(\text{ClNO}_2)$	Notes
	From	To			
Urban air masses	16th May 23:00	17th May 04:00	$0.022 \pm 0.005$	0.065	
	17th May 21:00	18th May 01:00	$0.013 \pm 0.006$	0.048	
	18th May 21:00	19th May 04:00	$0.030 \pm 0.009$	0.055 (21:26~22:41) 0.117 (01:06~03:31)	ClNO <sub>2</sub> yield changed
	20th May 21:00	21st May 04:00	$0.032 \pm 0.007$	0.082	
	22nd May 0:00	22nd May 04:00	$0.035 \pm 0.010$	0.312	
	27th May 20:00	28th May 04:00	$0.042 \pm 0.008$	0.084 (20:01~21:36) 0.319 (01:36~03:01)	ClNO <sub>2</sub> yield changed
	28th May 20:00	28th May 23:00	$0.023 \pm 0.007$	0.142	
Heavy sand storm events	4th May 04:00	4th May 06:00	$0.019 \pm 0.012$	0.677	Sand storm arrived
	4th May 23:00	5th May 05:00	$0.044 \pm 0.002$	0.129	Sand storm continued

The  $\gamma(\text{N}_2\text{O}_5)$  derived on the night of 3rd May (4th May 04:00~06:00) and 4th May (4th May 23:00 to 5th May 05:00) represents the N<sub>2</sub>O<sub>5</sub> uptake in the early and later stage of the sand storm event. Five-minute average  $\gamma(\text{N}_2\text{O}_5)$  was low (0.008) at the beginning of the dust storm at ~04:00 on 4th May (see Figure 3), but  $\gamma(\text{N}_2\text{O}_5)$  increased gradually to 0.039 at 06:00 when aerosols reached high levels. The  $\gamma(\text{N}_2\text{O}_5)$  continued to increase and remained at ~0.044 on the following night, with sustained high levels of aerosols. This stable value can be considered the  $\gamma(\text{N}_2\text{O}_5)$  on ambient dust particles in the region, and this field-derived value compares well with the laboratory-determined  $\gamma(\text{N}_2\text{O}_5)$  ( $(5 \pm 2) \times 10^{-2}$ ) on bulk CaCO<sub>3</sub> dust [21]. The  $\gamma(\text{N}_2\text{O}_5)$  on May 5th was higher than in urban air masses (see Table 1), although the aerosol water content ([H<sub>2</sub>O]) was relatively low (14–21 M) during the dust storm, according to E-AIM (Figure S5). Assuming a volume-limited mechanism, larger particle size

in the sand dust plumes might be responsible for the high  $\gamma(\text{N}_2\text{O}_5)$  on 5th May. Another possibility is that E-AIM (model III), which is used in the present work, underestimates the  $[\text{H}_2\text{O}]$  adsorbed by sand dust particles because it does not consider the significant enhancement of hygroscopicity in the conversion of  $\text{CaCO}_3$  to deliquescent  $\text{Ca}^{2+}$  [63].

To evaluate the applicability of the commonly used parameterizations, the field-determined 5-min average  $\gamma(\text{N}_2\text{O}_5)$  values were averaged to hourly values and compared with three parameterized  $\gamma(\text{N}_2\text{O}_5)$  values (Figure 5), calculated according to the approaches introduced in Section 2.4 and based on the hourly average of the input parameters. We also calculated and showed propagated errors of three parameterized  $\gamma(\text{N}_2\text{O}_5)$  by taking partial differentials of the variables in the parameterization formula and the measurement uncertainty for each variable. Because the measured  $V_a/S_a$  is invalid for the heavy sand storm event (method Section 2.2), parameterized  $\gamma(\text{N}_2\text{O}_5)$  was not calculated in that case. Overall, the parameterized  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$  ( $0.026 \pm 0.003$ ) was lower than the field-observed  $\gamma(\text{N}_2\text{O}_5)$  ( $0.032 \pm 0.010$ ) and had much less variability. This result contrasts with previous studies, which usually indicated higher parameterized  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$  [11,30,31,33]. The parameterization that considered only T and RH ( $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}}$ ) was systematically lower than the field-observed  $\gamma(\text{N}_2\text{O}_5)$ , which differs from the good fit of  $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}}$  at Wangdu in the humid summer period [11]. When the organic coating effect was considered and combined with  $\gamma(\text{N}_2\text{O}_5)_{\text{BT}}$ , the parameterized  $\gamma(\text{N}_2\text{O}_5)_A$  using (Equation (11)) was even lower. The significant underestimation of  $\gamma(\text{N}_2\text{O}_5)$  when organic coatings were considered is similar to the findings of previous studies (e.g., [11]).

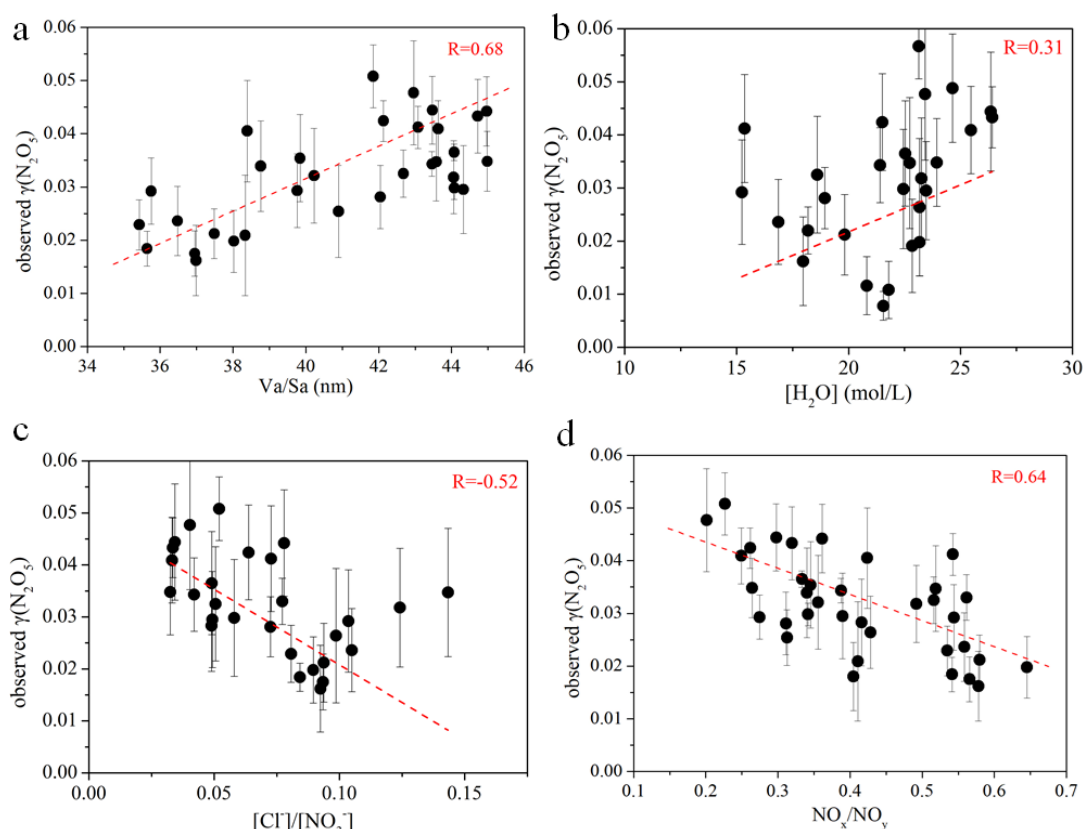


**Figure 5.** The relationship of parameterizations of  $\gamma(\text{N}_2\text{O}_5)$  to observed  $\gamma(\text{N}_2\text{O}_5)$  in urban air masses. Error bars of the observed  $\gamma(\text{N}_2\text{O}_5)$  represents the standard deviation of the 12  $\gamma(\text{N}_2\text{O}_5)$  values obtained within one hour. Error bars of the parameterized  $\gamma(\text{N}_2\text{O}_5)$  denote propagated uncertainty.

### 3.4. Influencing Factors of $\gamma(\text{N}_2\text{O}_5)$ and Implications

To further investigate the discrepancy between the observed  $\gamma(\text{N}_2\text{O}_5)$  and related parameterizations, various influencing factors of  $\gamma(\text{N}_2\text{O}_5)$  were examined, namely aerosol volume to surface ratio ( $V_a/S_a$ ), water content ( $[\text{H}_2\text{O}]$ ), and ratio of chloride to nitrate ( $[\text{Cl}^-]/[\text{NO}_3^-]$ ). The observed  $\gamma(\text{N}_2\text{O}_5)$  shows moderate correlation with  $V_a/S_a$  ( $R = 0.68$ , Figure 6a) but does not exhibit a clear

relationship with  $[\text{H}_2\text{O}]$  and  $[\text{Cl}^-]/[\text{NO}_3^-]$  (Figure 6b,c). It seems that the parameter  $V_a/S_a$  alone can explain the variation of  $\gamma(\text{N}_2\text{O}_5)$  in the present study. Including the chemical composition ( $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ , and  $\text{Cl}^-$ ) worsens the result of parameterizations. This result contrasts with those of previous studies, which were conducted in conditions with higher relative humidity. Positive correlations between  $\gamma(\text{N}_2\text{O}_5)$  and  $[\text{H}_2\text{O}]/[\text{NO}_3^-]$  were reported in Seattle, California, and over the eastern United States [10,28,33]. Our studies in China observed the enhancement effects of  $[\text{Cl}^-]$  and  $[\text{H}_2\text{O}]$  and the suppression effect of  $[\text{NO}_3^-]$  [11,32]. No correlation between  $\gamma(\text{N}_2\text{O}_5)$  and aerosol size ( $R^2 = 0.025$ ) was found in the northeastern US [10].

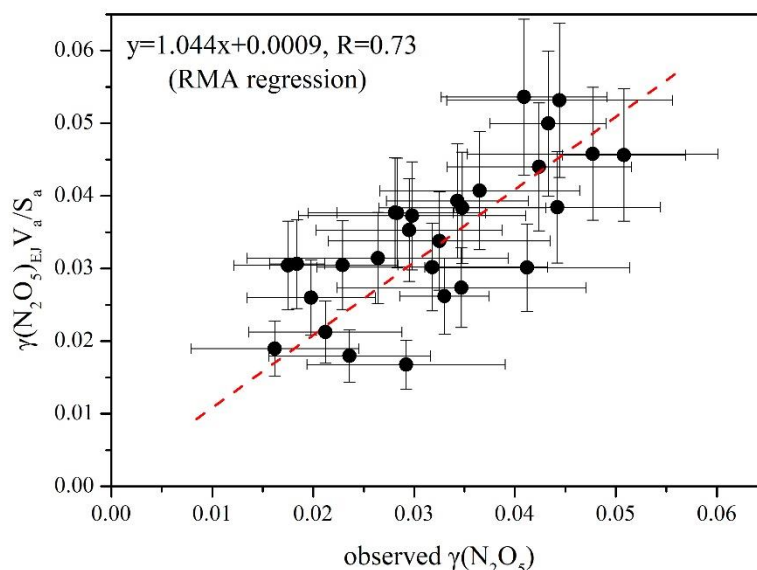


**Figure 6.** Dependence of  $\gamma(\text{N}_2\text{O}_5)$  on several parameters in urban air masses: (a)  $V_a/S_a$ ; (b) aerosol water content ( $[\text{H}_2\text{O}]$ ); (c) molar ratio of aerosol chloride to nitrate in the aqueous phase ( $[\text{Cl}^-]/[\text{NO}_3^-]$ ); (d) ratio of  $\text{NO}_x$  to  $\text{NO}_y$  ( $\text{NO}_x/\text{NO}_y$ ). The error bars of  $\gamma(\text{N}_2\text{O}_5)$  have the same meaning as in Figure 5.

The finding that  $\gamma(\text{N}_2\text{O}_5)$  is dependent on  $V_a/S_a$  but not chemical composition may be explained by the dry conditions encountered in this study. The deliquescence relative humidities (DRH) of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_4\text{NO}_3$  at 298 K are 79.9%, 80%, and 61.8% [64], respectively, which is much higher than the RH in this study. Thus, the inorganic components of aerosols ( $\text{Cl}^-$  and  $\text{NO}_3^-$ ) observed during our study may not be in the aqueous phase, making aqueous chemical reactions irrelevant to  $\text{N}_2\text{O}_5$  uptake. Another interesting observation is the negative correlation between  $\gamma(\text{N}_2\text{O}_5)$  and the  $\text{NO}_x/\text{NO}_y$  ratio ( $R = 0.64$ ) (Figure 6d). Because  $\text{NO}_x/\text{NO}_y$  is a measure of the chemical aging of air masses, the negative correlation between  $\gamma(\text{N}_2\text{O}_5)$  and  $\text{NO}_x/\text{NO}_y$  may imply a chemical enhancement effect of unknown secondary products on  $\text{N}_2\text{O}_5$  uptake or be explained by the larger particle size as the air masses age.

We then attempted to explore other forms of parameterizations that would better fit the observed  $\gamma(\text{N}_2\text{O}_5)$ . As the field-derived  $\gamma(\text{N}_2\text{O}_5)$  did not show dependence on chemical compositions (i.e.,  $\text{NO}_3^-$ ,  $\text{H}_2\text{O}$ , and  $\text{Cl}^-$ ) but exhibited positive correlation with  $V_a/S_a$ , it was desirable to have a parameterization without  $[\text{NO}_3^-]$ ,  $[\text{H}_2\text{O}]$ , or  $[\text{Cl}^-]$  but containing  $V_a/S_a$ . It turned out that multiplying  $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}}$  with

$V_a/S_a$  yielded a good representation of the observed  $\gamma(\text{N}_2\text{O}_5)$ , with a slope of 1.044, an intercept of 0.0009, and a correlation coefficient of 0.73 as shown in Figure 7 (RMA regression) [25].



**Figure 7.** Scatter plot of  $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}} V_a/S_a$  and the observed  $\gamma(\text{N}_2\text{O}_5)$ .

Therefore, we propose the following parameterization for dry conditions based on  $\gamma(\text{N}_2\text{O}_5)_{\text{EJ}}$ :

$$\begin{aligned} \gamma(\text{N}_2\text{O}_5)_{\text{dry}} &= 0.958 \times \frac{V_a}{S_a} \times \gamma(\text{N}_2\text{O}_5)_{\text{EJ}} \\ &= 0.958 \times \frac{V_a}{S_a} \times (2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times \text{RH} - 3.43 \times 10^{-6} \times \text{RH}^2 \\ &\quad + 7.52 \times 10^{-8} \times \text{RH}^3) \times 10^{(0.04 \times (T-294))} \end{aligned} \quad (15)$$

where the factor 0.958 is the inverse of the slope 1.044; the units of RH and T are the same as in (Equation (9)), and the unit of  $V_a/S_a$  is  $10^{-8}$  m. For example, the value 1.0 is used for  $V_a/S_a$  in (Equation (15)) when  $V_a/S_a = 10$  nm. This parameterization ( $\gamma(\text{N}_2\text{O}_5)_{\text{dry}}$ ) is valid for the observed RH range (20%–56%) and temperature above 282 K which are the conditions encountered in the present study. It is highly desirable to test its applicability in other regions/periods with low humidity.

#### 4. Concluding Remark

This work presents new observational insights into  $\text{N}_2\text{O}_5$  uptake on sand dust and urban aerosols under low-humidity conditions. The results reveal a dependence of  $\gamma(\text{N}_2\text{O}_5)$  on aerosol properties that differs from those obtained in previous investigations under humid conditions and suggest the important role of the aerosol volume to area ratio (i.e., aerosol diameter). The proposed new parameterization can be used in air quality models to improve simulations of the nighttime fate of  $\text{NO}_x$  and formation of nitrate aerosol in dry and dusty seasons. More investigation is needed to reappraise the controlling factors in  $\text{N}_2\text{O}_5$  uptake in dry environments.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4433/10/4/204/s1>.

**Author Contributions:** Conceptualization, T.W. and M.X.; formal analysis, M.X.; funding acquisition, T.W.; investigation, M.X., W.W., Z.W., Y.L., C.Y., Y.Z. (Yuechong Zhang), Y.Z. (Yujie Zhang), F.B., and X.C.; methodology, M.X., T.W., J.G., and Hong Li; project administration, J.G., H.L. and T.W.; resources, J.G., H.L., and T.W.; writing—original draft, M.X. and T.W.; writing—review and editing, M.X., W.W., Z.W., J.G., H.L., Y.L., C.Y., Y.Z. (Yuechong Zhang), P.W., Y.Z. (Yujie Zhang), F.B., X.C., and T.W.

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**Conflicts of Interest:** The authors declare that they have no conflict of interest.

**Data Availability:** To request the data described in this study, please contact the corresponding author (cetwang@polyu.edu.hk).

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