Reply on comments

We appreciate the reviewer for the careful reading and their constructive comments on our manuscript. **As detailed below, the reviewer's comments are** in normal font**, and our responses to the comments are shown in *italicized font*. New or modified text is in blue.**

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The authors directly measured the uptake coefficient of N_2O_5 using an aerosol flow tube reactor in Kumin, a highland environment, in China. The possible influence factors on the $\gamma(N_2O_5)$ were discussed by correlation analysis in this work. ALWC was the most important one affecting the measured $\gamma(N_2O_5)$. The comparison between the measured $\gamma(N_2O_5)$ and parameterized values. Overall, the results are well presented and discussed. It is publishable after the following questions have been well addressed.

1. Considering many studies on the $\gamma(N_2O_5)$ by measurement, modeling, and parameterization methods, I am wondering what scientific assumption is focused on in this work. The uptake kinetics in different environments? Crucial factors determining the $\gamma(N_2O_5)$? Or the uncertainties of the parameterization method for $\gamma(N_2O_5)$? The authors should clarify the highlights and the novelty of this study.

Thanks for the suggestions. We mainly focused on the main factors determining the $\gamma(N_2O_5)$ in a southwestern area of China with high sea level and low influence from industrial activities. No $\gamma(N_2O_5)$ observation has been reported in this region, which therefore provide us an opportunity to evaluate the general performance of current $\gamma(N_2O_5)$ parameterizations under this typical environment. We found that median $\gamma(N_2O_5)$ predicted by some parameterizations agreed well with observations, whereas the parameterizations failed to reproduce the range of observed values and showed poor correlations. We found significant discrepancies between observed and

parameterized values at extreme levels of aerosol water content, indicating the need for the improvement of the response coefficients of aerosol water content. In addition, the relationship between the measured γ(N_2O_5) values and impacting factors was consistent with previous laboratory results, except for aerosol chloride.

This study introduces several novel contributions: First, the γ(N_2O_5) values were quantified through direct measurements with high accuracy and reliability. Second, a significant relationship between key influencing factors and the measured values was identified, providing deeper insights into the underlying mechanisms. Finally, this study systematically analyzed the possible reasons of discrepancies between parameterized and measured values, offering an evaluation for existing models. These advancements enhance our understanding of N_2O_5 uptake dynamics and provide a new insight for improving parameterization performances.

According to the above discussion, we revised the abstract as follows.

"The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) is a critical process in assessing NO_x fate and secondary pollutants (e.g. particulate nitrate) formation. However, accurate quantification of the N_2O_5 uptake coefficient (γ(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 γ(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 γ(N_2O_5) parameterizations under this typical environmental condition. The nocturnal mean γ(N_2O_5) value ranged from 0.0018 to 0.12 with an average of 0.023±0.021. The relationship between the measured γ(N_2O_5) values 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 value 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. ”

And we revised the conclusion as follows.

“The $\gamma(N_2O_5)$ 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 $\gamma(N_2O_5)$ and impacting factors was consistent with previous laboratory results, except for aerosol chloride. The median of $\gamma(N_2O_5)$ 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 $\gamma(N_2O_5)$ 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 $\gamma(N_2O_5)$ 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.”

2. It is somewhat too weak about the correlation analysis between the measured $\gamma(N_2O_5)$ and possible factors such as chemical composition and ALWC. The dataset is too small

and the data points are too scattering. So, it is hard to observe the significant correlation.

Thanks for the valuable comments and we understand the reviewer's concern. To ensure accurate measurements, a rigorous data screening process was implemented. A 10% cutoff for N_2O_5 variation was applied to excluding air masses that were too unstable for valid analysis according to our data screening criteria. Cases showing more than a 2% variation in relative humidity (RH) between HEPA inline and bypass modes were excluded due to significant influence of RH on k_{wall} of N_2O_5 wihthin the aerosol flow tube. To ensure significant N_2O_5 concentration differences resulted from heterogeneous uptake reactions between the top and bottom of the flow tube, periods with low Sa conditions (<100 $\mu m^2 cm^{-3}$) were filtered out. Additionally, cases where NO concentration exceeded 7 ppbv were excluded to avoid significant changes in NO_3-N_2O_5 concentration due to NO titration in the flow tube. Therefore, we get a relatively small dataset during this 35-day observation.

The correlations between the measured values and impacting factors seem not so significant within this ambient dataset. Actually, $\gamma(N_2O_5)$ in a real atmosphere can be affected by a combination of factors, which results in lower correlations of them than laboratory studies. Even so, the correlation (R^2) between aerosol liquid water and $\gamma(N_2O_5)$ in this study was 0.74, which is still higher than previous studies in China (0.65) and USA (0.15)(Yu et al., 2020;McDuffie et al., 2018;Wang et al., 2020) (Figure R1). To further confirm the relationships, we divide each impacting factor into three groups from smallest to largest. The trends of $\gamma(N_2O_5)$ varying with factors are shown in Figure R2. We find that $\gamma(N_2O_5)$ decreases significantly with organic wet mass fraction and aerosol nitrate, and increases with aerosol liquid water as well as Cl^-/NO_3^-, which are consistent with previous laboratory studies.

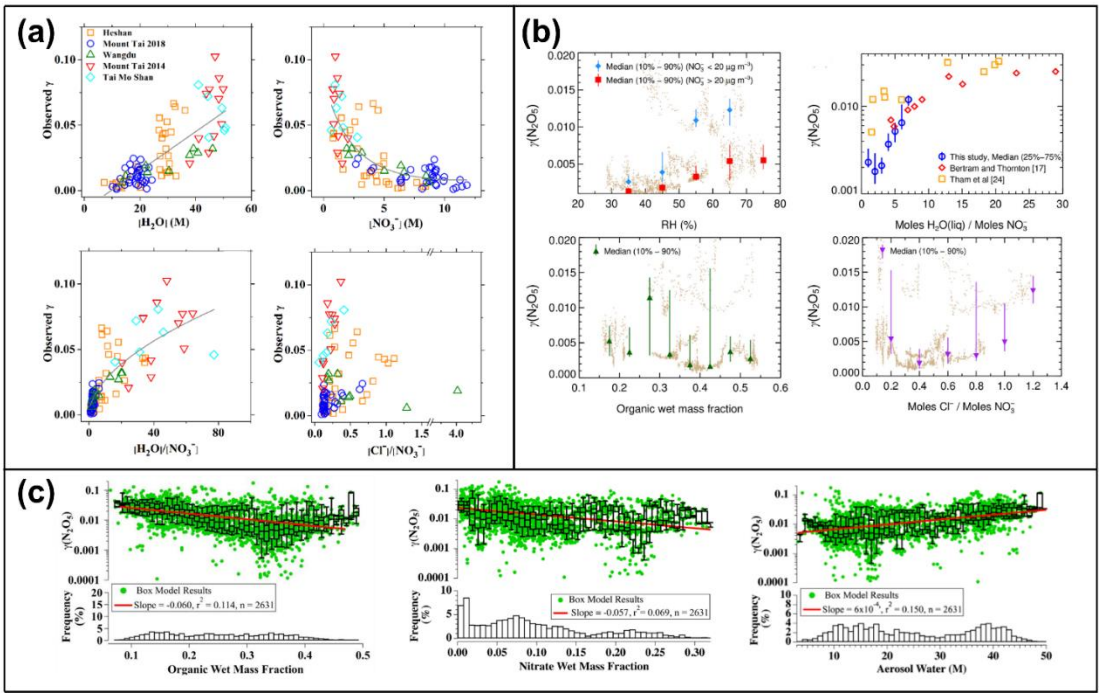

Figure R1. The correlations between γ(N_2O_5) and impacting factors in different field studies. *a:five field campaigns in China(Yu et al., 2020), b: field campaign in Beijing, China(Wang et al., 2020), c: field campaign in USA(McDuffie et al., 2018).*

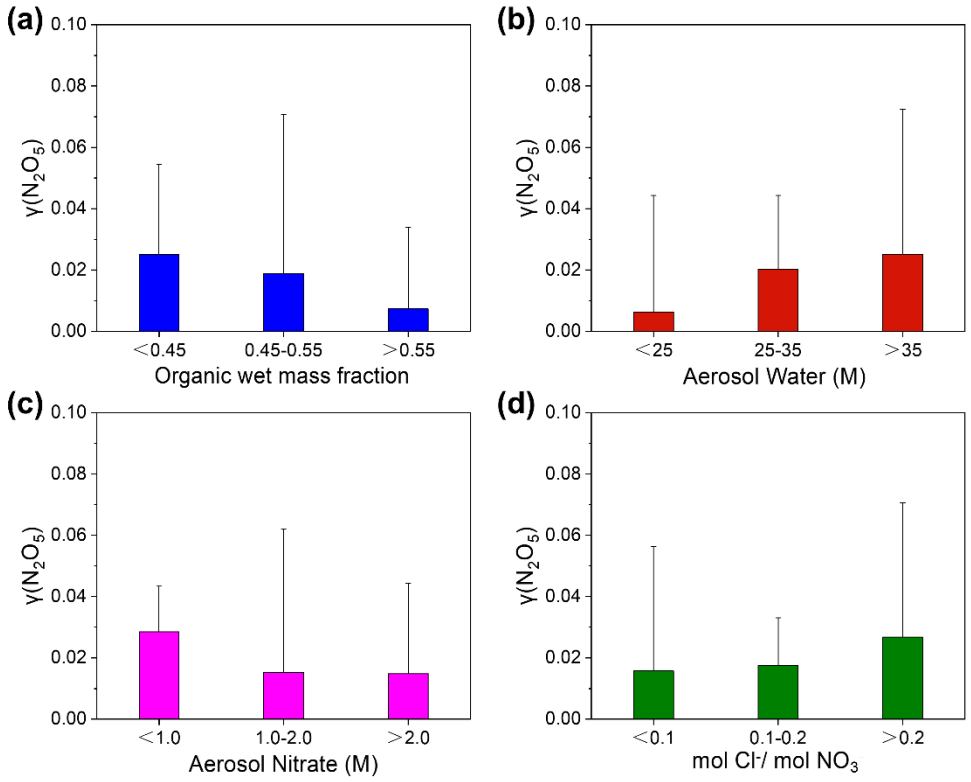

Figure R2. The correlations between measured γ(N_2O_5) values and impacting factors. *Variation of γ(N_2O_5) with organic wet mass fraction (a), the aerosol water*

content (b), the aerosol nitrate content (c), and molar ratio of chloride to nitrate (d). Each impacting factor was divided into three groups, the error bars represent the data range from 10th to 90th percentile in each bin.

3. About the negative correlation between organic aerosol and $\gamma(N_2O_5)$, is the $\gamma(N_2O_5)$ possibly affected by other factors when the concentration of organic is high along with a low $\gamma(N_2O_5)$? Unless organic aerosol is well mixed with other components, i.e., in an ideal inner mixed state.

Thanks for your comments. The negative correlation between organic wet mass fraction and $\gamma(N_2O_5)$ actually may not be influenced by other factors due to the possible formation of organic coating on aerosols when the concentration of organic is high in this study. Previous laboratory studies have proved that organics can suppress the uptake reaction by forming a coating on the surface of the particles and regulating the aerosol liquid water content and the passage rate of N_2O_5 molecules into particles (Folkers et al., 2003;Gaston et al., 2014;Anttila et al., 2006)). To investigate this problem, a table of Pearson Correlation Coefficient (r) among factors affecting $\gamma(N_2O_5)$ was calculated, as shown in Table S3, to find the covariations of organics and other aerosol components or impact factors. The organic wet mass fraction showed a negative correlation with aerosol water (r=-0.79), and the correlations with other factors were insignificant. It indicates that the organic coating may occur on most aerosols and limit the penetration of the liquid water into the bulk phase. Therefore, organics might affect $\gamma(N_2O_5)$ mainly by regulating aerosol liquid water content and thus limit the effects of other factors in this study.

We added the discussion in section 3.2 in the main text as follows.

"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 $\gamma(N_2O_5)$. 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 $\gamma(N_2O_5)$ 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."

The table added in supporting information is as follows.

***Table S3. Pearson Correlation Coefficient (r) among factors affecting $\gamma(N_2O_5)$**, the statistical data are limited to the period in which measured $\gamma(N_2O_5)$ is available.*

Factors	*Temp*	*RH*	*Aerosol Water*	*Aerosol Nitrate*	*H_2O/NO_3^- Molar ratio*	*Aerosol Chloride*	*Cl^-/NO_3^- Molar ratio*	*Org dry mass fraction*	*Org wet mass fraction*	*Org/SO_4^{2-}*
Temp	*1.00*	*-0.85*	*-0.45*	*-0.27*	*0.09*	*-0.30*	*-0.12*	*0.15*	*0.24*	*0.09*
RH	*-*	*1.00*	*0.49*	*0.45*	*-0.27*	*0.24*	*-0.09*	*-0.12*	*-0.23*	*-0.08*
Aerosol Water	*-*	*-*	*1.00*	*-0.40*	*0.62*	*-0.10*	*0.19*	*-0.66*	*-0.79*	*-0.68*
Aerosol Nitrate	*-*	*-*	*-*	*1.00*	*-0.80*	*0.24*	*-0.39*	*0.34*	*0.38*	*0.43*
H_2O/NO_3^- Molar ratio	*-*	*-*	*-*	*-*	*1.00*	*-0.21*	*0.45*	*-0.64*	*-0.67*	*-0.67*
Aerosol Chloride	*-*	*-*	*-*	*-*	*-*	*1.00*	*0.69*	*-0.02*	*0.01*	*0.06*
Cl^-/NO_3^- Molar ratio	*-*	*-*	*-*	*-*	*-*	*-*	*1.00*	*-0.37*	*-0.35*	*-0.33*
Org dry mass fraction	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*1.00*	*0.98*	*0.97*
Org wet mass fraction	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*1.00*	*0.96*
Org/SO_4^{2-}	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*-*	*1.00*

4. ALWC is the most important factor affecting $\gamma(N_2O_5)$. However, ALWC is greatly determined by nitrate concentration or fraction in PM2.5. Why does $\gamma(N_2O_5)$ show a different dependence on nitrate like ALWC?

ALWC can be affected by many factors, such as RH, particle sulfate, particle nitrate, and particle organics. In this study, as shown in Table S3, ALWC mainly correlates with organic dry mass fraction (r=-0.66) and RH (r=0.49). The relatively low nitrate mass fraction (5%) observed in Kunming suggests its potential contribution

to ALWC may be limited in this region.

For the reason of different dependence, particulate nitrate acts as a competing role to H_2O when participates in N_2O_5 uptake reaction in the bulk phase. The currently proposed mechanism for the N_2O_5 heterogeneous uptake (R1-R4) posits that upon entering the liquid phase, N_2O_5 initially decomposes into nitrate (NO_3^-) and the intermediate ion $H_2ONO_2^+$. Reactions R1 and R2 are reversible, and an increase in NO_3^- concentration inhibits the decomposition of N_2O_5 in the liquid phase, promoting its desorption back into the gas phase. Hence, particulate nitrate and $\gamma(N_2O_5)$ showed a negative correlation which is different from ALWC.

$$N_2O_5\ (g) \leftrightarrow N_2O_5\ (aq) \qquad (R1)$$

$$N_2O_5(aq) + H_2O(l) \leftrightarrow H_2ONO_2^+(aq) + NO_3^-\ (aq) \qquad (R2)$$

$$H_2ONO_2^+\ (aq) + H_2O(l) \rightarrow HNO_3(aq) + H_3O^+\ (aq) \qquad (R3)$$

$$H_2ONO_2^+\ (aq) + HX(aq) \rightarrow XNO_2(aq) + H_3O^+\ (aq) \qquad (R4)$$

We revised the discussion in section 3.2 to further clarify this point in the main text as follows.

"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)."

5. In Figure 2b, it is better to compare the $\gamma(N_2O_5)$ distribution among different methods.

According to the reviewer's suggestion, we attempted to calculate the uptake coefficient using indirect quantitative methods. However, previous studies have demonstrated that indirect quantitative methods have strict applicable scenarios. The steady-state method is more suitable for air masses with high aerosol concentrations, high temperatures, and moderate levels of kNO_3, making it more applicable in polluted regions with high aerosol loading during summertime(Chen et al., 2022). The box model method is significantly affected by uncertainties of N_2O_5 concentration and may cause order-of-magnitude overestimations under conditions of low air mass age, low O_3 concentration or high NO concentration, and high N_2O_5 uptake(Wagner et al.,

2013;Chen et al., 2022). During our observation, the measurements were influenced by NO concentration from traffic emissions. The air mass was relatively clean with low N_2O_5 concentration, which did not satisfy the necessary conditions for applying the iterative box model and steady-state method to calculate $\gamma(N_2O_5)$. Therefore, it is not feasible to obtain accurate $\gamma(N_2O_5)$ values using indirect quantitative methods in this study.

6. In Figure 4, the performances of these parameterization methods look too bad. I am wondering how about the performances of models widely used in literature.

The widely used parameterizations in models mainly include BT09, BT09w/oCl and MD18. The BT09 always overestimates the median $\gamma(N_2O_5)$ values, primarily attributable to its overestimated enhancement effect of chloride (Cl-)(Chang et al., 2016;Yu et al., 2020;Morgan et al., 2015). Similar results have also been found in this study with an 88% overestimation. In this study, BT09w/oCl and MD18 capture the median well, but fail to reproduce the range and variability of the measured values. Although these two parameterizations show less than 10% deviation compared to measured values, they exhibit notably low correlation coefficients (r^2 = 0.07 for BT09w/oCl and 0.05 for MD18). The low correlation has also been reported in the campaign in the United States (R^2 = 0.18 for BT09w/oCl and 0.17 for MD18)(McDuffie et al., 2018). In other regions, BT09w/oCl even showed different degrees of overestimations due to the absence of organic suppression or other influencing factors (Morgan et al., 2015;McDuffie et al., 2018). For instance, this parameterization overpredicts the median by 81% in Beijing, China (Wang et al., 2020).

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