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Direct measurement of N₂O₅ heterogeneous uptake coefficients on atmospheric aerosols in southwestern China and evaluation of current parameterizations

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Abstract. The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) is a critical process in assessing NO_x fate and secondary pollutant formation. However, accurate quantification of the N₂O₅ uptake coefficient (γ (N_2O_5)) in ambient conditions is a challenging problem that can cause unpredictable uncertainties in the predictions of air quality models. Here, the γ (N₂O₅) values were directly measured using an improved in situ aerosol flow tube system at a site located in a highland region in southwestern China to investigate influencing factors and the performance of current γ (N₂O₅) parameterizations under this typical environmental condition. The nocturnal mean γ (N₂O₅) value ranged from 0.0018 to 0.12 with an average of 0.023 ± 0.021. The relationship between the measured γ (N₂O₅) and impacting factors was consistent with previous laboratory results, except for aerosol chloride. The aerosol water significantly promoted N₂O₅ uptake, while particulate organics and nitrate showed suppression effects. We found that several parameterizations can capture the median of measured values, whereas none of the 10 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) (> 35 M) and low ALWC (< 25 M) levels with an underestimation of -37% to -1% and an overestimation of 34 % to 189 %, respectively. Such differences between the measured and parameterized γ (N_2O_5) would lead to a biased estimation (-77% to 74%) of the particulate nitrate production potential. Our findings suggest the need for more direct field quantifications of γ (N₂O₅) and laboratory measurements under extreme ALWC conditions to re-evaluate the response coefficients between γ (N₂O₅) and aerosol chemical compositions in parameterizations.

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Graphical abstract



ALWC Increasing

1 Introduction

Nitrate radical (NO₃) and dinitrogen pentoxide (N₂O₅) are dominant in nocturnal atmospheric chemistry as reactive nitrogen species that can strongly influence the concentration and distribution of ozone (O₃) 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). NO₃ is produced by the reaction of NO₂ and O₃ (Reaction R1), and there is a thermodynamic equilibrium between NO₃ and N_2O_5 (Reaction R2), which is the source of N₂O₅ (Brown and Stutz, 2012). There are two main pathways for NO₃ removal: the direct one is the reactions of NO₃ and VOCs (volatile organic compounds; Reaction R3), especially alkenes, and the indirect way is the heterogeneous hydrolysis of N₂O₅ (Asaf et al., 2009; Ng et al., 2017). N₂O₅ can react with H_2O and chloride (Cl⁻) in the particle phase and form soluble nitrate and nitryl chloride (ClNO2) (Reaction R4) (Osthoff et al., 2008; Chang et al., 2011). The uptake of N₂O₅ is the main pathway for the formation of particulate nitrate at night, which contributes to PM2.5 (particulate matter $< 2.5 \,\mu\text{m}$ in diameter) pollution. Meanwhile, chlorine radical is produced by ClNO₂ photodecomposition in the daytime and further regulates the O₃ 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 N₂O₅ heterogeneous hydrolysis reaction in ambient conditions.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R1}$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \tag{R2}$$

$$NO_3 + VOCs \rightarrow products$$
 (R3)

$$N_2O_5 + H_2O/Cl^-(p) \rightarrow NO_3^-(p) + CINO_2$$
(R4)

 γ (N₂O₅) is defined as the net probability of N₂O₅ irreversibly taken up onto an aerosol surface upon collision (McDuffie et al., 2018). According to the previous study, the process of the N₂O₅ heterogeneous hydrolysis reaction on aerosols was treated as a resistor model including three steps: gas diffusion (Reaction R5), surface accommo-

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dation, and aqueous reaction (Reactions 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 (NO₃⁻) 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 (Reactions R6–R8), and NO_3^- suppresses the reaction (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 γ (N₂O₅) and aerosol chemical compositions were generally weak mainly due to the coupling effects of particle morphology, size, the mixing state, and meteorological parameters (e.g., temperature and relative humidity) (Phillips et al., 2016; Wang et al., 2020b; Riedel et al., 2012).

$$N_2O_5(g) \leftrightarrow N_2O_5(aq)$$
 (R5)

 $N_2O_5(aq) + H_2O(l) \leftrightarrow H_2ONO_2^+(aq) + NO_3^-(aq)$ (R6)

$$H_2ONO_2^+(aq) + H_2O(l) \rightarrow HNO_3(aq) + H_3O^+(aq)$$
 (R7)

$$H_2ONO_2^+(aq) + HX(aq) \rightarrow XNO_2(aq) + H_3O^+(aq)$$
 (R8)

In order to accurately quantify the contribution of N₂O₅ heterogeneous hydrolysis to nitrate formation and NO_x regulation, a variety of parameterizations of γ (N₂O₅) 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 γ (N₂O₅) in varying environments (Brown et al., 2009; Ryder et al., 2014; McDuffie et al., 2018). Moreover, the overestimation or underestimation of the parameterized γ (N₂O₅) 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 γ (N₂O₅) values in ambient conditions (< 10⁻⁴ to 0.1) mostly by indirect quantification methods (Brown et al., 2016; Wang et al., 2018; X. R. Chen et al., 2020; Morgan et al., 2015; Tham et al., 2018), while some were quantified by direct measurements (Yu et al., 2020; Riedel et al., 2012; Bertram et al., 2009a). The N₂O₅ heterogeneous uptake process has been reported to be active in China. The γ (N₂O₅) values in the 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 those in Europe and North America (10⁻³-10⁻²) (Yan et al., 2023; H. C. Wang et al., 2017; X. F. Wang et al., 2017; Z. Wang et al., 2017; Niu



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

et al., 2022). To further investigate the N₂O₅ heterogeneous chemistry in China, the γ (N₂O₅) values were directly measured in a typical highland city in China, Kunming, using an improved in situ aerosol flow tube system from 15 April to 20 May 2021. The relationship between the γ (N₂O₅) values and impacting factors was determined. We then examine the performance of current γ (N₂O₅) 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 γ (N₂O₅) 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, $102^{\circ}39'40''$ E), about 20 m above the ground. As shown in Fig. 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 this, the particle composition was measured at the Guandu Forest Park (25°00'43" N, 102°45'55" E), which was about 9 km away from the Yijingyuan Hotel, 5.2 km from the city center, and also mainly surrounded by residential living area. Sunrise was around 06:30 CNST (China national standard time; UTC + 8 h), and sunset was at 19:30 CNST.

2.2 Instrument setup

Multiple gas phase and particulate parameters were measured during the campaign, including N_2O_5 , NO, NO₂, O₃, VOCs, PM_{2.5}, particle number size distribution (PNSD), particle composition, and meteorological parameters. Detailed information about the instruments is listed in Table 1. N_2O_5 concentration was measured by a cavity-enhanced absorption spectrometer (CEAS) developed by H. Wang et al. (2017), 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 into 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 limit of detection (LOD) of CEAS was 2.7 pptv (1 σ), and the uncertainty was 19 %.

NO, NO₂, and O₃ were monitored by commercial instruments (Thermo Fisher 42i and 49i). A total of 117 kinds of volatile organic compound (VOC) 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 the 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.

2.3 Measurement and calculation of γ (N₂O₅)

The γ (N₂O₅) was directly measured by an aerosol flow tube system (AFTS) coupled with a detailed box model developed by Chen et al. (2022). The detection limit and accuracy of the AFTS are listed in Table 1. Briefly, the AFTS mainly consists of an N2O5 generator; an aerosol flow tube; and detection instruments for N_2O_5 , NO_x , O_3 , and aerosol surface area (S_a) (Fig. S1 in the Supplement). N₂O₅ generated by O₃ and NO₂ (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 $2.08 \,\mathrm{L}\,\mathrm{min}^{-1}$, and the residence time was $259 \,\mathrm{s}$. 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, an RH-T sensor (Rotronic model HC2A-S) was utilized to monitor relative humidity and temperature inside the flow tube. During each duty cycle, N₂O₅ concentrations were recorded at both the inlet and the exit of the flow tube under conditions with and without aerosols to derive the wall loss of N₂O₅. NO, NO_2 , and O_3 concentrations were consistently measured at

Parameters	Detection limits	Methods	Accuracies
N ₂ O ₅	2.7 pptv $(1\sigma, 1 \min)$	CEAS	±19%
NO	50 pptv (2 min)	Chemiluminescence	$\pm 10\%$
NO ₂	50 pptv (2 min)	Chemiluminescence*	$\pm 10\%$
O ₃	$0.5 \text{ ppbv} (2\sigma, 1 \min)$	UV photometry	$\pm5\%$
VOCs	2-190 ppt (1 h)	GC-MS/FID	$\pm 5~\%$
PNSD	14–730 nm (5 min)	SMPS	$\pm 10\%$
Particle composition	m/z 10–219 (10 min)	ToF-ACSM	-
$\gamma (N_2O_5)$	0.0016 (40 min)	Aerosol flow tube system	± 16 %–43 %

Table 1. Detailed information about instruments used during the campaign.

* Photolytic conversion to NO through blue light before detection.

the inlet of the flow tube, and S_a concentrations were consistently measured at the exit of the flow tube. The loss rate coefficients of N₂O₅ were calculated by a time-dependent box model coupled with NO3-N2O5 chemistry under the constraint of the measurement of N2O5 concentrations and other auxiliary parameters to overcome the influence of homogeneous reactions (e.g., NO₂, O₃, and NO) and variations in air mass on γ (N₂O₅) retrieval. The N₂O₅ loss rate in the absence of aerosols was expected as wall loss rate coefficients $(k_{het}^{w/o \text{ aerosols}})$ of N₂O₅, and the loss rate in the presence of aerosols was expected as the loss rate on both the wall and aerosols $(k_{het}^{w/aerosols})$ of N₂O₅. Therefore, γ (N₂O₅) 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 (quality assurance/quality control) procedure is applied before model calculation based on the above-measured variables to retrieve robust γ (N₂O₅) values. Other detailed information about this system can be found in the Supplement and Chen et al. (2022).

$$\gamma (N_2 O_5) = \frac{4 \times \left(k_{het}^{w/aerosols} - k_{het}^{w/o aerosols}\right)}{c \times S_a}$$
(1)

2.4 Calculation of NO₃ and N₂O₅ reactivity

NO₃ production rate ($P(NO_3)$) was calculated by the measured NO₂ and O₃ concentrations via Eq. (2); $k_{NO_2+O_3}$ represents the reaction rate constant of NO₂ and O₃ (Atkinson et al., 2004). NO₃ concentration can be calculated by the measured N₂O₅ concentration with the temperature-dependent equilibrium relationship (Eq. 3). The steady-state lifetime of N₂O₅ (τ (N₂O₅)) and NO₃ (τ (NO₃)) was calculated by concentrations and $P(NO_3)$ as shown in Eqs. (4) and (5) (Brown and Stutz, 2012). The NO₃ reactivity with VOCs (k(NO₃)) can be calculated by Eq. (6); among them, k_i represents the bimolecular rate coefficients.

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

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

$$k_{eq} = 5.5 \times 10^{-27} \times e^{10724/T} \tau (N_2O_5) = [N_2O_5] / P(NO_3)$$
 (4)

$$\tau(\text{NO}_3) = [\text{NO}_3] / P(\text{NO}_3) \tag{5}$$

$$k(\text{NO}_3) = \sum k_i [\text{VOC}_i] \tag{6}$$

2.5 Calculation of the nitrate production rate

The N₂O₅ 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 γ (N₂O₅), where *C* is the mean molecular speed of N₂O₅. The yield ratio of ClNO₂ (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 northern China (Z. Wang et al., 2017; Wang et al., 2018). The nitrate production rate can be calculated by Eq. (8), where [N₂O₅] is the concentration of N₂O₅.

$$k_{\rm N2O5} = 0.25 \times S_{\rm a} \times \gamma (N_2 O_5) \times C \tag{7}$$

$$P(\mathrm{NO}_{3}^{-}) = k_{\mathrm{N2O5}} \times [\mathrm{N}_{2}\mathrm{O}_{5}] \times (2 - \varphi)$$
(8)

3 Results and discussion

3.1 γ (N₂O₅) measurement overview and comparison

The mean diurnal variation in the measured N₂O₅ concentration; γ (N₂O₅) values; RH; *T*; and concentrations of NO₂, O₃, NO, and PM_{2.5} from 15 April to 20 May 2021 are shown in Fig. 2a, and the time series are shown in Fig. S2 in the Supplement. A higher PM_{2.5} concentration was observed at night (average of 27.8 ± 14.3 µg m⁻³, peak of 81.0 µg m⁻³) than during the day (Figs. 2a and S2). The NO₂ (average of 6.5 ± 8.4 ppbv) and O₃ (average of 45.5 ± 19.7 ppbv) concentrations in Kunming are lower than in other regions in China (Z. Wang et al., 2017; Wang et al., 2020a; Niu et al., 2022; Li et al., 2020), indicating a lower atmospheric oxidation capacity. The mean nocturnal NO₃ production rate $(P(NO_3))$ was 0.6 ± 0.8 ppbv h⁻¹, which is also lower than previous reports in China (Tham et al., 2016; Zhai et al., 2023; Wang et al., 2022). During this campaign, a significant N₂O₅ concentration (at a maximum of 395.1 pptv) was only observed within 16-27 April, 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 $(\sim 20^{\circ}\text{C})$ favors the equilibrium shifting from N₂O₅ towards NO₃ and the site mainly received the emissions from vegetation in the surrounding parks. In that case, the major removal of NO₃-N₂O₅ at night was the reaction of NO₃ with VOCs represented by monoterpene (67%) and isoprene (4%), followed by N₂O₅ uptake (15 %) shown in Fig. 2c. Rapid depletion of daytime-emitted isoprene by NO₃ led to a low contribution of isoprene to NO₃ reactivity after sunset (Fig. S3). The steady-state lifetime of N₂O₅ (τ (N₂O₅)) was 185±294 s on average, and its diel pattern was similar to the N2O5 concentration. The τ (N₂O₅) in Kunming was higher than that in most other cities in China (Wang et al., 2020a; Li et al., 2020; Yan et al., 2019). Comparisons of NO₃ and N₂O₅ concentrations, P(NO₃), and other parameters from various regions around the world in recent years are summarized in Table S1.

The nocturnal mean γ (N₂O₅) value ranged from 0.0018 to 0.12 with an average of 0.023 ± 0.021. The diurnal profiles showed that the γ (N₂O₅) value decreased after sunset and then sharply increased with relative humidity after midnight, peaking at 05:00 CNST (Fig. 2a). The mean γ (N₂O₅) was lower than that in the North China Plain and eastern China and similar to that in the Pearl River Delta, China; Europe; and North America (Fig. 2b) (Yan et al., 2023; H. C. Wang et al., 2017; X. F. Wang et al., 2017; Z. Wang et al., 2017; 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 (N₂O₅) are summarized in Table S2.

3.2 Dependence of γ (N₂O₅) on impacting factors

The dependence of measured γ (N₂O₅) values on organics, ALWC, and NO₃⁻ and Cl⁻ concentration in the particle phase in this study are shown in Fig. 3. The organic wet mass fraction showed a significant negative correlation ($R^2 = 0.83$) with measured γ (N₂O₅) values (Fig. 3a), indicating that organics in the aerosol significantly inhibited the uptake of N₂O₅ during the measuring period in Kunming. While a large number of studies have observed evident suppression of particulate organics on N₂O₅ uptake of lab-generated aerosols (Escoreia et al., 2010; Cosman and Bertram, 2008; Gaston et al., 2014), the negative correlation of particulate organics and γ (N₂O₅) was usually weak as 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., 2020b; 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 (N₂O₅). 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 (N₂O₅) by forming an organic coating to limit the penetration of liquid water into the particle phase and hinder the reaction of N₂O₅ with the liquid phase.

Aerosol liquid water also exhibited a controlling role in the heterogeneous uptake of N2O5 in this study as demonstrated by the evidently positive correlation ($R^2 = 0.74$) of ALWC and γ (N₂O₅) (Fig. 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 (N₂O₅) values with ALWC or RH in most regions in China, indicating that ALWC may be one of the rate-limiting steps of a 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 (N₂O₅) 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 N₂O₅ heterogeneous uptake is mainly caused by the competition of aerosol nitrate with chloride and H₂O for the $H_2ONO_2^+$ intermediate (Reactions R5–R8) (Bertram and Thornton, 2009). The positive correlation $(R^2 = 0.48)$ between γ (N₂O₅) and the molar ratio of Cl⁻/NO₃⁻ values was weaker than that of ALWC (Fig. 3d), which indicates that Cl⁻ may promote the N₂O₅ uptake reaction instead of playing a critical role during our observation. The particulate Cl⁻ concentration also contributes to a weaker enhancement of γ (N₂O₅) compared to ALWC in other field observations (Wang et al., 2020b; Yu et al., 2020; McDuffie et al., 2018).

3.3 Comparison of parameterized γ (N₂O₅) values

The γ (N₂O₅) values were predicted using 10 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



Figure 2. Overview of γ (N₂O₅); gas phase and particulate parameters; meteorological parameters; and NO₃ loss pathways. (a) Mean diurnal profiles of measured γ (N₂O₅), N₂O₅, *T*, RH, NO₂, O₃, PM_{2.5}, and NO. (b) Comparison of γ (N₂O₅) values in China, Europe, and North America calculated from previous work with measured values in this work. (c) Percentage of the NO₃ loss pathway via VOCs and N₂O₅ uptake at night.



Figure 3. Correlations of measured γ (N₂O₅) values between the influencing factors. Variation in γ (N₂O₅) with (**a**) the organic wet mass fraction, (**b**) the aerosol water content, (**c**) the aerosol nitrate content, and (**d**) the molar ratio of chloride to nitrate. The gray points represent the measured values. The symbols in different colors represent the median in each bin, with a range from the 10th to 90th percentile in each bin denoted as lines.

and inorganic kernels with organic coating or organic mass (inorganic + organic).

The γ (N₂O₅) values predicted by inorganic-only parameterizations were generally larger than the measurements. Among these inorganic-only parameterizations, RIE03, BT09 w/o Cl, and Yu20 exhibited relatively low deviation in predicted median values from the measurements (Fig. 4a). However, the correlations of the predictions and measurements were bad for these three parameterizations ($R^2 = 0$ – 0.09, Fig. 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 DAV08, BT09, and GRI09 was 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 γ (N₂O₅). For the parameterizations with a median deviation less than 10%, the parameterized γ (N₂O₅) 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.

The inorganic + organic parameterizations tend to underestimate the measured γ (N₂O₅) due to the suppression effects of organics. Worse agreement and larger scatter were found for the parameterized γ (N₂O₅) ($R^2 = 0-0.07$, Fig. 4c) when the organic part was added into inorganic part. BT09 + Rie09(wG14) showed the best correlation with an 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 parameterizations, similar to the results of inorganic-only parameterizations.

The commonly used parameterizations mainly consist of the inorganic and inorganic + organic framework, such as



Figure 4. Comparison of parameterized and measured γ (N₂O₅). (a) Comparison of the median difference and root mean square error (RMSE) between measured γ (N₂O₅) and parameterized γ (N₂O₅) values. The error bars of BT09 + Rie09wG14 and MD18 show the range of the results of the atomic O/C ratio between 0.5 and 0.8. The distribution of parameterized γ (N₂O₅) values, including (**b**) inorganic-only parameterizations (RIE03, DAV08, BT09 w/o Cl⁻, YU20) and (**c**) inorganic + organic parameterizations (EJ05, BT09 + Rie09, BT09 + Rie09wG14, MD18) (O/C = 0.8). The solid black 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.

BT09 w/o Cl, YU20, and MD18. In this study, among all parameterizations, YU20 demonstrated the best performance, most likely because YU20 was optimized based on datasets observed in four rural regions in China. BT09 w/o Cl also performed well in this study, overestimating the median by only 7%. However, the poor performance of BT09 w/o Cl was still reported in the Pearl River Delta and North China Plain (Wang et al., 2022, 2020b). Conversely, BT09 w/o Cl performed well in northwestern Europe, mainly because γ (N_2O_5) in Europe is predominantly controlled by the ions in the bulk phase (Morgan et al., 2015; Chen et al., 2018; Phillips et al., 2016). In North America, γ (N₂O₅) 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 γ (N₂O₅) is controlled by aerosol liquid water content, are more suited to YU20. European regions, where gamma is controlled by H_2O/NO_3^- and less influenced by organics, are better served by BT09 w/o Cl. 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 γ (N₂O₅)

Although some parameterizations performed relatively well in reproducing the median values of γ (N₂O₅), none of the 10 parameterizations were able to reproduce the range of measured γ (N₂O₅) values, as indicated by poor correlations and a large RMSE. This phenomenon was possibly caused by several aspects, including the inaccurate estimation of response coefficients of aerosol compositions (representing the quantitative relationship between γ (N₂O₅) 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, the phase state, and the mixing state (You et al., 2014; Shiraiwa et al., 2017; Ng et al., 2010). These parameters, which are difficult to measure in field conditions with current methodologies, have been proven to affect γ (N₂O₅) and can contribute to the discrepancy between parameterized and measured values.

ALWC is one of the factors controlling N2O5 uptake during our observation, and the coefficients related to ALWC should play a critical role in reproducing the varying range of γ (N₂O₅). To investigate the accuracy of the ALWCrelated response coefficients in γ (N₂O₅) parameterizations, we compared the parameterized and measured γ (N₂O₅) 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 (Fig. 5). At low ALWC, all six parameterizations showed an overestimation with the maximum difference for EJ05 (189%) and the minimum for MD18 (34%). At medium ALWC, the deviation of parameterized γ (N₂O₅) reduced to -8%-4%. At high ALWC, the parameterizations tend to underestimate the measured γ (N₂O₅) with the difference ranging from -37% to -1%. The treatment of ALWC-related effects on γ (N₂O₅) following the BT09 and Rie09 parameterization framework was generally better than that following RIE03 and EJ05. YU20 and MD18 showed the best performance across all three ALWC levels among inorganiconly 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



Figure 5. Comparison of the median values of measured and parameterized γ (N₂O₅) at low, medium, and high ALWC levels. The O/C settings of BT09 + Rie09wG14 and MD18 were 0.8 and 0.5, respectively.



Figure 6. The median difference in the nitrate production rates P (NO₃⁻) between measured and parameterized γ (N₂O₅) values during low, medium, and high ALWC conditions. The O/C setting of BT09 + Rie09wG14 was 0.8, and that of MD18 was 0.5.

can hardly capture the response of γ (N₂O₅) to largely varied ALWC.

The biased prediction of γ (N₂O₅) at low and high ALWC levels might cause considerable uncertainties in estimating the impacts of N₂O₅ uptake when ALWC varies largely in ambient conditions. We calculated the particulate nitrate production potential contributed by N2O5 uptake based on measured γ (N₂O₅) 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 (Fig. 6). Our results indicate that current parameterizations may lead to large deviations in nitrate production potential predictions. The contribution of the N2O5 heterogeneous reaction to nitrate production is important in some regions (Wang et al., 2021; S. Chen et al., 2020; 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 (N₂O₅) measurements under extreme ALWC levels, which helps to improve the reliability of response coefficients between γ (N₂O₅) and ALWC in ambient conditions.

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4 Conclusions

The γ (N₂O₅) values of 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 (N₂O₅) and impacting factors was consistent with previous laboratory results, except for aerosol chloride. The median of γ (N₂O₅) 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 γ (N₂O₅) by 34 %-189 % at low ALWC and underestimate it by -37 %-1 % at high ALWC, respectively. Among the 10 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 (N₂O₅) directly on ambient aerosols to improve the performance of parameterizations and better elucidate the environmental impacts of the N₂O₅ uptake reaction. Meanwhile, further studies on the mechanism of N2O5 uptake under extreme ALWC conditions would help to improve the accuracy of its response coefficients in parameterizations.

Code and data availability. The code and datasets used in this study are available from the corresponding authors upon request (chenxr95@mail.sysu.edu.cn, k.lu@pku.edu.cn).

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Author contributions. XC and KL designed the study. KL organized the field campaign with the help from YG. TZ and XC measured the γ (N₂O₅) data. CL, SX, HD, and SC provided the field data of normal gases, particulate components, and other supporting parameters. JL, TZ, XC, and HW analyzed the data. JL, TZ, and XC wrote the paper with input from KL.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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