

Response to Referee #1

The authors present new measurements of the N₂O₅ uptake coefficient from field measurements in China. The additional measurements are of great value to the ongoing interpretation of N₂O₅ heterogeneous chemistry. The manuscript is well written and should be published following the authors attention to the following details:

Response: We appreciate the reviewer for the encouraging and helpful comments on our manuscript. We have made all of the suggested changes and clarifications. The reviewer's comments are in black, and our responses are in blue, and the changes in the manuscript are in red.

Line 78: It would be helpful to clarify what “rural” refers to. If this is meant to denote a chemical regime, it would be helpful to classify by chemical composition (e.g., PM_{2.5}, NO_x, O₃, CO, etc).

Response: Heshan site was considered as a semi-rural site because the site is located outside towns and far from the urban area. The site was mostly affected by natural emission and some agriculture activities, with limited influences from the transport of anthropogenic emissions (e.g., industry and vehicles). The average concentrations of PM_{2.5} and trace gases during the campaign were shown in Fig. 1b. We have revised the text to make it clearer, as follows,

“Field measurements of $\gamma_{\text{N}_2\text{O}_5}$ and related parameters were conducted at a semi-rural site (Heshan) in southern China from 22 February to 28 March 2017 and at a mountain site (Mt. Tai) in northern China from 11 March to 8 April 2018. Heshan site was located on a small hill (22.73°N, 112.92°E, 60 m a.s.l), surrounded by subtropical trees and some farmlands. A small city, Heshan, is 10 km to the northeast of the site, and three large cities, Guangzhou (the capital of Guangdong Province), Foshan and Jiangmen, are 80 km to the northeast, 50 km to the northeast and 30 km to the southwest of the site, respectively. The site is affected by vehicle emissions from three highways and two provincial roads within 10 km and some residential/agriculture activities in the area, and thus was considered as a semi-rural site.”

“All the sites are regionally representative sites, as they are situated in an area with limited anthropogenic influences (Tham et al., 2016; Wang et al., 2017a; Yun et al., 2018; Wang et al., 2016). The detailed information of the sampling sites, instrumentation, and $\gamma_{\text{N}_2\text{O}_5}$ determination approach have been described in the previous publications (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a), and site descriptions are briefly summarized in the SI. The locations of all the measurement sites are shown on the map in Fig. 1a. The statistics of the trace gases and PM_{2.5} measured during the campaigns were summarized in Fig. 1b, representing general pollution conditions at these sites. The mean concentration of O₃, NO_x and PM_{2.5} at these sites ranged from 43 to 80 ppbv, 2.4 to 14.5 ppbv and 9.9 to 80.2 $\mu\text{g m}^{-3}$, respectively.”

Lines 92 – 121: A reference to the original work of Bertram et al should be included here as the design and sampling approach appear to very closely replicate the technique described in

Bertram et al., AMT 2009. Also, the uncertainty is a function of the surface area and RH, I find it nearly impossible that the uncertainty ranges only between 37-40% for the range of atmospheric conditions sampled. If this is correct, more discussion should be included.

Response: Thanks for the suggestions. The reference to Bertram et al. has been added to the manuscript. The uncertainty was described in detail in our previous paper (Wang et al., 2018) and $\gamma_{\text{N}_2\text{O}_5}$ was found to be most sensitive to RH, and more discussion was added in the revised manuscript.

The revised text reads,

“The uptake coefficient of N_2O_5 , $\gamma_{\text{N}_2\text{O}_5}$, was derived from the direct measurement of the loss rate coefficient of N_2O_5 on ambient aerosols using an aerosol flow tube based on the design of Bertram et al. (2009), with some improvements and coupling with an iterative box model for polluted environments (Wang et al., 2018).”

“The uncertainty introduced by S_a measurement would be propagated to an uncertainty of 30% in the calculated $\gamma_{\text{N}_2\text{O}_5}$. The improvement with the use of the box model in the system could minimize the influences from the variability of ambient conditions as well as fresh NO emission, and a Monte Carlo approach was employed to evaluate the uncertainty from different parameters (Wang et al., 2018). The estimated uncertainty ranged from 37% to 40% at $\gamma_{\text{N}_2\text{O}_5}$ around 0.03 and from 34% to 65% at $\gamma_{\text{N}_2\text{O}_5}$ around 0.01 with $S_a = 1000 \mu\text{m}^2 \text{cm}^{-3}$ when RH varied from 20% to 70 %, and could be higher at $\text{RH} > 70\%$.”

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Line 156: It is not clear how the uptake coefficient at 50M H₂O which is essentially pure water is significantly larger than 0.03 (that measured for pure water in the laboratory). The authors should provide some discussion for how the ‘measured’ uptake coefficients are exceeding the rate for N_2O_5 with pure water? The limit observed in Hallquist, Thornton, ad Bertram and Thornton (all laboratory studies) correspond to reaching the upper limit of N_2O_5 uptake to pure water.

Response: Thanks for the suggestions. We were aware that many previous laboratory studies (Hallquist et al., 2000; Hallquist et al., 2003; Thornton et al., 2003; Thornton et al., 2005) had observed the N_2O_5 uptake on different particles (e.g., sulfuric acid, ammonium sulfate/bisulfate, malonic acid and sea salt) showing strong dependence on RH below 50% but reaching an upper

limit around 0.036 at RH around 50%-80%. However, there were also higher $\gamma_{\text{N}_2\text{O}_5}$ values measured by different laboratory studies. For example, Mozurkewich and Calvert (1988) reported an upper limit of $\gamma_{\text{N}_2\text{O}_5}$ on NH_4HSO_4 particles of 0.056 at RH = 55% at 293K, which increased to around 0.1 at 274K. Kane et al. (2001) observed a strong RH dependent $\gamma_{\text{N}_2\text{O}_5}$ on NH_4HSO_4 particles, increasing from 0.018 to 0.069 with RH from 56% to 99%. Moreover, several field measurements also reported the $\gamma_{\text{N}_2\text{O}_5}$ exceeding 0.04 at high RH or water molarity (e.g. Philips et al., 2016; McDuffie et. al, 2018; Wang H et al., 2017; Tham et. al, 2018), and some of them found the similar positive relationship between $\gamma_{\text{N}_2\text{O}_5}$ and water molarity (McDuffie et. al, 2018). Although uncertainties may exist in the calculation of aerosol surface and uptake coefficient at high ambient RH conditions, our results here indicate that the aerosol water content strongly affects the activity of N_2O_5 uptake, and the N_2O_5 hydrolysis is always limited by aerosol water content. It is unclear what exact mechanism or process (e.g., phase change different from laboratory-made particles, or acidity involved) promote more effective uptake on ambient aerosols at higher RH and water content condition due to the limited measurement data in laboratory and field. More detailed investigation of N_2O_5 uptake on nano-size water/aerosol droplets in the real (or close to real) ambient conditions are clearly warranted.

More discussion is added in the revised text, as follows:

“Although the positive correlation of $\gamma_{\text{N}_2\text{O}_5}$ with the humidity or aerosol water has been observed in the low range in previous laboratory studies, the $\gamma_{\text{N}_2\text{O}_5}$ reached plateaus at a value around 0.036 at RH > 50% or $[\text{H}_2\text{O}] > 15 \text{ M}$ (Hallquist et al., 2003; Thornton et al., 2003; Bertram & Thornton, 2009). In contrast, other laboratory studies also measured higher $\gamma_{\text{N}_2\text{O}_5}$ values on NH_4HSO_4 particles. For example, Mozurkewich and Calvert (1988) reported an upper limit of $\gamma_{\text{N}_2\text{O}_5}$ of 0.056 at RH = 55% at 293 K, which increased to around 0.1 at 274 K. Kane et al. (2001) observed a strong RH dependent $\gamma_{\text{N}_2\text{O}_5}$, increasing from 0.018 to 0.069 with RH from 56% to 99%, which is largely consistent with the field results in the present study. Moreover, several field measurements also observed $\gamma_{\text{N}_2\text{O}_5}$ value exceeding 0.04 at high RH or water molarity (e.g. Philips et al., 2016; McDuffie et. al, 2018a; Wang et al., 2017c; Tham et. al, 2018), and some of them also found the similar positive relationship between $\gamma_{\text{N}_2\text{O}_5}$ and water molarity (McDuffie et. al, 2018a). Although uncertainties may exist in the calculation of aerosol surface and uptake coefficient at high ambient RH conditions, our results with a consistently increasing trend of $\gamma_{\text{N}_2\text{O}_5}$ with $[\text{H}_2\text{O}]$ from below 10 M up to 50 M suggest that the aerosol water content strongly affects the activity of N_2O_5 uptake, and that N_2O_5 hydrolysis is always limited by aerosol water content under all the encountered ambient conditions. Since limited measurement data of $\gamma_{\text{N}_2\text{O}_5}$ from laboratory and fields are available at RH > 80% condition, it is unclear what exact mechanism or process (e.g., phase change different from laboratory-made particles or acidity involved) promote more effective uptake on ambient aerosols at higher aerosol water content condition. Therefore, more detailed investigations of N_2O_5 uptake on nano-size water/aerosol droplets in the real (or close to real) ambient conditions are clearly warranted.”

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Line 158: Linear not liner.

Response: Corrected.

Line 180: Correct use of the Bertram and Thornton parameterization involves calculating the aerosol water content for both the organic and inorganic components. Also, something doesn't seem to add up in the parameterization of the uptake coefficient. What value for V/S and KH were used and what temperature was this run at? It was my understanding that the parameterization could not exceed 0.03 based on the hydrolysis rate and Henry's law coefficient used in the parameterization.

A note on empirical parameterizations: I think there is an opportunity to use field measurements to tune mechanistic parameterizations. Although, it seems unlikely that field measurements will do a better job than laboratory measurements at constraining rate coefficients or ratios of rate coefficients for the inorganic reactions. Laboratory experiments are designed to do this, using targeted simple 1-2 component systems and 1000x the aerosol surface area. I would expect the

real power is looking at the variability in the hydrolysis rate or Henry's law terms that are required to match the measurements with the models. This is where the complexity of the atmospheric aerosol will cause issues in laboratory parameterizations.

Response: Thanks for the helpful comments. First, we want to clarify that the V_a/S_a values varied from 3.30×10^{-8} m to 9.29×10^{-8} m in different cases, and were measured from the particle number and size distribution by WPS or SMPS in different campaigns. The Henry's law dimensionless constant of K_H was taken as 51, following the Bertram and Thornton parameterization. The temperature ranged from 3°C to 28°C in different cases in the five campaigns.

Secondly, as shown in the Bertram and Thornton parameterization, $\gamma_{\text{N}_2\text{O}_5}$ was linearly dependent on the V_a/S_a value by assuming a volume-limited reaction. Because the average V_a/S_a of 3.75×10^{-8} m was used in their study, the upper limit of $\gamma_{\text{N}_2\text{O}_5}$ at high $[\text{H}_2\text{O}]$ from the parameterization was around 0.036. And the upper limit of $\gamma_{\text{N}_2\text{O}_5}$ would increase proportionally to the increase of V/S value.

In addition, since Bertram and Thornton observed that the $\gamma_{\text{N}_2\text{O}_5}$ was insensitive to RH above 50%, they treated the reaction rate coefficient of $[\text{N}_2\text{O}_5]$ with $[\text{H}_2\text{O}]$ as an inverse exponential function of $[\text{H}_2\text{O}]$. In the present study, we use the original second-order rate definition of water reaction term as $k_{2f}[\text{H}_2\text{O}]$, which leads to a linear dependence of $\gamma_{\text{N}_2\text{O}_5}$ on $[\text{H}_2\text{O}]$ and is consistent with our field observation results. The secondary order rate constant k_{2f} was fitted to be $(3.0 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, which is in reasonable agreement with the values of $(2.7\text{--}3.8) \times 10^4$, $\sim 3.9 \times 10^4$ and $2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ determined from ammonium bisulfate, ammonium sulfate (Gaston et al., 2016) and aqueous organic acid particles (Thornton et al. 2003), respectively.

We agree with the reviewer that it would be an opportunity to use the field data to tune mechanistic parameters such as Henry's law term. Different K_H values have been used in previous studies, e.g., ~ 50 (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009) or ~ 120 (corresponding to a Henry's law of 5M/atm at 298K) (e.g., Gaston et al., 2014; 2016; Griffiths et al., 2009). The $\gamma_{\text{N}_2\text{O}_5}$ in the parameterization is also linearly dependent on the K_H , and thus an increase of K_H value would proportionally increase the $\gamma_{\text{N}_2\text{O}_5}$ value but cannot account for the large variability of measured $\gamma_{\text{N}_2\text{O}_5}$ comparing to the parameterized values. In addition, there is lack of an explicit function of effective Henry's law constant for N_2O_5 to include the 'salting-in' effect and other processes, therefore in the present study, we use the value of 51 suggested by Bertram and Thornton and enclosed the influences from the aerosol composition in the last 'chemical' term. The derived empirical ratios in the last 'chemical' term not only represent the competing ratio of these reactions but also include other unspecified effects or influences (e.g., organic coating, mixing state, other nucleophiles reactions, etc.).

We have clarified this and added more discussion in the revised text, as follows,

“where V_a/S_a is the measured aerosol volume to surface area ratio, ranging from 3.30×10^{-8} to 9.29×10^{-8} m in the five campaigns; K_H is Henry's law coefficient, taken as 51 (Bertram &

Thornton, 2009; Fried et al., 1994);”

“In view of the linear dependence of $\gamma_{\text{N}_2\text{O}_5}$ on the aerosol water content in this study and reaction mechanism (Bertram & Thornton, 2009), the second-order reaction rate coefficient with water (refer to k'_{2f} in Eq. (2) and Eq. (3)) was fitted as a linear function of $[\text{H}_2\text{O}]$, as $(3.0 \pm 0.4) \times 10^4 \times [\text{H}_2\text{O}]$. This value is in reasonable agreement with the values of $(2.7\text{--}3.8) \times 10^4$, $\sim 3.9 \times 10^4$, and $2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ determined from ammonium bisulfate, ammonium sulfate (Gaston et al., 2016) and aqueous organic acid particles (Thornton et al. 2003), respectively. Compared to original BT09 (Eq. (3)), the newly fitted k'_{2f} is smaller for $[\text{H}_2\text{O}] < 38 \text{ M}$, but become higher with the increasing of aerosol water content (Fig. S2). Different dimensionless K_{H} values have been used in previous studies, e.g., ~ 50 (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009) or ~ 120 (e.g., Gaston et al., 2014; 2016; Griffiths et al., 2009), which correspond to a Henry’s law constant of 2 or 5 M atm^{-1} at 298K. As $\gamma_{\text{N}_2\text{O}_5}$ in the parameterization is linearly dependent on the K_{H} , an increase of K_{H} value would proportionally increase the $\gamma_{\text{N}_2\text{O}_5}$ value but cannot account for the large variability of measured $\gamma_{\text{N}_2\text{O}_5}$ values. Given the lack of an explicit function of effective Henry’s law constant for N_2O_5 to include the different process (e.g., ‘salting-in’ effect and surface processes), we use the value of 51 suggested by Bertram and Thornton (2009) and enclose those effects from the aerosol composition in the last ‘chemical’ term. The derived empirical ratios in the last ‘chemical’ term not only represent the competing ratio of these reactions but also include other unspecified effects or processes (e.g., organic coating, mixing state, other nucleophiles reactions, etc.).

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Response to Anonymous Referee #2

This study developed an improved observation-based parameterization of N₂O₅ uptake coefficient and showed that the new parameterization improved the simulation results of NO₂ and NO₃- by the WRF-CMAQ model. The manuscript is generally well written. I think that it can be considered for publication after the authors address the following comments and suggestions.

Response: We appreciate the reviewer for the helpful comments on our manuscript. We have made all of the suggested changes and clarifications. The reviewer's comments are in black and our responses are in blue, and the changes in the manuscript are in red.

1. Please clearly indicate the scope of application of the new parameterization. Is it applicable to China only or the whole world? I suggest that you apply the parameterization to all the sites shown in Fig. 3 to examine how it performs in other regions of the world. Even within China, please comment on whether the five sites used in this study are representative of China's general environmental conditions.

Response: We think the empirical parameterization should be applicable to different areas in China, especially those polluted regions. The four sites were all located in semi-rural areas with regional representativeness in north or south China. For the sites other than described in this study in Fig. 3, the detailed experimental data such as inorganic compositions and V_a/S_a of each data points are not available in the literature, and thus it is not possible for us to evaluate and compare the new empirical parameters at all other sites in the world. We advocate further validation of the parameterization derived from the present study in other regions of the world.

We added more information to clarify it, as follows,

“All the sites are regionally representative sites, as they are situated in an area with limited anthropogenic influences (Tham et al., 2016; Wang et al., 2017a; Yun et al., 2018; Wang et al., 2016). The detailed information of the sampling sites, instrumentation and $\gamma_{N_2O_5}$ determination approach have been described in the previous publications (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a), and site descriptions are briefly summarized in the SI. The locations of all the measurement sites are shown on the map in Fig. 1a. The statistics of the trace gases and PM_{2.5} measured during the campaigns were summarized in Fig. 1b, representing general pollution conditions at these sites. The mean concentration of O₃, NO_x and PM_{2.5} at these sites ranged from 43 to 80 ppbv, 2.4 to 14.5 ppbv and 9.9 to 80.2 $\mu\text{g m}^{-3}$, respectively.”

“More tests of this empirical parameterization are warranted for other locations/seasons in China and other parts of the world.”

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2. You only evaluated the CMAQ simulation results against NO₂ and NO₃⁻ observations. Since you made many N₂O₅ and ClNO₂ measurements in this study, I strongly suggest that you also compare the simulation results with these data to better evaluate the performance of the new parameterization in CMAQ. In fact, I think the evaluation results of N₂O₅ may more directly reflect the performance of the N₂O₅ uptake parameterization.

Response: We agree with the reviewer that the comparison of simulated N₂O₅ could provide a more direct evaluation of the performance of the new parameterization. Because of the short lifetime of N₂O₅ (usually several to ten minutes) (Tham et al., 2018; Yun et al., 2019), it is more prone to be affected by local emissions and fluctuation of meteorological parameters. For the regional models with a grid resolution of tens of kilometers, it is difficult for the regional model to capture the variation of N₂O₅. We made a comparison of the statistic results of simulated N₂O₅ concentrations in winter 2017 with those observed in the wintertime at various locations of China, including two in the North China Plain (Beijing and Wangdu in Hebei province) and two in southern China (Tai Mao Shan and Heshan). With the new parameterization, the WRF-Chem model can better simulate the average concentrations and variation ranges of N₂O₅ at these locations. The results were added as the new Figure 6, and the discussions were also added, as follows,

“In addition to NO₂ and NO₃⁻, we also compared the simulated N₂O₅ concentrations for December 2017 with those observed in the wintertime at various locations of China, including two in the North China Plain (Beijing and Wangdu in Hebei province) and two in southern China (Tai Mao Shan and Heshan). As shown in Figure 6, with the new parameterization, the WRF-CMAQ model can better simulate the average concentration and variation range of N₂O₅ at these locations. Overall, the new parameterization has significantly reduced the discrepancies between the modelled and observed concentrations of NO₂, N₂O₅ and NO₃⁻ at our study sites and periods in both northern and southern China. More tests of this empirical parameterization are warranted for other locations/seasons in China and other parts of the world.”

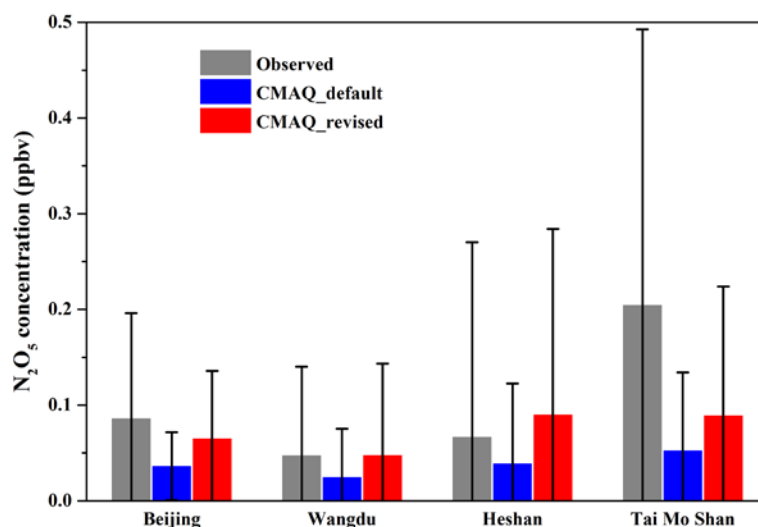


Figure 6. Comparison of the simulated N_2O_5 concentrations by the CMAQ model for December 2017 with the wintertime observation results from four sites in China. The field observations were conducted in December 2017 at Wangdu, January 2018 at Beijing, January 2018 at Heshan and November 2013 at Tai Mo Shan. The columns and error bars represent the average value and standard deviation, respectively.

3. Line 246-249: Your modeling domain covers the whole China and this sentence implies that you do have observational data in southern China. In this case, it looks strange that you only evaluated the simulation results over the North China Plain. I suggest that you provide a quantitative evaluation in southern China rather than just a speculation here.

Response: We focused on northern China for Dec 2017 in evaluating the new parameterization in part because of the availability of the unique regional observations of $PM_{2.5}$ nitrate aerosol. We agree that comparisons with N_2O_5 observations are valuable. As responded to comment #2, we have further compared the model simulation in southern China with our previous field observations at Heshan and Tai Mo Shan, and the comparison results of N_2O_5 are now included in the revised text, see the response to above comment #2.

4. Line 130-132: Although the detailed configuration of CMAQ has been described in a previous paper, I think it is still helpful to briefly describe some key configurations, especially those related to $NO_2/N_2O_5/CINO_2/NO_3$ - chemistry.

Response: Adopted and a brief description of CMAQ configuration is added.

“In addition, the Community Multiscale Air Quality (CMAQ) model (v5.1) was employed to evaluate the uptake parameterization. Two simulations (default and revised) were conducted. In the default case, the N_2O_5 uptake and $CINO_2$ production were calculated based on the parameterization of Bertram and Thornton (2009). In the revised case, the new parameterization derived in this study was used. Other model configurations were the same. The SAPRC07tic

gas mechanism and AERO6i aerosol mechanism was used. Weather Research and Forecasting (WRF) (v4.0) was applied to generate the meteorological inputs for the CMAQ simulations. The anthropogenic emission inputs were generated based on the local Chinese emission inventory (Zhao et al. 2018) and the INTEX-B dataset for Asia (Zhang et al., 2009). The high-resolution chloride emission inventory for China from Fu et al. (2018) was also included. More details for model configuration can be found in Fu et al. (2019). The simulation domain covers China with a resolution of 36×36 km (Fig. S1), based on a Lambert projection with two true latitudes of 25°N and 40°N.”

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5. Fig. 2d: Obviously the curve does not fit the data points well. Could you justify why you select this formula?

Response: Thanks for pointing this out. The curve was fitted just to check whether the trend following the relationship between $\gamma_{\text{N}_2\text{O}_5}$ and $\text{Cl}^-/\text{NO}_3^-$ derived from laboratory studies. The discrepancy of the data and the curve shows the Cl^- enhancement in our study is not as strong or obvious as that found in other laboratory studies. To avoid misleading the reader, the fitting curve is removed from Fig. 2d.

Heterogeneous N_2O_5 reactions on atmospheric aerosols at four Chinese sites: Improving model representation of uptake parameters

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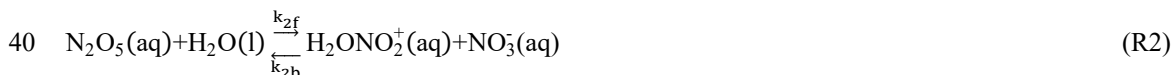
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Abstract. Heterogeneous reactivity of N_2O_5 on aerosols is a critical parameter in assessing NO_x fate, nitrate production, and particulate chloride activation. Accurate measurement of its uptake coefficient ($\gamma_{\text{N}_2\text{O}_5}$) and representation in air quality model are challenging, especially in the polluted environment. With an in-situ aerosol flow tube system, the $\gamma_{\text{N}_2\text{O}_5}$ was directly
20 measured on ambient aerosols at two rural sites in northern and southern China. The results were analyzed together with the $\gamma_{\text{N}_2\text{O}_5}$ derived from previous field studies in China to obtain a holistic picture of N_2O_5 uptake and the influencing factors under various climatic and chemical conditions. The field derived/measured $\gamma_{\text{N}_2\text{O}_5}$ was generally promoted by the aerosol water content and suppressed by particle nitrate. Significant discrepancies were found between the measured $\gamma_{\text{N}_2\text{O}_5}$ and that estimated
25 from laboratory-determined parameterizations. An observation-based empirical parameterization was derived in the present work, which better reproduced the mean value and variability of the observed $\gamma_{\text{N}_2\text{O}_5}$. Incorporating this new parameterization in a regional air quality model (WRF-CMAQ) has improved the simulation of nitrogen oxides and secondary nitrate in the polluted regions of China.

1 Introduction

30 Heterogeneous reaction of dinitrogen pentoxide (N_2O_5) on aerosol surfaces plays an important role in the nocturnal removal of nitrogen oxides (NO_x), secondary nitrate formation, and chlorine activation through nitryl chloride (ClNO_2) production on chloride-containing aerosols (Brown et al., 2006; Osthoff et al., 2008; Thornton et al., 2010; Wang et al., 2016). Realistically representing this process in air quality models is therefore necessary for the prediction and mitigation of ground-level ozone

and particulate pollution. The currently accepted mechanism of the heterogeneous reaction of N_2O_5 on aqueous aerosols starts with the mass accommodation of N_2O_5 on aerosol surface (R1), followed by reversible N_2O_5 hydrolysis to form nitrate and intermediate $H_2ONO_2^+$ in the aqueous phase (R2). The intermediate $H_2ONO_2^+$ will react with H_2O or Cl^- to form HNO_3 or $ClNO_2$, respectively (R3 and R4) (Behnke et al., 1997; Finlayson-Pitts et al., 1989; Schweitzer et al., 1998; Thornton and Abbatt, 2005; Bertram and Thornton, 2009).



The reaction probability of N_2O_5 , the so-called uptake coefficient $\gamma_{N_2O_5}$, is the fraction of N_2O_5 net removal upon collisions on aerosols, and is a key parameter to describe the heterogeneous loss rate of N_2O_5 on ambient aerosols. $\gamma_{N_2O_5}$ was first measured using aerosol flow tube in the laboratory and was shown dependent on aerosol chemical compositions such as water content, nitrate concentration, chloride concentration and organic coatings. Specifically, the aerosol water content can enhance the N_2O_5 uptake by promoting the hydrolysis of N_2O_5 (e.g. Hallquist et al., 2003; Thornton et al., 2003), while ~~high~~-nitrate favors the reverse of reaction (R2) and thus suppress the N_2O_5 uptake (e.g. Wahner et al., 1998; Bertram & Thornton, 2009). On the contrary, chloride in the aqueous aerosol will react with the intermediate $H_2ONO_2^+$ faster than NO_3^- and negate the nitrate suppression effect (e.g. Behnke et al., 1997; Bertram & Thornton, 2009). Organic coatings also can suppress N_2O_5 uptake by inhibiting the mass accommodation of N_2O_5 or limiting the availability of liquid water on the aerosol surface (e.g. Thornton & Abbatt, 2005; Anttila et al., 2006; Cosman et al., 2008; Gaston et al., 2014). Based on the laboratory studies, several parameterizations have been proposed to predict the variations of $\gamma_{N_2O_5}$, with considerations of temperature, RH, aerosol water content, nitrate, chloride, aerosol volume to surface area ratio and organic coatings (Davis et al., 2008; Evans & Jacob, 2005; Anttila et al., 2006; Riemer et al., 2009; Griffiths et al., 2009; Bertram & Thornton, 2009).

To investigate the heterogeneous process of N_2O_5 in ambient environments, $\gamma_{N_2O_5}$ was also derived from ambient concentrations of N_2O_5 with several methods, including steady-state lifetime estimation (Brown et al., 2006; Brown et al., 2009; Brown et al., 2016), secondary products formation rate determination (Phillips et al., 2016), and inverse iterative box model calculation (Wagner et al., 2013). In addition, aerosol flow tubes have been deployed to the field solely or in combination with an iterative model to directly ‘measure’ $\gamma_{N_2O_5}$ on ambient aerosols (Bertram et al., 2009a; Wang et al., 2018). Several studies have compared the field-derived/measured $\gamma_{N_2O_5}$ with that calculated from the parameterizations based on the laboratory results, ~~which revealed significant revealing large~~ discrepancies between them, and large variations ~~were found~~ in the relationship between $\gamma_{N_2O_5}$ and aerosol chemical composition (e.g. Bertram et al., 2009b; Riedel et al., 2016; Morgan et al.,

2015; Wang et al., 2017a; Tham et al., 2018; McDuffie et al., 2018a). Recently, McDuffie et al. (2018a) proposed an empirical parameterization based on the aircraft measurements of N_2O_5 in the eastern United States, which can reproduce the mean value of the field-derived $\gamma_{\text{N}_2\text{O}_5}$ but still has difficulty in explaining its large variability. The discrepancies between the field-derived/measured and parameterized $\gamma_{\text{N}_2\text{O}_5}$ lie in the differences between the complex aerosols in ambient conditions and the simple proxies used in laboratory studies, for example, more complex organic matters or mixing state of ambient aerosols, and highlight the demand for the further comprehensive investigation of N_2O_5 uptake in diverse atmospheric conditions.

70 ~~To further investigate~~ Given the active N_2O_5 heterogeneous process revealed in ~~previously studies the polluted environments~~ in China (e.g., Wang et al., 2017a; Wang et al., 2017c; Tham et al., 2018; Yun et al., 2019), direct measurements of $\gamma_{\text{N}_2\text{O}_5}$ at two rural sites in northern and southern China were conducted in this work, by using the recently improved aerosol flow-tube system (Wang et al., 2018). Integrating them with ~~the~~ previous field results in various regions of China, we examine in detail the key factors ~~that determine determining~~ the $\gamma_{\text{N}_2\text{O}_5}$ and compare them with laboratory-derived parameterizations. Then we

75 propose improved parameters for $\gamma_{\text{N}_2\text{O}_5}$ to better represent the N_2O_5 reactivity in polluted regions of China, and model simulations with incorporation of the new parameters were also performed to evaluate its representativeness and applicability.

2 Method

Field measurements of $\gamma_{\text{N}_2\text{O}_5}$ and related parameters were conducted at a semi-rural site (Heshan) in southern China from 22 February to 28 March 2017 and at a mountain site (Mt. Tai) in northern China from 11 March to 8 April 2018. Heshan site

80 was located on a small hill (22.73°N, 112.92°E, 60m a.s.l), ~~surrounded by subtropical trees and some farmlands. A small city, Heshan, is 10 km to the northeast of the site, and three large cities, Guangzhou (the capital of Guangdong Province), Foshan and Jiangmen, are 80 km to the northeast, 50 km to the northeast and 30 km to the southwest of the site, respectively. The site is affected by vehicle emissions from three highways and two provincial roads within 10 km and some residential/agriculture activities in the area, and thus was considered as a semi-rural site.~~ ~~10 km northeast of Heshan city in Guangdong Province, and~~

85 ~~three large cities of Guangzhou (the capital of Guangdong Province), Foshan and Jiangmen are 80 km to the northeast, 50 km to the northeast and 30 km to the southwest of the site, respectively. Heshan site is often affected by vehicle emission from five highways within 10 km and some residential activities at the foot of the hill.~~ Mt. Tai site was located on the top of Mount Tai (36.25°N, 117.10°E, 1545 m a.s.l) in Shandong Province, and is ~~regionally representative and~~ affected by regional air pollution ~~with limited impact from local sources~~. Two cities of Tai'an and Jinan (the capital of Shandong Province) are 15 km

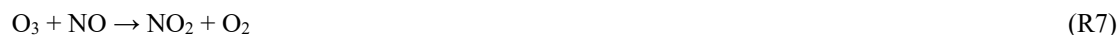
90 and 60 km to the south and north, respectively.

N_2O_5 and ClNO_2 ~~were was~~ measured using an iodide-adduct chemical ionization mass spectrometer (CIMS; THS Instrument, Atlanta), which has been deployed in several field campaigns (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a; Wang et al., 2017b; Yun et al., 2018). The related trace gases (O_3 , NO/NO_2 , etc.), aerosols size distribution, aerosol composition, and meteorological parameters were concurrently measured during the campaigns. Detailed descriptions of the measurement site

95 and instrumentation can be found in Yun et al. (2018) and Wang et al. (2017a), and the measurement techniques, uncertainties and detection limits of the instruments are summarized in Table S1.

The uptake coefficient of N₂O₅, $\gamma_{N_2O_5}$, was derived from the direct measurement of the loss rate coefficient of N₂O₅ on ambient aerosols using an aerosol flow tube based on the design of Bertram et al. (2009), with some improvements and coupling with an iterative box model for polluted environments (Wang et al., 2018)~~a newly improved aerosol flow tube coupled with an iterative box model~~ (Wang et al., 2018). Briefly, the flow tube consisted of a cylindrical stainless-steel tube of 12.5 cm inner diameter and 120 cm length, with two 10 cm deep 60° tapered caps. The inner wall of the flow tube was coated with ~~a~~ Teflon ~~coating~~ to reduce the wall loss of N₂O₅. The inlet was equipped with parallel sampling pass ways with one ~~having of them has~~ a filter to remove aerosols. ~~and the~~ The switch of stainless steel valves allows the ambient air with or without aerosols to be introduced into the flow tube. The in-situ generated N₂O₅ (4.3 ppbv at 120 mL min⁻¹, produced from the reaction of O₃ with excess NO₂) was added to the ambient air after the valves and prior to the flow tube by a side port. The total flow rate in the flow tube was 4.6 L min⁻¹, corresponding to a residence time of 149 s. During the flow tube experiments, the N₂O₅, NO, NO₂, O₃, particle number and size distribution, and RH were simultaneously measured at the base of the flow tube, and ambient NO, NO₂, and O₃ were also measured at the same time.

105 An iterative box model considering multiple reactions of production and loss of N₂O₅ (Reactions R5–R10) was used to determine the loss rate of N₂O₅ in both aerosol and non-aerosol modes (Wang et. al. 2018).



The rate constants of reactions (R5) to (R8) were adopted from Sander et al. (2009), and that of reaction (R9) was from Atkinson and Arey (2003). With the constraint of measurement data at the entrance of the flow tube reactor in the model, the exit concentrations of NO₂, O₃, and N₂O₅ can be predicted by integrating these reactions. The N₂O₅ loss rate coefficient, k_{10} , was adjusted until the N₂O₅ concentration predicted by the iterative box model matched with the measured N₂O₅ value ~~concentration~~ at the exit. Then the loss rate coefficient of N₂O₅ on aerosols surfaces can be determined from the differences of k_{10} with or without aerosol, assuming a constant k_{wall} in both modes. The uptake coefficient of N₂O₅ on ambient aerosol is then calculated by:

$$\gamma_{N_2O_5} = (k_{10}^{\text{w/aerosol}} - k_{10}^{\text{wo/aerosol}})/(cS_a). \quad \text{Eq. (1)}$$

125 The $k_{10}^{w/aerosol}$ and $k_{10}^{wo/aerosol}$ are the N_2O_5 loss rate coefficient with or without aerosol, and c is the mean molecular speed of N_2O_5 , and S_a is the particle surface area. The ambient aerosol surface area density was calculated from the dry particle size distributions corrected with a size-resolved kappa-Köhler function and ambient RH (Hennig et al., 2005; Liu et al., 2014; Yun et al., 2018). The uncertainty introduced by S_a measurement would be propagated to an uncertainty of 30% in the calculated $\gamma_{N_2O_5}$. The improvement with the use of the box model in the system could minimize the influences from the variability of ambient conditions as well as fresh NO emission, and a Monte Carlo approach was employed to evaluate the uncertainty from different parameters (Wang et al., 2018). The estimated uncertainty ranged from 37% to 40% at $\gamma_{N_2O_5}$ around 0.03 and from 34% to 65% at $\gamma_{N_2O_5}$ around 0.01 with $S_a = 1000 \mu m^2 cm^{-3}$ when RH varied from 20% to 70 %, and could be higher at $RH > 70\%$. The uncertainty of the measured $\gamma_{N_2O_5}$ is estimated to be 37% to 40 % for RH ranging from 20% to 70 %.

To obtain a holistic picture of the $\gamma_{N_2O_5}$ in different geographic regions of China, field measurement results from three previous campaigns are also used in the present study. These measurements were conducted at a sub-rural site at Wangdu and same mountain site at Mt. Tai in 2014, and a mountain site at Mt. Tai Mo Shan in South China in 2016. All the sites are regionally representative sites, as they are situated in an area with limited anthropogenic influences (Tham et al., 2016; Wang et al., 2017a; Yun et al., 2018; Wang et al., 2016). The detailed information of the sampling sites, instrumentation and $\gamma_{N_2O_5}$ determination approach have been described in the previous publications (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a), and site descriptions are briefly summarized in the SI. The locations of all the measurement sites are shown on the map in Fig. 1a. The statistics of the trace gases and $PM_{2.5}$ measured during the campaigns were summarized in Fig. 1b, representing general pollution conditions at these sites. The mean concentration of O_3 , NO_x and $PM_{2.5}$ at these sites ranged from 43 to 80 ppbv, 2.4 to 14.5 ppbv and 9.9 to 80.2 $\mu g m^{-3}$, respectively. The detailed information of sampling sites, instrumentation and $\gamma_{N_2O_5}$ determination have been described in the previous publications (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a), and site descriptions are briefly summarized in the SI. The locations of all the measurement sites in China are shown on the map in Fig. 1a.

In addition, the Community Multiscale Air Quality (CMAQ) model (v5.1) ~~and Weather Research and Forecasting (WRF) (v3.7) were~~ was employed to evaluate the uptake parameterization. Two simulations (default and revised) were conducted. In the default case, the N_2O_5 uptake and $ClNO_2$ production were calculated based on the parameterization of Bertram and Thornton (2009). In the revised case, the new parameterization derived in this study was used. Other model configurations were the same. The SAPRC07tic gas mechanism and AERO6i aerosol mechanism was used. Weather Research and Forecasting (WRF) (v4.0) was applied to generate the meteorological inputs for the CMAQ simulations. The anthropogenic emission inputs were generated based on the local Chinese emission inventory (Zhao et al. 2018) and the INTEX-B dataset for Asia (Zhang et al., 2009). The high-resolution chloride emission inventory for China from Fu et al. (2018) was also included. More details for model configuration can be found in Fu et al. (2019). ~~and simulate the concentrations of NO_2 and NO_3^- in the North China Plain.~~ The simulation domain covers China with a resolution of 36×36 km (Fig. S1), based on a Lambert projection with two true latitudes of $25^\circ N$ and $40^\circ N$. ~~The detailed model configuration and parameters of WRF and CMAQ models can~~

be found in our previous paper (Fu et al., 2019). The simulation period was from 1 to 31 December 2017, with five days before as a spin-up time.

160 3 Results and discussion

3.1 Field measured $\gamma_{\text{N}_2\text{O}_5}$ and ~~influencing affecting~~ factors

During the field measurements at Heshan and Mt. Tai, the air was characterized as moderately polluted for O_3 (43 ± 22 ppbv at Heshan and 63 ± 14 ppbv at Mt. Tai), NO_x (14.0 ± 11.5 ppbv at Heshan and 2.2 ± 2.1 ppbv at Mt. Tai), and $\text{PM}_{2.5}$ (66.7 ± 41.9 $\mu\text{g m}^{-3}$ at Heshan and 33.7 ± 26.7 $\mu\text{g m}^{-3}$ at Mt. Tai), as summarized in Table S2 and shown in Fig 1b. $\gamma_{\text{N}_2\text{O}_5}$, which was directly

165 measured using the aerosol flow tube, showed a large variation ranging from 0.002 to 0.067 with an average of 0.020 ± 0.019 at Heshan, and from 0.001 to 0.019 with an average of 0.011 ± 0.005 at Mt. Tai. These values are within the range of 10^{-5} to > 0.1 derived from the ambient N_2O_5 concentrations around the world (e.g. Brow et al., 2006; Bertram et al., 2009b; Riedel et al., 2016; Morgan et al., 2015; Wang et al., 2017a; Tham et al., 2018; McDuffie et al., 2018a), but slightly lower than the previous results in the polluted regions in China (0.021 to 0.102) (Wang et al., 2017a; Wang et al., 2017b; Wang et al., 2017c).

170 The field measured $\gamma_{\text{N}_2\text{O}_5}$ and relevant pollutants at the two sites and those derived from three previous studies in China are summarized in Fig 1b, covering diverse atmospheric conditions from moderately humid to humid conditions and from clean to polluted conditions.

Figure 2 shows the relationship of the field measured $\gamma_{\text{N}_2\text{O}_5}$ with the aerosol composition during five campaigns at those four sites in China. It can be seen that the $\gamma_{\text{N}_2\text{O}_5}$ had a good positive correlation with the aerosol water content ($r^2 = 0.65$) (Fig. 2a),

175 suggesting a common controlling role of aerosol water in the reactivity of N_2O_5 in both northern and southern China. Although the positive correlation of $\gamma_{\text{N}_2\text{O}_5}$ with aerosol water has been observed in the low range in previous laboratory studies, the $\gamma_{\text{N}_2\text{O}_5}$ reached plateaus at a value around 0.036 at $\text{RH} > 50\%$ or (McDuffie et al., 2018a), such strong dependence was not obvious in other studies in Europe and America, and also different from some laboratory studies indicating that $\gamma_{\text{N}_2\text{O}_5}$ increases with the humidity or water content in the low range but plateaus after $[\text{H}_2\text{O}] > 15$ M (Hallquist et al., 2003; Thornton et al., 2003;

180 Bertram & Thornton, 2009). In contrast, other laboratory studies also measured higher $\gamma_{\text{N}_2\text{O}_5}$ values on NH_4HSO_4 particles. For example, Mozurkewich and Calvert (1988) reported an upper limit of $\gamma_{\text{N}_2\text{O}_5}$ of 0.056 at $\text{RH} = 55\%$ at 293 K, which increased to around 0.1 at 274 K. Kane et al. (2001) observed a strong RH dependent $\gamma_{\text{N}_2\text{O}_5}$ increasing from 0.018 to 0.069 with RH from 56% to 99%, which is largely consistent with the field results in the present study. Moreover, several field measurements also

185 observed $\gamma_{\text{N}_2\text{O}_5}$ value exceeding 0.04 at high RH or water molarity (e.g. Philips et al., 2016; McDuffie et al., 2018a; Wang et al., 2017c; Tham et al., 2018), and some of them also found the similar positive relationship between $\gamma_{\text{N}_2\text{O}_5}$ and water molarity (McDuffie et al., 2018a). Although uncertainties may exist in the calculation of aerosol surface and uptake coefficient at high ambient RH conditions, Our results show with a consistently increasing trend of $\gamma_{\text{N}_2\text{O}_5}$ with $[\text{H}_2\text{O}]$ from below 10 M up to 50 M suggest that the aerosol water content strongly affects the activity of N_2O_5 uptake, and that N_2O_5 hydrolysis is always limited by aerosol water content under all the encountered ambient conditions. Since limited measurement data of $\gamma_{\text{N}_2\text{O}_5}$ from

190 laboratory and fields are available at RH > 80% condition, it is unclear what exact mechanism or process (e.g., phase change
different from laboratory-made particles or acidity involved) promote more effective uptake on ambient aerosols at higher
aerosol water content condition. Therefore, more detailed investigations of N₂O₅ uptake on nano-size water/aerosol droplets
in the real (or close to real) ambient conditions are clearly warranted, ~~suggesting the consistent limitation of aerosol water
content on N₂O₅ uptake under all the encountered ambient conditions and that the hygroscopicity of the ambient aerosols seems~~
195 ~~a critical property affecting the heterogeneous uptake. On the other hand, similar to most of the previous field and laboratory
studies, -For nitrate,~~ a clear ~~nitrate~~-suppression effect can be found at the Chinese sites (Fig. 2b), which is similar to most of
the previous field and laboratory studies. The decrease of $\gamma_{\text{N}_2\text{O}_5}$ with increasing nitrate concentration seems to be better captured
by an ‘exponential-decay’ curve, with almost ~~linear~~ suppression for [NO₃⁻] below 5 M. The observed $\gamma_{\text{N}_2\text{O}_5}$ under high
nitrate condition (> 5 M) was generally below 0.025 and became nitrate independent as the nitrate levels further increased.

200 The $\gamma_{\text{N}_2\text{O}_5}$ variation was affected by the additive effects from both [NO₃⁻] and [H₂O], which could not be easily isolated because
of their competition reactions with the reactive intermediate H₂ONO₂⁺. This is further supported by the positive dependence
of $\gamma_{\text{N}_2\text{O}_5}$ on the molar ratio of [H₂O]/[NO₃⁻] (Fig. 2c). Different from the previously reported plateauing of $\gamma_{\text{N}_2\text{O}_5}$ with increasing
[H₂O]/[NO₃⁻] ratio in laboratory studies (Hallquist et al., 2003; Bertram & Thornton, 2009), no decrease in $\gamma_{\text{N}_2\text{O}_5}$ suppression
was found in the present study for [H₂O]/[NO₃⁻] ratio of up to 60. The more scattered data at higher [H₂O]/[NO₃⁻] range implies
205 that the variation of $\gamma_{\text{N}_2\text{O}_5}$ become more sensitive to other factors in the diluted aqueous aerosols. Although the $\gamma_{\text{N}_2\text{O}_5}$ measured
at two mountain sites showed a positive relationship with [Cl⁻]/[NO₃⁻], the overall results from five sites did not exhibit an
obvious pattern (Fig. 2d). These results suggest that chloride concentration may not play a critical role in $\gamma_{\text{N}_2\text{O}_5}$ during our
observations as laboratory studies have observed (Bertram & Thornton, 2009), possibly due to the complex effect of aerosol
mixing state. Though the measured $\gamma_{\text{N}_2\text{O}_5}$ exhibited nonlinear relationship and complex dependence on different factors at a
210 single site, the general consistent patterns at different sites in this study suggests the feasibility of a common parameterization
representing the N₂O₅ uptake in these regions.

3.2 Comparison to parameterizations

Current regional air quality models such as WRF-Chem and CMAQ mainly use the $\gamma_{\text{N}_2\text{O}_5}$ parameterization recommended by
Bertram and Thornton (2009) (hereafter referred to BT09), which links $\gamma_{\text{N}_2\text{O}_5}$ to aerosol water content, nitrate and chloride as
215 well as the aerosol size and ambient temperature. The BT09 parameterization based on the above-mentioned reaction
mechanism (R1-R5) was expressed as follows:

$$\gamma_{\text{N}_2\text{O}_5} = \frac{4 V_a}{c S_a} K_H k'_{2f} \left(1 - \frac{1}{\left(\frac{k_3 [\text{H}_2\text{O}]}{k_{2b} [\text{NO}_3^-]} \right) + 1 + \left(\frac{k_4 [\text{Cl}^-]}{k_{2b} [\text{NO}_3^-]} \right)} \right) \quad \text{Eq. (2)}$$

$$k'_{2f} = \beta - \beta e^{-\delta [\text{H}_2\text{O}]} \quad \text{Eq. (3)}$$

where V_a/S_a is the measured aerosol volume to surface area ratio, ranging from 3.30×10^{-8} to 9.29×10^{-8} m in the five campaigns; K_H is Henry's law coefficient, taken as 51 (Bertram & Thornton, 2009; Fried et al., 1994); $\beta = 1.15 \times 10^6$; $\delta = -0.13$. k_3/k_{2b} (= 0.06) and k_4/k_{2b} (= 29) represent the relative rates of competing reactions of intermediate $\text{H}_2\text{ONO}_2^+(\text{aq})$ with H_2O (R3) and Cl^- (R4) over NO_3^- (R2), respectively. $[\text{H}_2\text{O}]$, $[\text{NO}_3^-]$ and $[\text{Cl}^-]$ are the aerosol water content, aerosol nitrate and chloride molarity, respectively, calculated by the E-AIM model with the measured ionic compositions of $\text{PM}_{2.5}$ and RH (<http://www.aim.env.uca.ac.uk/aim/aim.php>) (Wexler and Clegg, 2002).

We calculate the $\gamma_{\text{N}_2\text{O}_5}$ values from BT09 with the measured aerosol composition at the five sites. The parameterized $\gamma_{\text{N}_2\text{O}_5}$ ranged from 0.021 to 0.075, with an average of 0.047 ± 0.015 , which overestimates the observed values by a factor of 1.8. When the chloride effect was excluded, the parameterized $\gamma_{\text{N}_2\text{O}_5}$ mean value decreased to 0.020 ± 0.018 , which was better correlated with but underestimated (by 30%) the measurements (Table 1). Figure 3 compares the observation-derived and parameterized $\gamma_{\text{N}_2\text{O}_5}$ at five sites in China and in different parts of the world. The BT09 parameterization (blue markers in Fig. 3) generally overestimates the observed $\gamma_{\text{N}_2\text{O}_5}$ values in the range of 0.001 to 0.03, but is closer (within a factor of 1.5) to the observed value for $\gamma_{\text{N}_2\text{O}_5}$ above 0.03 in Germany (Phillips et al., 2016) and Mt. Tai (Wang et al., 2017a). The BT09 parameterization excluding chloride effects (yellow markers) gives much better agreement, with more values located in the range within a factor of 2, though the $\gamma_{\text{N}_2\text{O}_5}$ was still overpredicted in most of the studies in North America (Bertram et al., 2009b; Riedel et al., 2012; McDuffie et al., 2018a) except for Boulder (Wagner et al., 2013). The improvement indicates that the efficiency of chloride in competing for the H_2ONO_2^+ intermediate and the effects on N_2O_5 uptake on ambient aerosols might be overestimated, possibly due to the existence of other nucleophiles competing with Cl^- (McDuffie et al., 2018b; Staudt et al., 2019), or different mixing states of particle and non-uniform distribution of available chlorine in the aerosols.

Organic matter/coating on the aerosols can suppress the uptake of N_2O_5 (Thornton & Abbatt, 2005; McNeill et al., 2006; Park et al., 2007), and previous studies have attempted to account for this effect by treating organics as a coating on the inorganic core (Anttila et al., 2006; Riemer et al., 2009). However, significant underpredictions were found from the parameterization of BT09 combined with the organic effect (Morgan et al., 2015; McDuffie et al., 2018a; Tham et al., 2018) (green and purple markers in Fig. 3). One reason could be that the parameterization does not differentiate the water-soluble organic fractions and simplifies the morphology and phase state, which leads to the underestimation of the solubility and/or diffusivity of N_2O_5 in the organics. The complex effects of organic matter on N_2O_5 uptake remain poorly quantified (McDuffie et al., 2018a), and the prediction of composition, morphology and phase state of the organic fractions are still difficult in current air quality models. Therefore, we do not consider the organic effect in deriving a new parameterization in the next section.

3.3 Observation-based empirical parameterization of $\gamma_{\text{N}_2\text{O}_5}$

Based on the above discussion and comparison, we attempt to derive a new empirical parameterization of $\gamma_{\text{N}_2\text{O}_5}$ following the BT09 framework (Eq. (2)) and using the measurement data from five field campaigns in China. The variables in the

parameterization (i.e., reaction rates) were fitted with multiple regression to obtain the best representation of observations in China. The derived empirical parameterization of $\gamma_{\text{N}_2\text{O}_5}$ is shown as Eq. (4) and the fitted $\gamma_{\text{N}_2\text{O}_5}$ are summarized in Table 1.

$$\gamma_{\text{N}_2\text{O}_5} = \frac{4V_a}{cS_a} K_H \times 3.0 \times 10^4 \times [\text{H}_2\text{O}] \left(1 - \frac{1}{\left(0.033 \times \frac{[\text{H}_2\text{O}]}{[\text{NO}_3^-]} + 1 + \left(3.4 \times \frac{[\text{Cl}^-]}{[\text{NO}_3^-]}\right)\right)} \right) \quad \text{Eq. (4)}$$

In view of the linear dependence of $\gamma_{\text{N}_2\text{O}_5}$ on the aerosol water content in this study and reaction mechanism (Bertram & Thornton, 2009), the second-order reaction rate coefficient with water (refer to k'_{2f} in Eq. (2) and Eq. (3)) was fitted as a linear function of $[\text{H}_2\text{O}]$, as $(3.0 \pm 0.4) \times 10^4 \times [\text{H}_2\text{O}]$. This value is in reasonable agreement with the values of $(2.7\text{--}3.8) \times 10^4$, $\sim 3.9 \times 10^4$, and $2.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ determined from ammonium bisulfate, ammonium sulfate (Gaston et al., 2016) and aqueous organic acid particles (Thornton et al. 2003), respectively. Compared to original BT09 (Eq. (3)), the newly fitted k'_{2f} is smaller for $[\text{H}_2\text{O}] < 38 \text{ M}$, but become higher with the increasing of aerosol water content (Fig. S2). Different dimensionless K_H values have been used in previous studies, e.g., ~ 50 (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009) or ~ 120 (e.g., Gaston et al., 2014; 2016; Griffiths et al., 2009), which correspond to a Henry's law constant of 2 or 5 M atm^{-1} at 298K. As $\gamma_{\text{N}_2\text{O}_5}$ in the parameterization is linearly dependent on the K_H , an increase of K_H value would proportionally increase the $\gamma_{\text{N}_2\text{O}_5}$ value but cannot account for the large variability of measured $\gamma_{\text{N}_2\text{O}_5}$ values. Given the lack of an explicit function of effective Henry's law constant for N_2O_5 to include the different process (e.g., 'salting-in' effect and surface processes), we use the value of 51 suggested by Bertram and Thornton (2009) and enclose those effects from the aerosol composition in the last 'chemical' term. The derived empirical ratios in the last 'chemical' term not only represent the competing ratio of these reactions but also include other unspecified effects or processes (e.g., organic coating, mixing state, other nucleophiles reactions, etc.). The fitted relative rates of competing reactions, i.e., k_3/k_{2b} and k_4/k_{2b} , were 0.033 ± 0.017 and 3.4 ± 1.4 , respectively, which are smaller than the original BT09 parameters by with a factor of 1.8 and 8.5, respectively. The smaller ratios of the reaction rates indicate a smaller enhancement effect of chloride or but a larger suppression effect by nitrate, which is consistent with the above-observed relationship of $\gamma_{\text{N}_2\text{O}_5}$ with the aerosol composition. Other suppression effects such as organic coating and mixing state that was not specified in the parameterization also may contribute to, and are reflected in the smaller fitted values. As compared in Fig. 4 and Table 1, the new empirical parameterization can better reproduce the average values and the large variability of the observed $\gamma_{\text{N}_2\text{O}_5}$ than the original BT09 both with and without considering Cl^- effects.

As suggested by the previous studies, the production yield of ClNO_2 (Φ_{ClNO_2}) from N_2O_5 uptake is also a function of competing reactions of H_2O and Cl^- content in aerosols, and can be estimated from $\Phi_{\text{ClNO}_2} = 1/(1+k_3/k_4 \times [\text{H}_2\text{O}]/[\text{Cl}^-])$ (Bertram & Thornton, 2009). Based on the above-fitted results for $\gamma_{\text{N}_2\text{O}_5}$, k_4/k_3 is determined to be 105 ± 37 for the five sites, which is smaller than the values of 450 ± 100 (Roberts et al., 2009), 483 ± 175 (Bertram & Thornton, 2009) and 836 ± 32 (Behnke et al., 1997) derived from laboratory experiments and used in previous parameterizations. As compared in Fig. S3 and Table 1, although the newly fitted values improve the estimated ClNO_2 yield comparing to the original BT09 (with k_4/k_3 of 483), overestimation remains, and the large variability of observed Φ_{ClNO_2} in different campaigns still cannot be well captured. As shown in Fig. 5, the new

fits can better catch the Φ_{ClNO_2} trend at $[\text{H}_2\text{O}]/[\text{Cl}^-] > 750$, but discrepancy is still obvious at $[\text{H}_2\text{O}]/[\text{Cl}^-] < 750$. The discrepancy could be due to aqueous-phase competition reactions of intermediate H_2ONO_2^+ with other compounds (e.g., phenol) (Heal et al., 2007), and ClNO_2 loss/reaction mechanisms (e.g., reaction with Cl^- to form Cl_2) (Roberts et al., 2008, 2009). A recent laboratory study (Staudt et al. 2019) has reported that sulfate and acetate can suppress Φ_{ClNO_2} for Cl^- containing solutions, but such sulfate suppression effect was not observed in our results. Further studies are needed to identify and quantify these effects for better parameterizing the heterogeneous ClNO_2 production. Nonetheless, the revised k_3/k_4 from fitting the field data has improved the estimates of Φ_{ClNO_2} at our study sites.

3.4 Evaluation of the empirical parameterization

To further evaluate the representativeness and validity of the newly fitted empirical parameterization of $\gamma_{\text{N}_2\text{O}_5}$ in predicting N_2O_5 heterogeneous process in air quality models, simulation tests were performed with the WRF-CMAQ model. The simulations were conducted with the incorporation of newly fitted and original BT09 parameterizations, respectively. The ~~model~~-simulated concentrations of NO_2 and NO_3^- , as the key precursor and a product of the N_2O_5 uptake, were compared with the observed daily NO_3^- concentrations at 28 sites and hourly NO_2 concentrations at 472 sites in the North China Plain during December of 2017. As summarized in Table 2 and shown in Fig. S4, the simulation with original BT09 parameterization overestimated the regionally averaged NO_3^- concentrations by 18.7% ~~on average~~ compared to the observations, whereas the new parameterization gave more consistent results with the observations ($20.98 \pm 18.77 \mu\text{g m}^{-3}$ vs $20.94 \pm 17.16 \mu\text{g m}^{-3}$), reducing the normalized mean bias (NMB) of simulated NO_3^- concentration from 18.72% to 0.19%. The simulated NO_2 concentrations were also in better agreement with the observations, with the NMB changed from -12.25% to -8.06%. In addition to NO_2 and NO_3^- , we also compared the simulated N_2O_5 concentrations for December 2017 with those observed in the wintertime at various locations of China, including two in the North China Plain (Beijing and Wangdu in Hebei province) and two in southern China (Tai Mao Shan and Heshan). As shown in Figure 6, with the new parameterization, the WRF-CMAQ model can better simulate the average concentration and variation range of N_2O_5 at these locations. Overall, the new parameterization has significantly reduced the discrepancies between the modeled and observed concentrations of NO_2 , N_2O_5 and NO_3^- at our study sites and periods in both northern and southern China. More tests of this empirical parameterization are warranted for other locations/seasons in China and other parts of the world. ~~In southern China, our previous modeling study with the original BT09 parameterization underpredicted the N_2O_5 but overpredicted the ClNO_2 mixing ratios (Li et al., 2016). The new parameterization, which gives smaller values of $\gamma_{\text{N}_2\text{O}_5}$ and Φ_{ClNO_2} , would therefore also reduce the discrepancies from the observation and improve the model performance in southern China.~~

310 4 Conclusion

Nitrate is becoming the predominant component of $\text{PM}_{2.5}$ during severe haze events in China ~~in during~~ recent years (Zhang et al., 2015; Li et al., 2018), and ground-level ozone pollution in urban areas is also worsening (Wang et al., 2017d). Despite

extensive research, current air quality models still have difficulties in accurately simulating the N_2O_5 uptake on aerosols, which limits their ability in predicting the lifetime and fate of NO_x and therefore the productions of aerosol nitrate and ozone. Based on the measurements from five field campaigns at four sites across China with different atmospheric conditions, our study examined the factors influencing N_2O_5 uptake processes and derived an observation-based empirical parameterization of N_2O_5 uptake. While further research is still needed on the additional factors affecting $\gamma_{\text{N}_2\text{O}_5}$ and Φ_{ClNO_2} , the empirical parameterization derived here can be used in air quality models to improve the prediction of $\text{PM}_{2.5}$ and photochemical pollution in China and similar polluted regions of the world.

320 **Author contributions**

TW and ZW designed the study. WW, CY and ZW designed the aerosol flow tube and CY carried out the aerosol flow tube measurements. MX, TC, PZ, HL, YS, YZ, and DY conducted the field measurement of relevant species and data analysis. XF performed the model simulation. CY, ZW, and TW wrote the manuscript, with discussions and comments from all co-authors.

Competing interests.

325 The authors declare that they have no conflict of interest.

Data availability

The data used in this study are available upon request from Zhe Wang (z.wang@ust.hk) and Tao Wang (cetwang@polyu.edu.hk).

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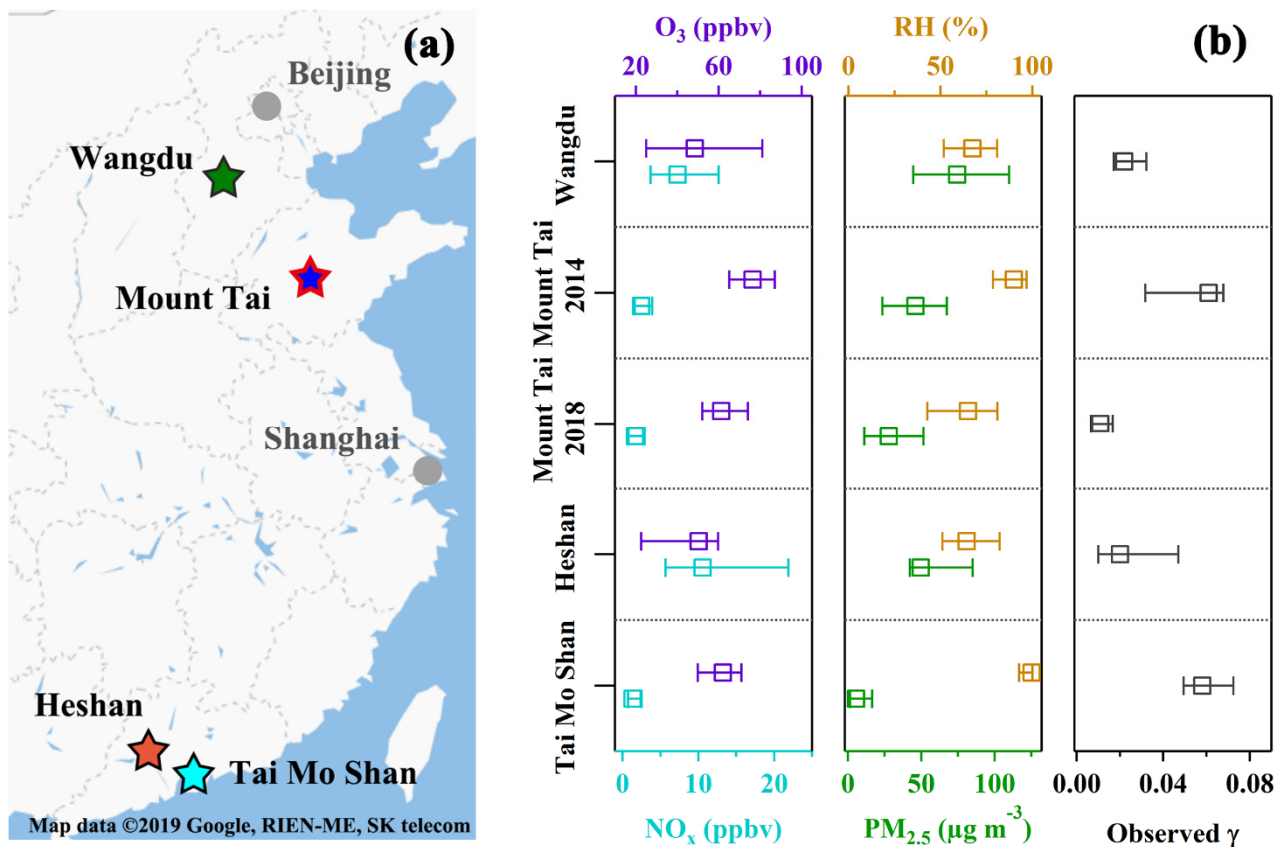
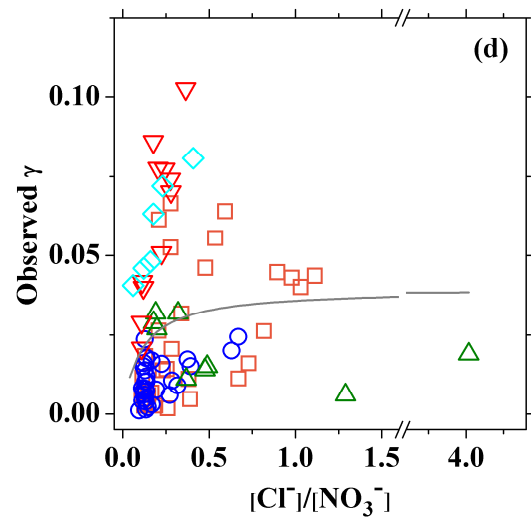
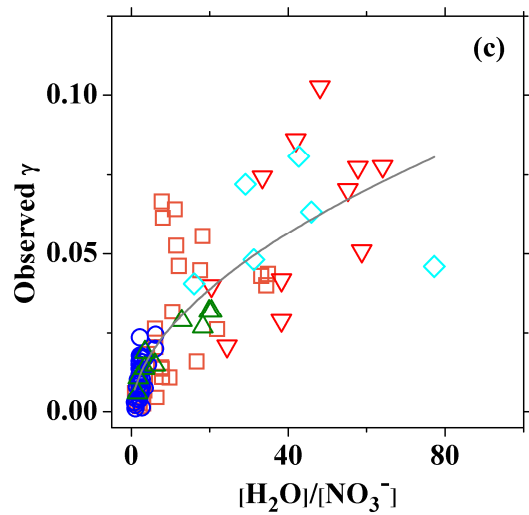
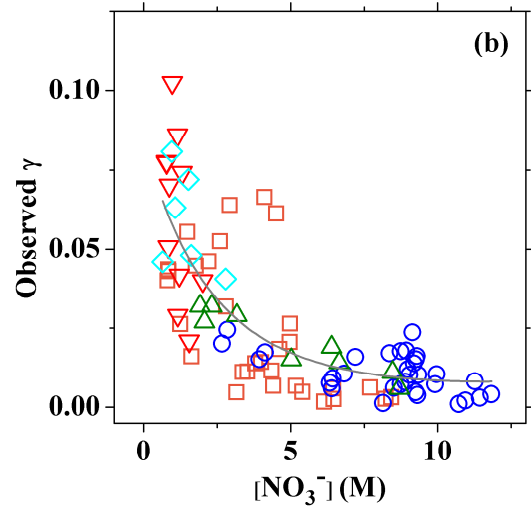
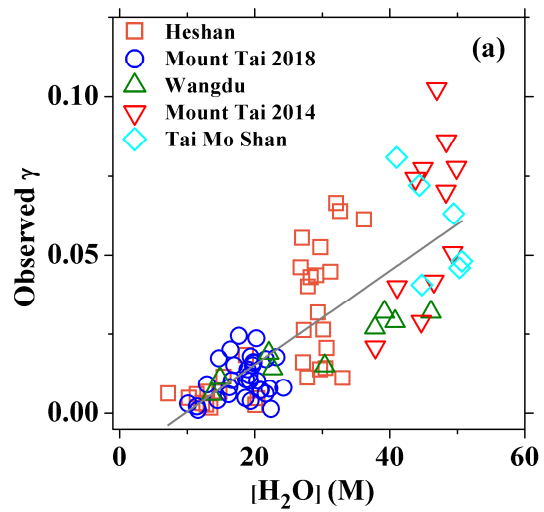


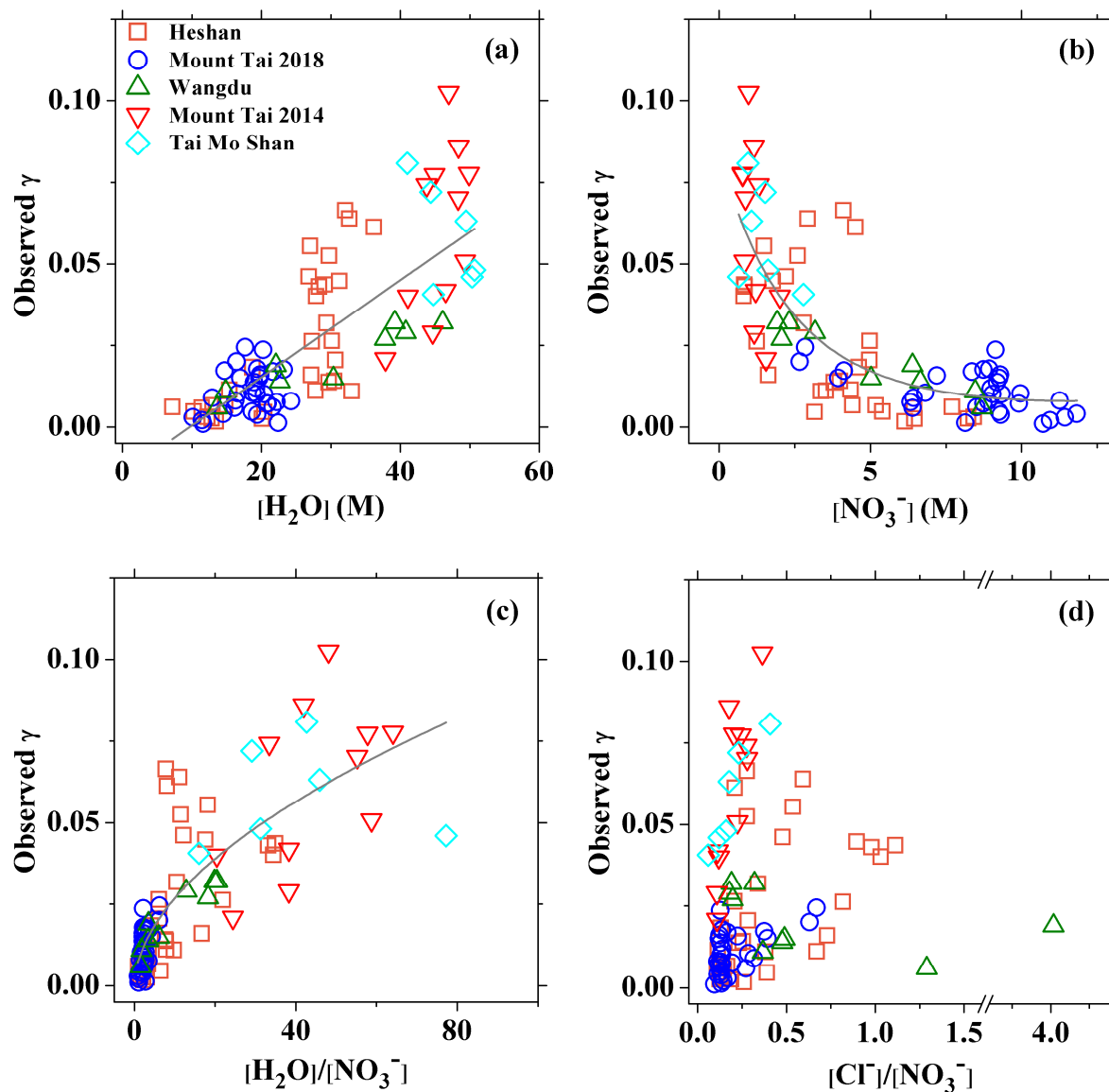
Figure 1. (a) The locations of the four field measurement sites (pentagram markers) in China. (b) Comparisons of the concentrations of O₃, NO_x, PM_{2.5}, and observed RH and γ_{N2O5} during the five campaigns in China. Squares represent the median values and bars represent the interquartile ranges of the values in the five measurements. It should be noted that the high RH in both Mt. Tai 2014 and Tai Mo Shan campaigns were caused by frequent cloud/fog events, and the γ_{N2O5} was determined only during non-cloudy periods in these two campaigns.

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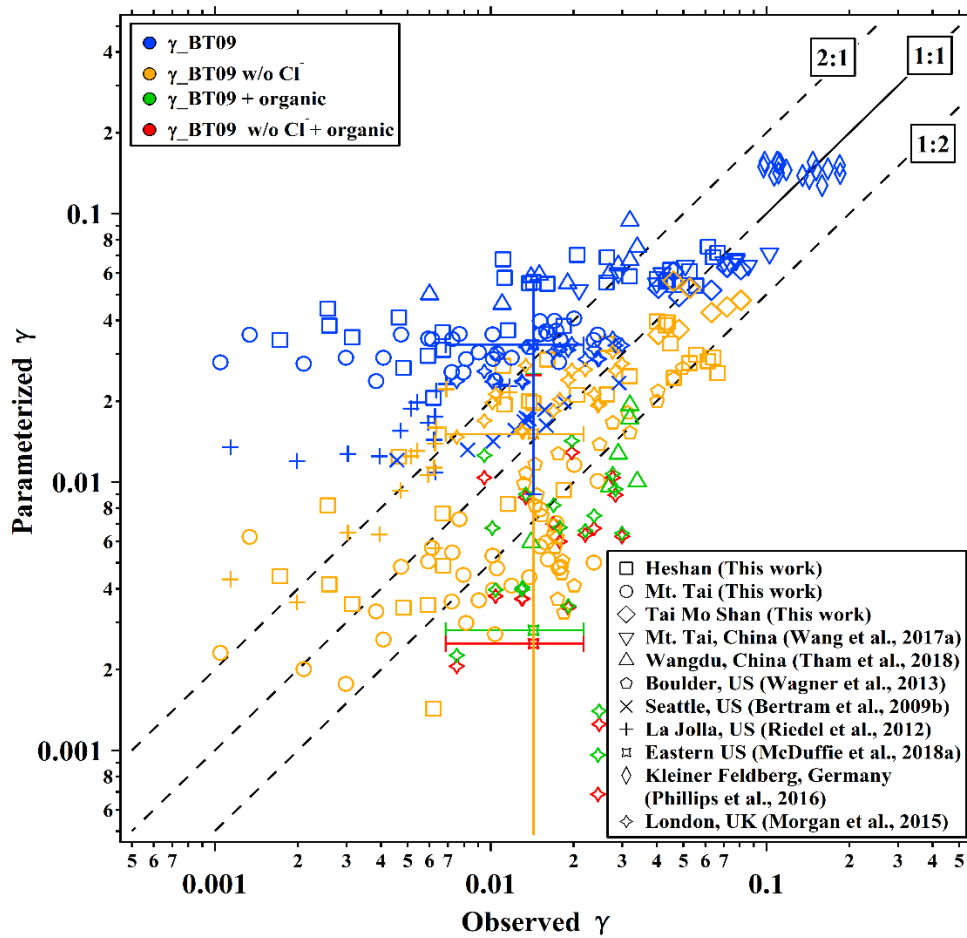
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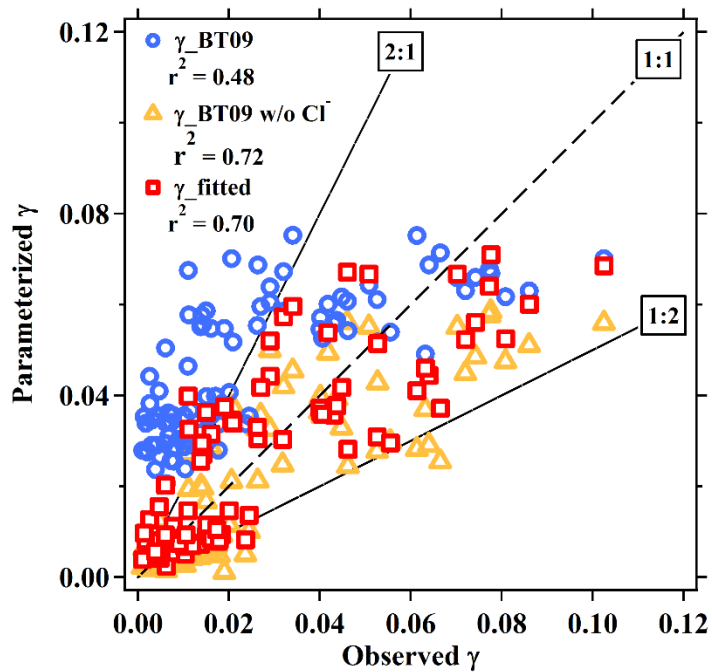


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Figure 2. Relationship between the field measured/derived N_2O_5 uptake coefficient $\gamma_{\text{N}_2\text{O}_5}$ and (a) aerosol water content, (b) particle nitrate, (c) H_2O to NO_3^- molarity ratio, and (d) Cl^- to NO_3^- molarity ratio. Green triangles, red triangles, cyan squares, yellow squares and blue circles represent the results of Wangdu in 2014, Mount Tai in 2014, Tai Mo Shan in 2016, Heshan in 2017 and Mount Tai in 2018, respectively. The solid lines are linear or exponential regressions.

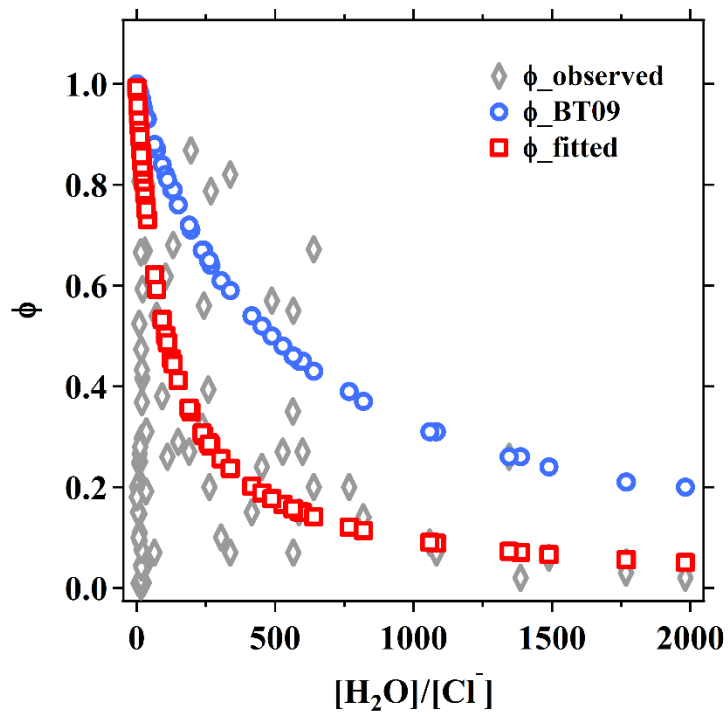


520 Figure 3. Summary of the comparisons of field measured/derived $\gamma_{\text{N}_2\text{O}_5}$ and values estimated from parameterizations from the literature. Blue, yellow, green and purple markers represent the results calculated from parameterizations of original BT09, BT09 excluding chloride effect, BT09 plus organic effect, and BT09 excluding chloride but with organic effect, respectively.



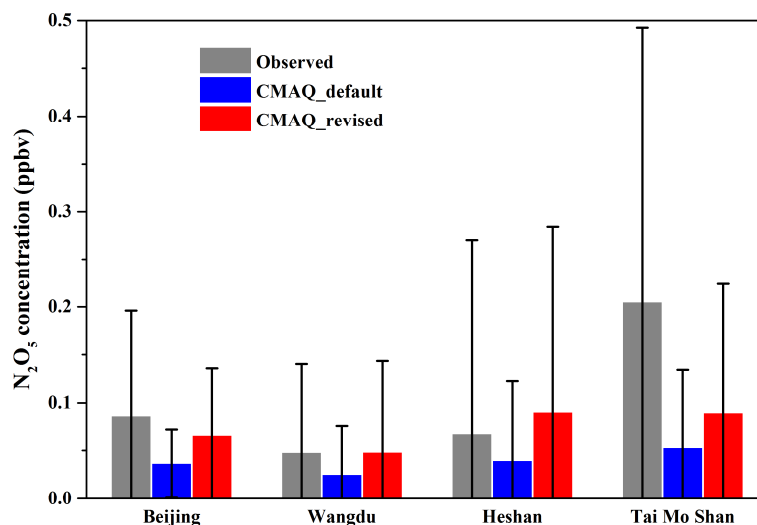
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Figure 4. Comparison of the field measured/derived γ_{N2O5} with the values estimated from parameterizations for the five sites in the present study. The dashed line represents the 1:1 line. Blue circles, yellow triangles, and red squares are results estimated by BT09 parameterization, BT09 excluding chloride effect and the derived observation-based empirical parameterization, respectively.



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Figure 5. Relationship between the ClNO_2 yield, Φ_{ClNO_2} , and the molarity ratio of H_2O to Cl^- . Grey rhombi, blue circles, and red squares represent the observed Φ_{ClNO_2} , values from BT09 parameterization and fitted from the empirical parameters derived in the present study, respectively.



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Figure 6. Comparison of the simulated N₂O₅ concentrations by the CMAQ model for December 2017 with the wintertime observation results from four sites in China. The field observations were conducted in December 2017 at Wangdu, January 2018 at Beijing, January 2018 at Heshan and November 2013 at Tai Mo Shan. The columns and error bars represent the average value and standard deviation, respectively.

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Table 1. Statistical summary and comparison of the observed parameters (N₂O₅ uptake coefficient, $\gamma_{\text{N}_2\text{O}_5}$; ClNO₂ yield, Φ_{ClNO_2}) with values predicted from different parameterizations.

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Parameters		Average \pm SD	Maximum	Minimum	r ²
$\gamma_{\text{N}_2\text{O}_5}$	Observed	0.026 \pm 0.024	0.10	0.001	-
	BT09	0.047 \pm 0.015	0.075	0.021	0.54
	BT09 w/o Cl ⁻	0.020 \pm 0.018	0.058	0.001	0.72
	Fitted	0.026 \pm 0.020	0.071	0.002	0.70
Φ_{ClNO_2}	Observed	0.31 \pm 0.27	1.04	0.004	-
	BT09	0.74 \pm 0.26	1.00	0.20	0.025
	Fitted	0.57 \pm 0.33	0.99	0.05	0.003

550 **Table 2. Statistical summary and comparison of the observed species (nitrate and NO₂ concentrations) with values predicted from different parameterization. NMB represents the normalized mean bias.**

Species		Simulated average \pm SD ($\mu\text{g m}^{-3}$)	Observed average \pm SD ($\mu\text{g m}^{-3}$)	NMB (%)	r ²
NO ₃ ⁻	CMAQ_default (BT09)	24.86 \pm 20.48	20.94 \pm 17.16	18.72	0.56
	CMAQ_revised (Fitted)	20.98 \pm 18.77		0.19	0.56
NO ₂	CMAQ_default (BT09)	45.71 \pm 31.21	52.09 \pm 27.25	-12.25	0.31
	CMAQ_revised (Fitted)	47.89 \pm 32.10		-8.06	0.34