Direct measurement of N_2O_5 heterogeneous uptake coefficients on atmospheric aerosols in southwestern China and evaluation of current parameterizations

Jiayin Li [a⊥], Tianyu Zhai [a,b⊥], Xiaorui Chen [c*], Haichao Wang [c], Shuyang Xie [a], Shiyi Chen [a], Chunmeng Li [a,d], Huabin, Dong [a], Keding Lu [a*]

[a] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China

[b] Key Laboratory for Vehicle Emission Control and Simulation of Ministry of Ecology and Environment, Beijing, 100012, China

[c] School of Atmospheric Sciences, Sun Yat-sen University, and Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China

[d] The National Institute of Metrology, Center for Environmental Metrology, Beijing 100029, China

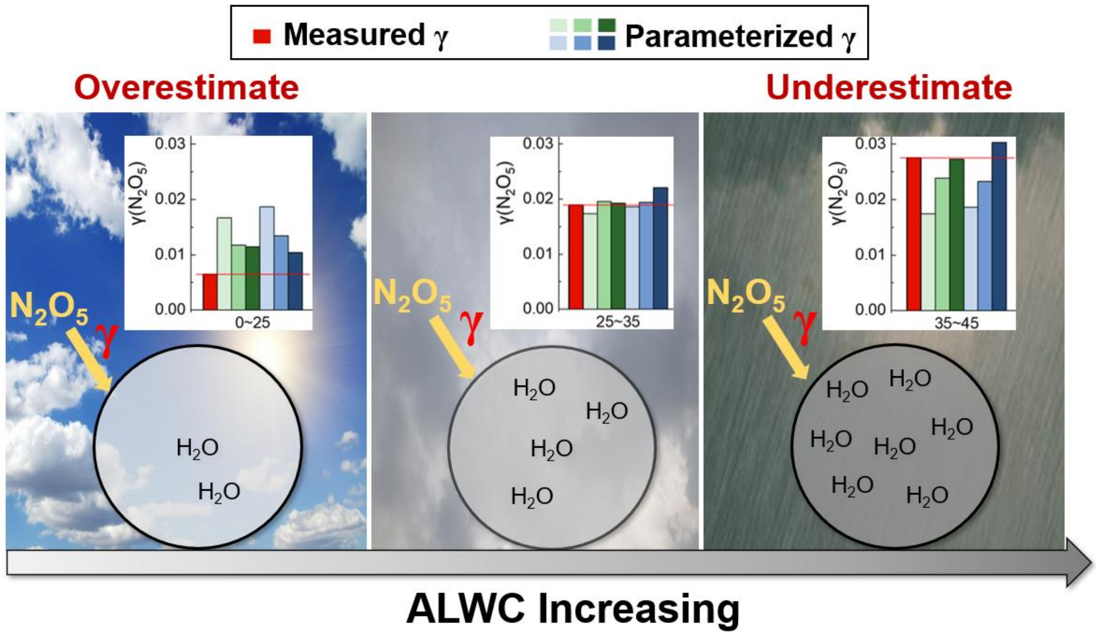
[⊥] Jiayin Li and Tianyu Zhai contributed equally to this work.

Corresponding author: Xiaorui Chen (chenxr95@mail.sysu.edu.cn) and Keding Lu (k.lu@pku.edu.cn)

Abstract: The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) is a critical process in assessing NO_x fate and secondary pollutants formation. However, accurate quantification of the N_2O_5 uptake coefficient ($\gamma(N_2O_5)$) in ambient conditions is a challenging problem that can cause unpredictable uncertainties in the predictions of the air quality models. Here, the $\gamma(N_2O_5)$ values were directly measured using an improved in situ aerosol flow tube system at a site located on a highland region in southwestern China to investigate its influencing factors and performances of current $\gamma(N_2O_5)$ parameterizations under this typical environmental condition. The nocturnal mean $\gamma(N_2O_5)$ value ranged from 0.0018 to 0.12 with an average of 0.023±0.021. The relationship between the measured $\gamma(N_2O_5)$ and impacting factors was consistent with previous laboratory results, except for aerosol chloride. The aerosol water significantly promoted N_2O_5 uptake, while particulate organic and nitrate showed suppression effects.

We found that several parameterizations can capture the median of measured values, whereas none of the ten parameterizations were able to reproduce the variabilities and showed poor correlations (R^2=0.00~0.09). Elevated biases of predictions specifically occurred at high aerosol liquid water content (ALWC) (>35M) and low ALWC (<25M) with an underestimation of -37%~-1% and an overestimation of 34~189%, respectively. Such differences between the measured and parameterized $\gamma(N_2O_5)$ would lead to biased estimation (-77%~74%) on particulate nitrate production potential. Our findings suggest the need for more direct field quantifications of $\gamma(N_2O_5)$ and the laboratory measurements under extreme ALWC conditions to re-evaluate the response coefficients between $\gamma(N_2O_5)$ and aerosol chemical compositions in parameterizations.

Keywords: N_2O_5 uptake coefficient, $\gamma(N_2O_5)$ parameterizations, particulate nitrate formation, nighttime chemistry



Graphic Abstract

1. Introduction

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) are dominant in nocturnal atmospheric chemistry as reactive nitrogen species that can strongly influence the concentration and distribution of ozone (O_3) and nitrogen oxides (NO_x=NO+NO_2), and the air quality (Brown et al., 2006;Wang et al., 2023;Decker et al., 2019;Dentener and Crutzen, 1993). NO_3 is produced by the reaction of NO_2 and O_3 (R1), and there is a thermodynamic equilibrium between NO_3 and N_2O_5 (R2), which is the source of N_2O_5 (Brown and Stutz, 2012). There are two main pathways for NO_3 removal: the direct one is reactions of NO_3 and VOCs (R3), especially alkenes, and the indirect way is the heterogeneous hydrolysis of N_2O_5 (Asaf et al., 2009;Ng et al., 2017). N_2O_5 can react with H_2O and chloride (Cl^-) in the particle phase and form soluble nitrate and nitryl chloride ($ClNO_2$) (R4) (Osthoff et al., 2008;Chang et al., 2011). The uptake of N_2O_5 is the main pathway for the formation of particulate nitrate at night, which contributes to $PM_{2.5}$ (<2.5 μm in diameter) pollution. Meanwhile, chlorine radical is produced by $ClNO_2$ photodecomposition in the daytime and further regulates the O_3 pollution production by promoting the oxidation of VOCs (Finlaysonpitts et al., 1989;Riedel et al., 2014). Thus, it is important to quantify the rate of the N_2O_5 heterogeneous hydrolysis reaction in ambient conditions.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad \text{(R2)}$$

$$NO_3 + VOCs \rightarrow \text{Products} \quad \text{(R3)}$$

$$N_2O_5 + H_2O/Cl^-(p) \rightarrow NO_3^-(p) + ClNO_2 \quad \text{(R4)}$$

$\gamma(N_2O_5)$ is defined as the net probability of N_2O_5 irreversibly taken up onto an aerosol surface upon collision (McDuffie et al., 2018). According to the previous study, the process of N_2O_5 heterogeneous hydrolysis reaction on aerosols was treated as a resistor model including three steps: gas diffusion (R5), surface accommodation, and aqueous reaction (R6~R8) (Abbatt et al., 2012;Fang et al., 2024). This process can be influenced by aerosol chemical compositions (e.g. aerosol liquid water content (ALWC), nitrate (NO_3^-) concentration, Cl^- concentration, and organics), morphology and ambient meteorological factors (Bertram and Thornton, 2009;Mozurkewich and Calvert, 1988;Roberts et al., 2009;Thornton et al., 2003). High concentrations of aerosol water and Cl^- can promote the uptake reaction (R6~R8), and NO_3^- suppress the reaction (R6). Organics also can suppress the reaction by forming a coating on the surface of the particles and regulating the ALWC and the passage rate of N_2O_5 molecules (Folkers et al., 2003;Gaston et al., 2014;Anttila et al., 2006). However, the above results are mainly based on laboratory studies. In ambient conditions, the correlations between $\gamma(N_2O_5)$ and aerosol chemical compositions were generally weak mainly due to the coupling effects of particle morphology, size, mixing state, and meteorological parameters (e.g. temperature and relative humidity) (Phillips et al., 2016;Wang et al., 2020b;Riedel et al., 2012).

$$N_2O_5\,(g) \leftrightarrow N_2O_5\,(aq) \tag{R5}$$

$$N_2O_5(aq) + H_2O(l) \leftrightarrow H_2ONO_2^+(aq) + NO_3^-\,(aq) \tag{R6}$$

$$H_2ONO_2^+\,(aq) + H_2O(l) \rightarrow HNO_3(aq) + H_3O^+\,(aq) \tag{R7}$$

$$H_2ONO_2^+\,(aq) + HX(aq) \rightarrow XNO_2(aq) + H_3O^+\,(aq) \tag{R8}$$

In order to accurately quantify the contribution of N_2O_5 heterogeneous hydrolysis to nitrate formation and NO_x regulation, a variety of parameterizations of $\gamma(N_2O_5)$ have been established based on laboratory and field studies (Evans and Jacob, 2005;Davis et al., 2008;Yu et al., 2020;Bertram and Thornton, 2009). The parameters in parameterizations mainly include the meteorological parameters, concentrations of aerosol chemical compositions, and particle physicochemical parameters. However, these parameterizations usually exhibit low correlations with observed $\gamma(N_2O_5)$ in varying environments (Brown et al., 2009; Ryder et al., 2014; McDuffie et al., 2018). Moreover, the overestimation or underestimation of the parameterized $\gamma(N_2O_5)$ can lead to unpredictable biases in the simulations of the chemical transport models (Murray et al., 2021;Chen et al., 2018;Ryder et al., 2014).

Until now, only a few studies have quantified $\gamma(N_2O_5)$ values in ambient conditions ($<10^{-4}$ to 0.1) mostly by indirect quantification methods (Brown et al., 2016;Wang et al., 2018;Chen et al., 2020b;Morgan et al., 2015;Tham et al., 2018) while some by direct measurements (Yu et al., 2020;Riedel et al., 2012;Bertram et al., 2009a). The N_2O_5 heterogeneous uptake process has been reported to be active in China. The $\gamma(N_2O_5)$ values in North China Plain, Yangtze River Delta and Pearl River Delta in China (10^{-2}~10^{-1}) were generally about 1 to 2 orders of magnitude larger than that in Europe and North America (10^{-3}~10^{-2}) (Yan et al., 2023;Wang et al., 2017b;Wang et al., 2017d;Wang et al., 2017c;Niu et al., 2022). To further investigate the N_2O_5 heterogeneous chemistry in China, the $\gamma(N_2O_5)$ values were directly measured in a typical highland city, Kunming, in China using an improved in situ aerosol flow tube system from 15 April to 20 May 2021. The relationship between the $\gamma(N_2O_5)$ values and impacting factors was determined. We then examine the performance of current $\gamma(N_2O_5)$ parameterizations by comparing them to the observed values and analyze the causes of discrepancies in extreme ALWC conditions. We further observe significant biases when estimating particulate nitrate formation potential based on current $\gamma(N_2O_5)$ parameterization.

2. Methods

2.1. Site description

The field campaign was conducted in Kunming, China from 15 April to 20 May 2021. The main sampling site was on the roof of the Yihe Building, Yijingyuan Hotel (24°59′05″ N, 102°39′40″ E), about 20 m above the ground. As shown in Figure 1, the measurement site was located approximately 1890 m above sea level, 8 km away from the city center, and 1 km from Dianchi Lake to the west. The site receives traffic emissions from two roads within a radius of 500 m. The site was mainly surrounded by residential areas and there was no major industrial source around. Besides, the particle composition was measured at Guandu Forest Park (25°00′43″ N, 102°45′55″ E), which was about 9 km away from Yijingyuan Hotel, 5.2 km from the city center and was also mainly surrounded by residential living area. Sunrise was around 06:30 CNST (Chinese National Standard Time = UTC + 8 h) and sunset was at 19:30 CNST.

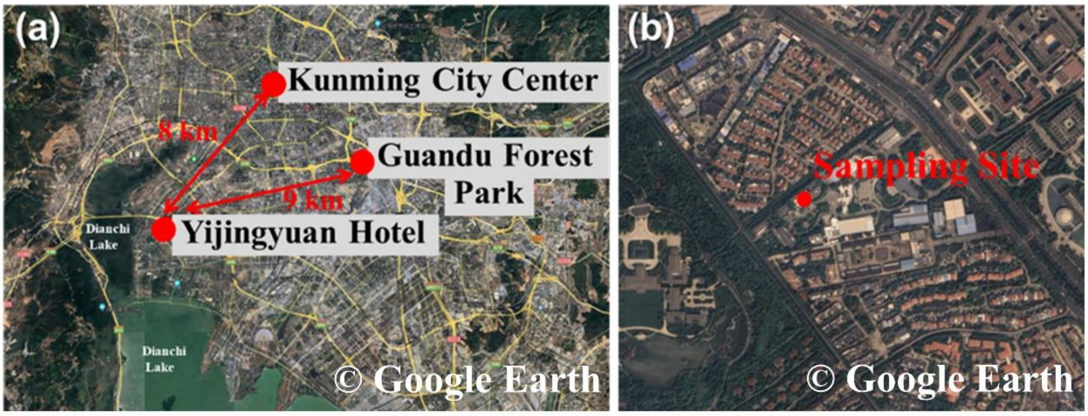


Figure 1. Google Map images showing the locations of the experimental sites. (a) The location of the Yijingyuan Hotel and Guandu Forest Park. (b) The surrounding environment of Yijingyuan Hotel.

2.2. Instrument setup

Multiple gas phase and particulate parameters were measured during the campaign, including N_2O_5, NO, NO_2, O_3, VOCs, $PM_{2.5}$, particle number size distribution (PNSD), particle composition, and meteorological parameters. The detailed information of the instruments is listed in Table 1.

N_2O_5 concentration was measured by a cavity-enhanced absorption spectrometer

(CEAS) developed by Wang et al. (Wang et al., 2017a), which has been used in several field campaigns. N_2O_5 in the sampling gas was thermally decomposed to NO_3 in a preheated perfluoroalkoxy alkane (PFA) tube (130 °C), and then detected in a resonator cavity maintained at 110 °C to avoid the reversible reaction of N_2O_5 and NO_3. Excess NO was injected to the cavity every 5 min to obtain the reference spectrum by eliminating the influence of water vapor. The N_2O_5 loss in the sampling system and detection system were also calibrated and corrected during data processing. The detection of limit (LOD) of CEAS was 2.7 pptv (1σ), and the uncertainty was 19%.

NO, NO_2 and O_3 were monitored by commercial instruments (Thermo-Fisher 42i and 49i). A total of 117 kinds of volatile organic compounds (VOCs) species were measured by an automated gas chromatograph equipped with a mass spectrometer and flame ionization detector (GC-MS/FID). The particle composition was measured by a time-of-flight aerosol chemical speciation monitor (ToF-ACSM), including sulfate, nitrate, ammonium, chloride and organics. The ALWC was calculated by ISORROPA-II model and did not consider the hygroscopicity of organic compounds (Fountoukis and Nenes, 2007). PNSD were measured by a scanning mobility particle sizer (SMPS, TSI Model 3938), including an Electrostatic Classifier (Model 3082) and a condensation particle counter (CPC, Model 3776). Meteorological parameters, including relative humidity (RH), temperature (T), pressure, wind speed and wind direction, were available during the campaign.

Table 1. The detailed information of instruments during the campaign.

Parameters	Detection limits	Methods	Accuracies
N_2O_5	2.7 pptv (1σ, 1min)	CEAS	± 19%
NO	50 pptv (2min)	Chemiluminescence	± 10%
NO_2	50 pptv (2min)	Chemiluminescence[a]	± 10%
O_3	0.5 ppbv (2σ, 1min)	UV photometry	± 5%
VOCs	2–190 ppt (1 h)	GC-MS/FID	± 5%
PNSD	14–730 nm (5 min)	SMPS	± 10%
Particle composition	m/z 10 – 219 (10 min)	ToF-ACSM	-
$\gamma(N_2O_5)$	0.0016 (40 min)	Aerosol flow tube system	± 16~43 %

[a] Photolytic conversion to NO through blue light before detection.

2.3. Measurement and calculation of $\gamma(N_2O_5)$

The $\gamma(N_2O_5)$ was directly measured by an aerosol flow tube system (AFTS) coupled with a detailed box model developed by Chen et al. (Chen et al., 2022). The detection limit and accuracy of the AFTS are listed in Table 1. Briefly, the AFTS mainly consists of a N_2O_5 generator, an aerosol flow tube, and detection instruments for N_2O_5, NO_x, O_3 and S_a (Figure S1). N_2O_5 generated by O_3 and NO_2 (in excess) was added to the sampling gas in the front of the aerosol flow tube. The aerosol flow tube consists of two cones at both ends with a vertex angle of 15° and a straight cylinder in the middle with an inner diameter of 140 mm and a length of 343 mm. The total flow rate in the tube was 2.08 L min^{-1}, and the residence time was 259 s. The detection instruments used for measurements of N_2O_5, NO_x, O_3 and S_a are CEAS-PKU, Thermo 42i-TL, Teledyne T265 and SMPS (TSI Model 3938). Additionally, a RH&T sensor (Rotronic, Model HC2A-S) was utilized to monitor relative humidity and temperature inside the flow tube. During each duty cycle, N_2O_5 concentrations were recorded both at the inlet and exit of the flow tube under the condition with and without aerosols to derive the wall loss of N_2O_5. NO, NO_2, and O_3 concentrations were consistently measured at the inlet of the flow tube, and Sa concentrations were consistently measured at the exit of the flow tube. The loss rate coefficients of N_2O_5 were calculated by a time-dependent box model coupled with NO_3-N_2O_5 chemistry under the constraint of the measurement of N_2O_5 concentrations and other auxiliary parameters to overcome the influence of homogeneous reactions (e.g., NO_2, O_3 and NO) and variations of air mass on $\gamma(N_2O_5)$ retrieval. The N_2O_5 loss rate in the absence of aerosols was expected as wall loss rate coefficients ($k_{het}^{wo/aerosols}$) of N_2O_5, and the loss rate in the presence of aerosols was expected as the loss rate both on wall and aerosols ($k_{het}^{w/aerosols}$) of N_2O_5. Therefore, $\gamma(N_2O_5)$ could be calculated by Eq (1). Among them, the loss of S_a concentration in the aerosol flow tube was corrected by the penetration efficiency derived in our previous study (Chen et al., 2022), and the dry-state S_a was corrected to ambient (wet) S_a by a hygroscopic growth factor (Liu et al., 2013). A stringent data QA/QC procedure is applied before model calculation based on the above measured variables to retrieve robust $\gamma(N_2O_5)$ values. Other detailed information about this system can be found in Supplementary Information and Chen et al. 2022.

$$\gamma(N_2O_5) = \frac{4 \times (k_{het}^{w/aerosols} - k_{het}^{wo/aerosols})}{c \times S_a} \quad (1)$$

2.4 Calculation of NO_3 and N_2O_5 reactivity

NO_3 production rate ($P(NO_3)$) was calculated by the measured NO_2 and O_3 concentrations via Eq.(2), $k_{NO_2+O_3}$ represents the reaction rate constant of NO_2 and O_3 (Atkinson et al., 2004). NO_3 concentration can be calculated by the measured N_2O_5 concentration with the temperature-dependent equilibrium relationship (Eq.3). The steady-state lifetime of N_2O_5 ($\tau(N_2O_5)$) and NO_3 ($\tau(NO_3)$) was calculated by concentrations and $P(NO_3)$ as shown in Eq.(4) and Eq.(5) (Brown and Stutz, 2012). The NO_3 reactivity with VOCs ($k(NO_3)$) can be calculated by Eq.(6), among them k_i represents the bimolecular rate coefficients.

$$P(NO_3) = k_{NO_2+O_3}[NO_2][O_3] \quad (2)$$

$$[NO_3] = [N_2O_5]/k_{eq}[NO_2], \quad (3)$$

$$k_{eq} = 5.5 \times 10^{-27} \times e^{10724/T}$$

$$\tau(N_2O_5) = [N_2O_5]/P(NO_3) \quad (4)$$

$$\tau(NO_3) = [NO_3]/P(NO_3) \quad (5)$$

$$k(NO_3) = \sum k_i [VOC_i] \quad (6)$$

2.5 Calculation of nitrate production rate

The N_2O_5 uptake for nighttime particulate nitrate production is regarded as a pseudo-first-order reaction, the rate constant (k_{N2O5}) of which can be calculated from Eq 7 with measured or parameterized $\gamma(N_2O_5)$, where C is the mean molecular speed of N_2O_5. The yield ratio of $ClNO_2$ (φ) was set as a constant of 0.5 in all calculations, which is consistent with the previously observed yield range of 0.3~0.73 in North China (Wang et al., 2017d;Wang et al., 2018). The nitrate production rate can be calculated by Eq 8, where $[N_2O_5]$ is the concentration of N_2O_5.

$$k_{N2O5} = 0.25 \times S_a \times \gamma(N_2O_5) \times C \quad (7)$$

$$P(NO_3^-) = k_{N2O5} \times [N_2O_5] \times (2-\varphi) \quad (8)$$

3. Results and discussion

3.1. γ(N_2O_5) measurement overview and comparison

The mean diurnal variation of the measured N_2O_5 concentration, γ(N_2O_5) values, RH, T, concentrations of NO_2, O_3, NO, $PM_{2.5}$ from 15 April to 20 May 2021 are shown in Figure 2a, and the time series are shown in Figure S2. Higher $PM_{2.5}$ concentration was observed at night (average of 27.8±14.3 ug/m^3, peak of 81.0 ug/m^3) than during the day (Figure 2a & Figure S2). The NO_2 (average of 6.5±8.4 ppbv) and O_3 (average of 45.5±19.7 ppbv) concentrations in Kunming are lower than in other regions in China (Wang et al., 2017d;Wang et al., 2020a;Niu et al., 2022;Li et al., 2020), indicating a lower atmospheric oxidation capacity. The mean nocturnal NO_3 production rate (P(NO_3)) was 0.6± 0.8 ppbv/h, which is also lower than previous reports in China (Tham et al., 2016;Zhai et al., 2023;Wang et al., 2022). During this campaign, significant N_2O_5 concentration (at a maximum of 395.1 pptv) was only observed within April 16-27, mainly with low humidity and high precursor concentrations, while the concentrations fluctuated around the detection limit during other periods. The nocturnal mean concentration of N_2O_5 was 33.4±75.2 pptv, which is lower than reported concentrations in other regions of China (Wang et al., 2018;Brown et al., 2016;Zhai et al., 2023). During the field measurement, high temperature (~20°C) favors the equilibrium shifting from N_2O_5 towards NO_3 and the site mainly received the emissions from vegetation in the surrounding parks. In that case, the major removal of NO_3-N_2O_5 at night was the reaction of NO_3 with VOCs represented by monoterpene (67%) and isoprene (4%), followed by N_2O_5 uptake (15%) shown in Figure 2c. Rapid depletion of daytime-emitted isoprene by NO_3 led to a low contribution of isoprene to NO_3 reactivity after sunset (Figure S3). The steady-state lifetime of N_2O_5 (τ(N_2O_5)) was 185±294 s on average and its diel pattern was similar to N_2O_5 concentration. The τ(N_2O_5) in Kunming was higher than most other cities in China (Wang et al., 2020a;Li et al., 2020;Yan et al., 2019). Comparisons of NO_3 and N_2O_5 concentrations, P(NO_3), and other parameters from various regions around the world in recent years are summarized in Table S1.

The nocturnal mean γ(N_2O_5) value ranged from 0.0018 to 0.12 with an average of 0.023±0.021. The diurnal profiles showed that the γ(N_2O_5) value decreased after sunset and then sharply increased with relative humidity after midnight, peaking at 5:00 am (Figure 2a). The mean γ(N_2O_5) was lower than that in North China Plain and Eastern

China, and similar to that in Pearl River Delta China, Europe and North America (Figure.2b) (Yan et al., 2023;Wang et al., 2017b;Wang et al., 2017d;Wang et al., 2017c;Niu et al., 2022;Morgan et al., 2015;Phillips et al., 2016;Bertram et al., 2009a;McDuffie et al., 2018). The detailed comparisons of field-derived γ(N_2O_5) were summarized in Table S2.

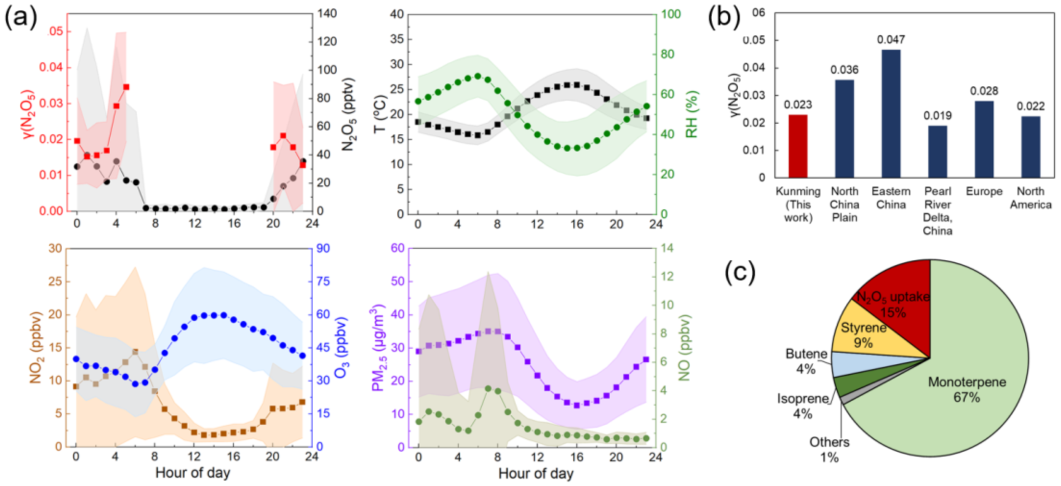


Figure 2. The overview of γ(N_2O_5), gas phase and particulate parameters, meteorological parameters, and NO_3 loss pathways. (a) Mean diurnal profiles of measured γ(N_2O_5), N_2O_5, T, RH, NO_2, O_3, $PM_{2.5}$ and NO. (b) Comparison of γ(N_2O_5) values in China, Europe, and North America calculated from previous work with measured value in this work. (c) The percentage of NO_3 loss pathway via VOCs and N_2O_5 uptake at night.

3.2. Dependence of γ(N_2O_5) on impacting factors

The dependence of measured γ(N_2O_5) values on organics, ALWC, NO_3^- and Cl^- concentration in the particle phase in this study are shown in Figure 3. The organic wet mass fraction showed a significant negative correlation (R^2=0.83) with measured γ(N_2O_5) values (Figure 3a), indicating that organics in the aerosol significantly inhibited the uptake of N_2O_5 during the measuring period in Kunming. While a large number of studies have observed evident suppression of particulate organic on N_2O_5 uptake on lab-generated aerosols (Escoreia et al., 2010;Cosman and Bertram, 2008;Gaston et al., 2014), the negative correlation of particulate organic and γ(N_2O_5) was usually weak derived from field measurements (Brown et al., 2009;McDuffie et al., 2018;Chen et al., 2018;Wang et al., 2020b). The organic wet mass fraction in this study varies between 0.3 and 0.8, while other previous studies have reported a variation range of 0.1 to 0.5 (McDuffie et al., 2018;Wang et al., 2020;Brown et al., 2009). The large proportion and variation range of organics in the aerosols may lead to a more significant inhibition effect on γ(N_2O_5). Additionally, we found that both the dry and wet mass fractions of organics in this study showed significant negative correlations with ALWC, with Pearson coefficients of -0.66 and -0.79 (Table S3), respectively. Therefore, organics might decrease γ(N_2O_5) by forming an organic coating to limit the penetration of liquid water into the particle phase and hinder the reaction between N_2O_5 with liquid phase.

Aerosol liquid water also exhibited a controlling role in the heterogeneous uptake of N_2O_5 in this study as demonstrated by the evidently positive correlation (R^2=0.74) of ALWC and γ(N_2O_5) (Figure 3b). A weak correlation was observed with ALWC below 25 M and a significant correlation was observed with ALWC higher than 25 M. A similar trend has been reported by previous laboratory studies (Mozurkewich and Calvert, 1988;Bertram and Thornton, 2009;Folkers et al., 2003;Hallquist et al., 2003). When RH is low, the aerosols mainly exist in the solid state with low ALWC, limiting the uptake reaction. Whereas the aerosols become deliquesced as the RH (also ALWC) increases, which greatly promotes the uptake reaction. Previous field studies also found good correlations of γ(N_2O_5) values with ALWC or RH in most regions in China, indicating that ALWC may be one of the rate-limiting steps of heterogeneous reaction in China (McDuffie et al., 2018;Yu et al., 2020;Tham et al., 2018;Wang et al., 2022).

Figure 3c shows the negative dependence of measured γ(N_2O_5) values on aerosol nitrate concentration, similar to the results of previous laboratory studies and most field observations (Tham et al., 2018;Bertram et al., 2009b;Morgan et al., 2015;Yu et al., 2020). The suppression effect of NO_3^- on the N_2O_5 heterogeneous uptake is mainly caused by the competition of aerosol nitrate with chloride and H_2O for the $H_2ONO_2^+$ intermediate (R5~R8) (Bertram and Thornton, 2009). The positive correlation (R^2=0.48) between γ(N_2O_5) and the molar ratio of Cl^-/NO_3^- values was weaker than that of ALWC (Figure 3d), which indicates that Cl^- may promote the N_2O_5 uptake reaction instead of playing a critical role during our observation. The particulate Cl^- concentration also contributes to a weaker enhancement of γ(N_2O_5) compared to ALWC in other field observations (Wang et al., 2020b;Yu et al., 2020;McDuffie et al., 2018).

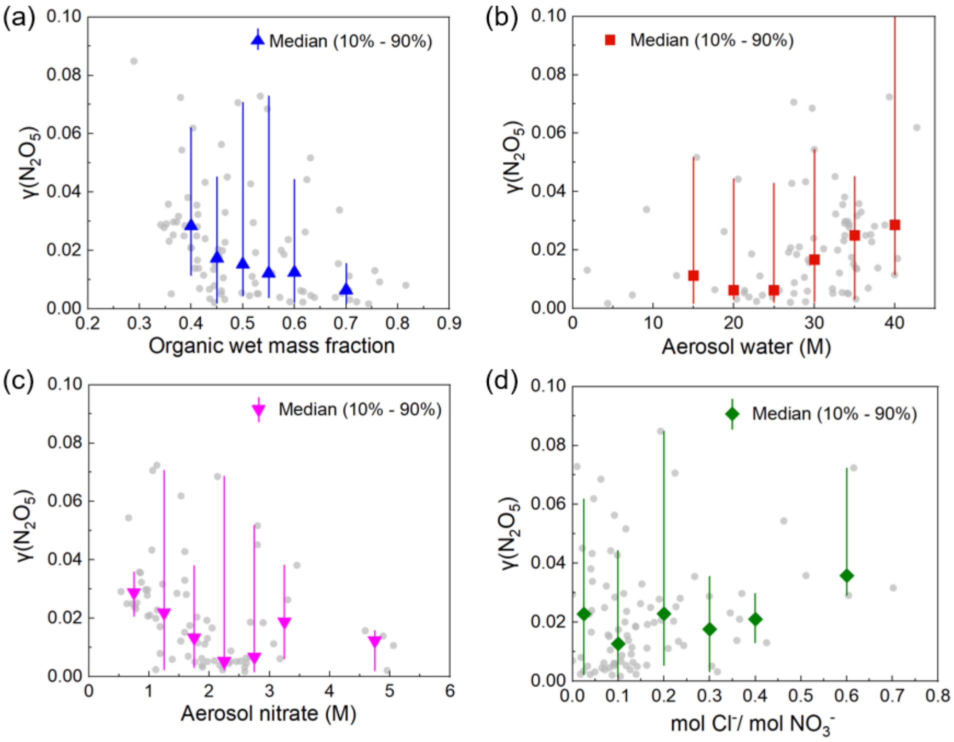


Figure 3. The correlations of measured γ(N_2O_5) values between the influencing factors. Variation of γ(N_2O_5) with the organic wet mass fraction (a), the aerosol water content (b), the aerosol nitrate content (c), and the molar ratio of chloride to nitrate (d). The gray points represent the measured values. The symbols in different colors represent the median in each bin with range from the 10th to 90th percentile in each bin denoted as lines.

3.3. Comparison of parameterized γ(N_2O_5) values

The γ(N_2O_5) values were predicted using ten widely used parameterizations and compared with the measured results. The details of the parameterizations are summarized in Table S4. Parameterizations were categorized into inorganic-only and inorganic kernels with organic coating or organic mass (inorganic+organic).

The γ(N_2O_5) predicted by inorganic-only parameterizations were generally larger than measurements. Among these inorganic-only parameterizations, RIE03, BT09 w/o Cl and Yu20 exhibited relatively low deviation in predicted median values from measurements (Figure 4a). However, the correlations of the predictions and measurements were bad for these three parameterizations (R^2=0~0.09, Figure 4b). The empirical parameterization Yu20 derived from several field campaigns in China showed the best performance with a median difference of 4%, the lowest RMSE (0.0200) and the highest correlation coefficient (R^2=0.09) in Kunming, indicating the effectiveness of the improvement by the localized field results. The overestimation of the DAV08, BT09 and GRI09 were also reported by previous studies (Bertram et al., 2009b;Brown et al., 2009;Chang et al., 2016;Griffiths et al., 2009;McDuffie et al., 2018). All parameterizations had difficulties in predicting the low and high values of measured $\gamma(N_2O_5)$. For the parameterizations with a median deviation less than 10%, the parameterized $\gamma(N_2O_5)$ values mainly fell in the range of 0.0036~0.035, while the measured values varied from 0.0018 to 0.12, indicating that the relevant parameters in the parameterizations were still inappropriate and cannot reproduce the range of the measurements.

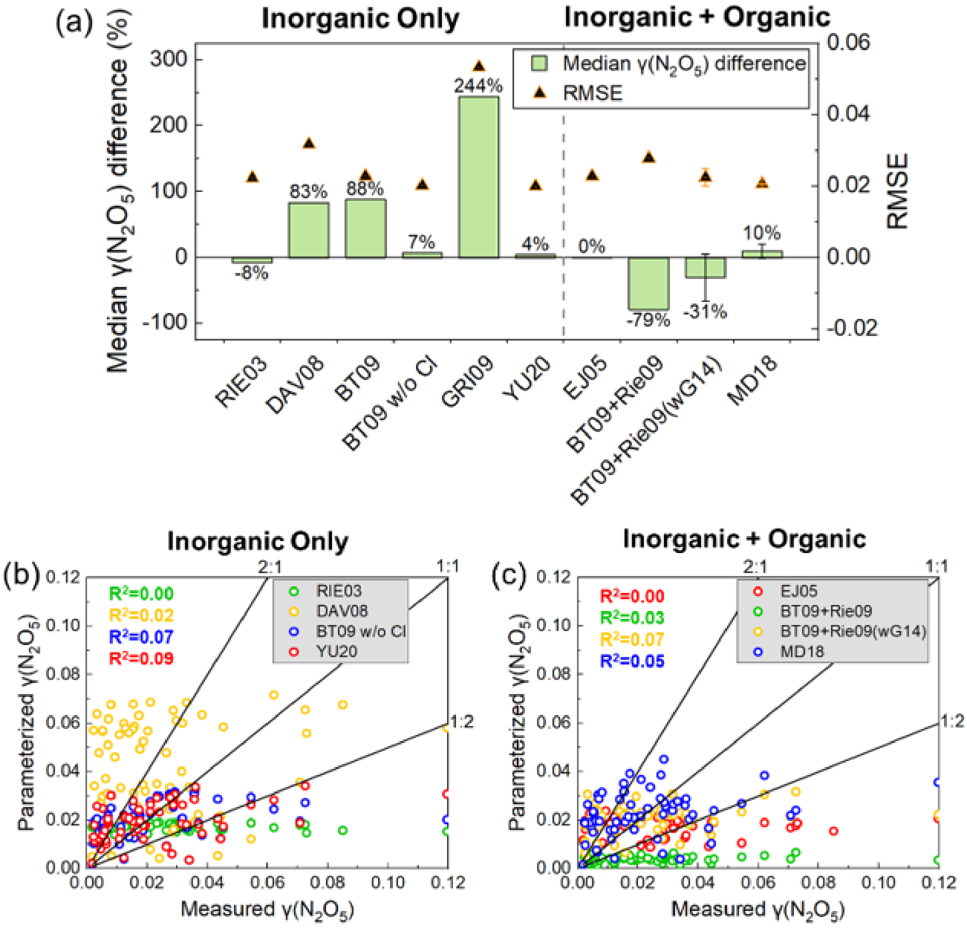


Figure 4. Comparison of parameterized and measured $\gamma(N_2O_5)$. (a) Comparison of median difference and root-mean-square-error (RMSE) between measured $\gamma(N_2O_5)$ and parameterized $\gamma(N_2O_5)$ values. The error bars of BT09+Rie09wG14 and MD18 showed the range of the results of O/C setting between 0.5 and 0.8. The distribution of parameterized $\gamma(N_2O_5)$ values, including inorganic-only parameterizations (RIE03, DAV08, BT09 w/o Cl^-, YU20) (b), and inorganic+organic parameterizations (EJ05, BT09+Rie09, BT09+Rie09wG14, MD18) (O/C=0.8) (c). The black solid line

represents the 1:1, 1:2 and 2:1 lines, respectively. The R^2 displayed in different colors corresponds to the parameterization of the same color.

The inorganic+organic parameterizations tend to underestimate the measured $\gamma(N_2O_5)$ due to the suppression effects of organics. Worse agreement and larger scatter were found for the parameterized $\gamma(N_2O_5)$ (R^2=0~0.07, Figure 4c) when the organics part was added into inorganic. BT09+Rie09(wG14) showed the best correlation with R^2 of 0.07 but a relatively large median deviation (-66~5%). EJ05 and MD18 showed the lowest deviations among the four parameterizations, while EJ05 showed the worst correlation (R^2=0.00). Among them, the empirical parameterization MD18, derived from field observations, exhibited the best performance with a deviation of -1~20% and the lowest RMSE (0.0207), which also indicates that parameterization can be improved by fitting to field observations, similar to the results of inorganic-only parameterizations.

The commonly used parameterizations mainly consist of inorganic and inorganic+organic framework, such as BT09w/oCl, YU20, and MD18. In this study, among all parameterizations, YU20 demonstrated the best performance, most likely because YU20 was optimized based ondatasets observed in four rural regions in China. BT09w/oCl also performed well in this study, overestimating the median by only 7%. However, poor performances of BT09w/oCl were still reported in Pearl River Delta and North China Plain (Wang et al., 2022;Wang et al., 2020). Conversely, the BT09w/oCl performed well in Northwestern Europe, mainly because $\gamma(N_2O_5)$ in Europe is predominantly controlled by the ions in bulk phase (Morgan et al., 2015;Chen et al., 2018;Phillips et al., 2016). In North America, $\gamma(N_2O_5)$ is significantly inhibited by organic effects (Chang et al., 2016). The parameterizations considering organic effects, like MD18, might be more suitable for the conditions in North America. However, in this study, MD18 showed an overestimation of up to 20%, suggesting that this parameterization is not suitable for China, but more applicable to North American regions.

Hence, most regions in China, where $\gamma(N_2O_5)$ is controlled by aerosol liquid water content, are more suited to the YU20. European regions, where gamma is controlled by H_2O/NO_3^- and less influenced by organics, are better served by the BT09w/oCl. Meanwhile, MD18 is more appropriate for North American regions. Localized parameterizations established on the basis of local measurements can exhibit superior performance within the respective regions. Parameterizations incorporating organic effects generally exhibit larger errors than others, underscoring the importance of further improving the consideration of organic effects in parameterizations.

3.4. Impact of ALWC on parameterized $\gamma(N_2O_5)$

Although some parameterizations performed relatively well in reproducing the median values of $\gamma(N_2O_5)$, none of the ten parameterizations were able to reproduce the range of measured $\gamma(N_2O_5)$ values, as indicated by poor correlations and large RMSE. This phenomenon was possibly caused by several aspects, including the inaccurate estimation of response coefficients of aerosol compositions (represents the quantitative relationship between $\gamma(N_2O_5)$ and aerosol chemical compositions), relative rates of competitive reactions, and the missing parameters. The missing influencing factors in current parameterizations include parameters such as particle morphology, phase state, and mixing state (You et al., 2014;Shiraiwa et al., 2017;Ng et al., 2010). These parameters, which current methodologies are difficult to measure in field conditions, have been proven to affect $\gamma(N_2O_5)$, and can contribute to the discrepancy between parameterized and measured values.

ALWC is one of the factors controlling N_2O_5 uptake during our observation and the coefficients related to ALWC should play a critical role in reproducing the varying range of $\gamma(N_2O_5)$. To investigate the accuracy of the ALWC-related response coefficients in $\gamma(N_2O_5)$ parameterizations, we compared the parameterized and measured $\gamma(N_2O_5)$ values at three ALWC levels: low concentration (0~25 M), medium concentration (25~35 M), and high concentration (35~45 M). Six parameterizations were selected for the comparison at different ALWC levels due to their low deviations (below 10% of median values) over the entire observation (Figure 5). At low ALWC, all six parameterizations showed overestimation with the maximum difference for EJ05 (189%) and the minimum for MD18 (34%). At median ALWC, the deviation of parameterized $\gamma(N_2O_5)$ reduced to -8~4%. At high ALWC, the parameterizations tend to underestimate the measured $\gamma(N_2O_5)$ with the difference ranging from -37% to -1%. The treatment of ALWC-related effects on the $\gamma(N_2O_5)$ following BT09 and Rie09 parameterizations framework was generally better than those following RIE03 and EJ05. The YU20 and MD18 showed the best performance across all three ALWC levels among inorganic-only parameterizations and inorganic+organic parameterizations, respectively. The overestimation at low ALWC and underestimation at high ALWC suggest that the treatment of coefficients related to ALWC in most parameterizations can hardly capture the response of $\gamma(N_2O_5)$ to largely varied ALWC.

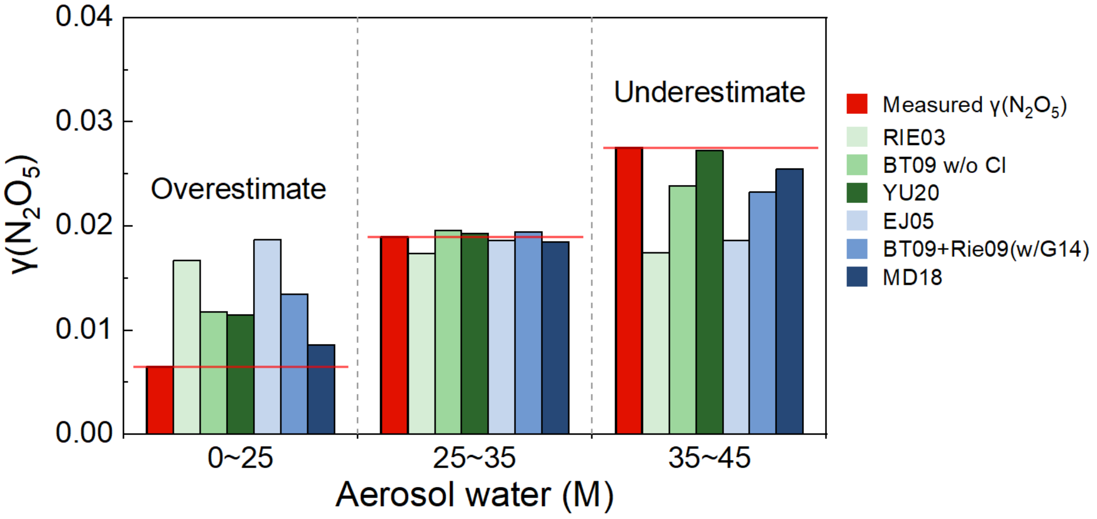


Figure 5. Comparison of the median values of measured and parameterized γ(N_2O_5) at low, median and high ALWC levels. The O/C settings of BT09+Rie09wG14 and MD18 were 0.8 and 0.5, respectively.

The biased prediction of γ(N_2O_5) at low and high ALWC levels might cause considerable uncertainties in estimating the impacts of N_2O_5 uptake when ALWC varies largely in ambient conditions. We calculated the particulate nitrate production potential contributed by N_2O_5 uptake based on measured γ(N_2O_5) and six selected parameterizations at low and high ALWC levels, respectively. The maximum deviations of median nitrate production rates were 74% and -77% at low and high ALWC levels, respectively (Figure 6). Our results indicate that current parameterizations may lead to large deviations in nitrate production potential predictions. The contribution of the N_2O_5 heterogeneous reaction to nitrate production is important in some regions (Wang et al., 2021;Chen et al., 2020a;Fan et al., 2020;Wagner et al., 2013), and can be comparable with that of OH+NO_2 pathway (Alexander et al., 2020;Fan et al., 2022;Zhai et al., 2023). Therefore, we suggest that future studies should conduct more γ(N_2O_5) measurements under extreme ALWC levels, which helps to improve the reliability of response coefficients between γ(N_2O_5) and ALWC in ambient conditions.

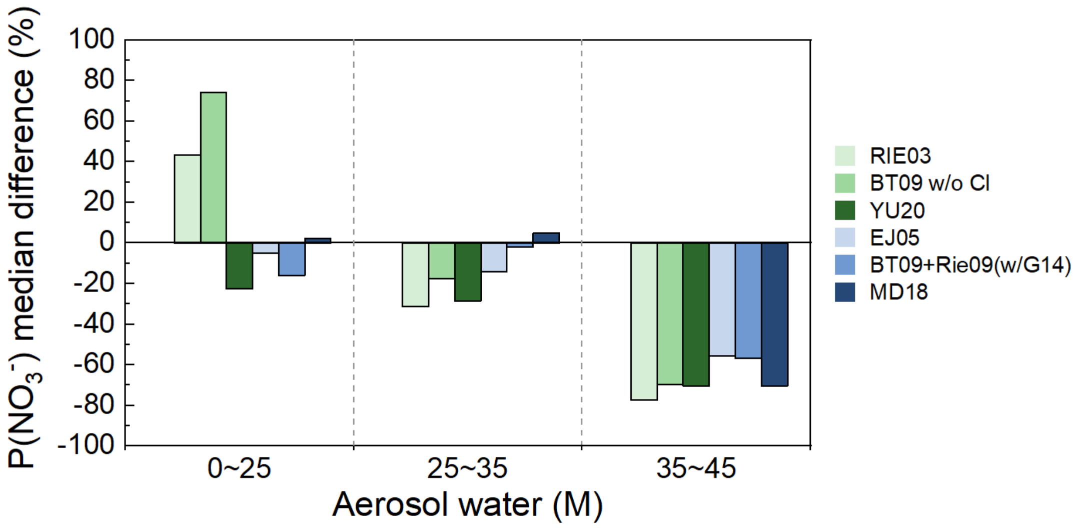


Figure 6. The median difference of the nitrate production rates P(NO_3^-) between measured and parameterized γ(N_2O_5) values during low, median and high ALWC conditions. The O/C setting of BT09+Rie09wG14 was 0.8 and that of MD18 was 0.5.

4. Conclusions

The γ(N_2O_5) values on ambient aerosols were directly measured by an improved in situ aerosol flow tube system in Kunming, which represents a typical highland environment. The relationship between the measured γ(N_2O_5) and impacting factors was consistent with previous laboratory results, except for aerosol chloride. The median of γ(N_2O_5) predicted by inorganic-only and inorganic+organic parameterizations generally overestimate and underestimate the measurements, respectively. While some parameterizations agreed well with the measurements on median values, they failed to reproduce the variabilities and showed low correlations. In particular, parameterizations overestimate the γ(N_2O_5) by 34~189% at low ALWC and underestimate by -37%~-1% at high ALWC, respectively. Among the ten parameterizations, the empirical parameterizations YU20 and MD18 performed relatively well with lower deviations in median values and RMSE. The suggestions on how to choose the different parameterization scenarios under various conditions were given. Our result reveals that using ambient measurements can effectively improve parameterizations derived from laboratory experiments. Therefore, we call for the need to conduct more field observations of γ(N_2O_5) directly on ambient aerosols to improve the performance of parameterizations and better elucidate the environmental impacts of N_2O_5 uptake reaction. Meanwhile, further studies on the mechanism of N_2O_5 uptake under extreme ALWC conditions would help to improve the accuracy of its response coefficients in parameterizations.

Author information

Corresponding Authors

Keding Lu – State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China; Email: k.lu@pku.edu.cn

Xiaorui Chen – School of Atmospheric Sciences, Sun Yat-sen University, and Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China; Email: chenxr95@mail.sysu.edu.cn

Authors

Jiayin Li⊥ – State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China

Tianyu Zhai⊥ – State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China; Key Laboratory for Vehicle Emission Control and Simulation of Ministry of Ecology and Environment, Beijing, 100012, China

Haichao Wang – School of Atmospheric Sciences, Sun Yat-sen University, and Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, 519082, China

Shuyang Xie – State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China

Shiyi Chen– State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China

Chunmeng Li– State Key Joint Laboratory of Environmental Simulation and

Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China; The National Institute of Metrology, Center for Environmental Metrology, Beijing 100029, China

Huabin Dong– State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Science and Engineering, Peking University, Beijing 100871, China

Author Contributions

X.R.C. and K.D.L. designed the study. K.D.L organized the field campaign with the help from Y.J.G. T.Y.Z and X.R.C measured the $\gamma(N_2O_5)$ data. C.M.L, S.Y.X, H.B.D and S.Y.C provide the field data of normal gases, particulate components and other supporting parameters. J.Y.L, T.Y.Z, X.R.C and H.C.W analyze the data. J.Y.L, T.Y.Z and X.R.C wrote the paper with the input from K.D.L.

Competing Interests

The authors declare no competing financial interest.

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