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

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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 (γ_{N2O5}) and representation in air quality model are challenging, especially in the polluted environment. With an in-situ aerosol flow tube system, the γ_{N2O5} was directly measured on ambient aerosols at two rural sites in northern and southern China. The results were analyzed together with the γ_{N2O5} 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 γ_{N2O5} was generally promoted by the aerosol water content and suppressed by particle nitrate. Significant discrepancies were found between the measured γ_{N2O5} and that estimated 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 γ_{N2O5}. 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

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

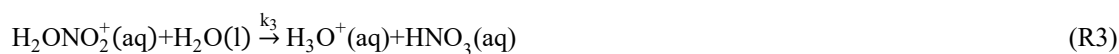
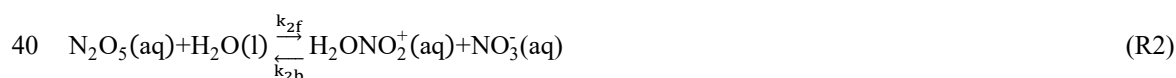
and particulate pollution. The currently accepted mechanism of the heterogeneous reaction of N_2O_5 on aqueous aerosols starts

35   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).

$$N_2O_5(g) \xrightarrow{k_1} N_2O_5(aq) \qquad\qquad (R1)$$

40    $$N_2O_5(aq)+H_2O(l) \underset{k_{2b}}{\overset{k_{2f}}{\rightleftarrows}} H_2ONO_2^+(aq)+NO_3^-(aq) \qquad\qquad (R2)$$

$$H_2ONO_2^+(aq)+H_2O(l) \xrightarrow{k_3} H_3O^+(aq)+HNO_3(aq) \qquad\qquad (R3)$$

$$H_2ONO_2^+(aq)+Cl^-(aq) \xrightarrow{k_4} ClNO_2(g)+H_2O(l) \qquad\qquad (R4)$$

The reaction probability of N_2O_5, the so-called uptake coefficient γ_{N2O5}, 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. γ_{N2O5} was first measured

45   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

50   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 γ_{N2O5}, 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;

55   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, γ_{N2O5} 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

60   with an iterative model to directly 'measure' γ_{N2O5} on ambient aerosols (Bertram et al., 2009a; Wang et al., 2018). Several studies have compared the field-derived/measured γ_{N2O5} with that calculated from the parameterizations based on the laboratory results, revealing large discrepancies between them, and large variations were found in the relationship between γ_{N2O5} 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
65   aircraft measurements of N_2O_5 in the eastern United States, which can reproduce the mean value of the field-derived γ_{N2O5} but
still has difficulty in explaining its large variability. The discrepancies between the field-derived/measured and parameterized
γ_{N2O5} 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   Given the active N_2O_5 heterogeneous process revealed in 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 γ_{N2O5} 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 previous field results in various regions of China, we examine in detail the key factors determining the γ_{N2O5} and
compare them with laboratory-derived parameterizations. Then we propose improved parameters for γ_{N2O5} to better represent
75   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 γ_{N2O5} 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), 10 km northeast of Heshan city in Guangdong Province, and 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.
85   Two cities of Tai'an and Jinan (the capital of Shandong Province) are 15 km and 60 km to the south and north, respectively.
N_2O_5 and $ClNO_2$ 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
90   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 N_2O_5, γ_{N2O5}, was derived from the direct measurement of the loss rate coefficient of N_2O_5 on ambient
aerosols using 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°
95   tapered caps. The inner wall of the flow tube was coated with a Teflon coating to reduce the wall loss of N_2O_5. The inlet was

equipped with parallel sampling pass ways with one of them has a filter to remove aerosols, and 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 N_2O_5 (4.3 ppbv at 120 mL min^{-1}, produced from the reaction of O_3 with excess NO_2) 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

100   149 s. During the flow tube experiments, the N_2O_5, NO, NO_2, O_3, particle number and size distribution, and RH were simultaneously measured at the base of the flow tube, and ambient NO, NO_2, and O_3 were also measured at the same time. An iterative box model considering multiple reactions of production and loss of N_2O_5 (Reactions R5–R10) was used to determine the loss rate of N_2O_5 in both aerosol and non-aerosol modes (Wang et. al).

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \hspace{4cm} \text{(R5)}$$

105     $$NO_3 + NO_2 \rightarrow N_2O_5 \hspace{4cm} \text{(R6)}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \hspace{4cm} \text{(R7)}$$

$$NO_3 + NO \rightarrow 2NO_2 \hspace{4cm} \text{(R8)}$$

$$NO_3 + VOC \rightarrow products \hspace{4cm} \text{(R9)}$$

$$N_2O_5 + aerosol/wall \rightarrow products \hspace{4cm} \text{(R10)}$$

110   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 NO_2, O_3, and N_2O_5 can be predicted by integrating these reactions. The N_2O_5 loss rate coefficient, k_{10}, was adjusted until the N_2O_5 concentration predicted by the iterative box model matched with the measured N_2O_5 concentration at the exit. Then the loss rate coefficient of N_2O_5 on aerosols surfaces can be determined from the differences of k_{10} with or

115   without aerosol, assuming a constant k_{wall} in both modes. The uptake coefficient of N_2O_5 on ambient aerosol is then calculated by:

$$\gamma_{N2O5} = (k_{10}^{w/aerosol} - k_{10}^{wo/aerosol})/(cS_a). \hspace{3cm} \text{Eq. (1)}$$

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

120   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 of the measured γ_{N2O5} is estimated to be 37% to 40 % for RH ranging from 20% to 70 %.

To obtain a holistic picture of the γ_{N2O5} 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. The detailed information of

125   sampling sites, instrumentation and γ_{N2O5} 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 employed to evaluate the uptake parameterization and simulate the concentrations of NO_2 and NO_3^- in the North

130   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°N and 40°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.

3 Results and discussion

135   ### 3.1 Field measured γ_{N2O5} and 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 $PM_{2.5}$ (66.7±41.9 μg m^{-3} at Heshan and 33.7±26.7 μg m^{-3} at Mt. Tai), as summarized in Table S2 and shown in Fig 1b. γ_{N2O5}, which was directly 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

140   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). The field measured γ_{N2O5} and relevant pollutants at the two sites and derived from three previous studies in China are

145   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 γ_{N2O5} with the aerosol composition during five campaigns at those four sites in China. It can be seen that the γ_{N2O5} had a good positive correlation with the aerosol water content (r^2 = 0.65) (Fig. 2a), suggesting a common controlling role of aerosol water in the reactivity of N_2O_5 in both northern and southern China. Although

150   the positive correlation of γ_{N2O5} with aerosol water has been observed (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 γ_{N2O5} increases with the humidity or water content in the low range but plateaus after [H_2O] > 15 M (Hallquist et al., 2003; Thornton et al., 2003; Bertram & Thornton, 2009). Our results show a consistently increasing trend of γ_{N2O5} with [H_2O] from below 10 M up to 50 M, suggesting the consistent limitation of aerosol water content on N_2O_5 uptake under all the encountered ambient

155   conditions and that the hygroscopicity of the ambient aerosols seems a critical property affecting the heterogeneous uptake. On the other hand, similar to most of the previous field and laboratory studies, a clear nitrate suppression effect can be found at the Chinese sites (Fig. 2b). The decrease of γ_{N2O5} with increasing nitrate concentration seems to be better captured by an

'exponential-decay' curve, with almost liner suppression for $[NO_3^-]$ below 5 M. The observed γ_{N2O5} under high nitrate condition (> 5 M) was generally below 0.025 and became nitrate independent as the nitrate levels further increased.

160 The γ_{N2O5} variation was affected by the additive effects from both $[NO_3^-]$ and $[H_2O]$, which could not be easily isolated because of their competition reactions with the reactive intermediate $H_2ONO_2^+$. This is further supported by the positive dependence of γ_{N2O5} on the molar ratio of $[H_2O]/[NO_3^-]$ (Fig. 2c). Different from the previously reported plateau of γ_{N2O5} with increasing $[H_2O]/[NO_3^-]$ ratio in laboratory studies (Hallquist et al., 2003; Bertram & Thornton, 2009), no decrease in γ_{N2O5} suppression was found in the present study for $[H_2O]/[NO_3^-]$ ratio of up to 60. The more scattered data at higher $[H_2O]/[NO_3^-]$ range implies

165 that the variation of γ_{N2O5} become more sensitive to other factors in the diluted aqueous aerosols. Although the γ_{N2O5} measured at two mountain sites showed a positive relationship with $[Cl^-]/[NO_3^-]$, 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 γ_{N2O5} during our observations as laboratory studies have observed (Bertram & Thornton, 2009), possibly due to the complex effect of aerosol mixing state. Though the measured γ_{N2O5} exhibited nonlinear relationship and complex dependence on different factors at a

170 single site, the general consistent patterns at different sites in this study suggests the feasibility of a common parameterization representing the N_2O_5 uptake in these regions.

3.2 Comparison to parameterizations

Current regional air quality models such as WRF-Chem and CMAQ mainly use the γ_{N2O5} parameterization recommended by Bertram and Thornton (2009) (hereafter referred to BT09), which links γ_{N2O5} to aerosol water content, nitrate and chloride as

175 well as the aerosol size and ambient temperature. The BT09 parameterization based on the above-mentioned reaction mechanism (R1-R5) was expressed as follows:

$$\gamma_{N2O5} = \frac{4}{c}\frac{V_a}{S_a}K_H k'_{2f}\left(1 - \frac{1}{\left(\frac{k_3[H_2O]}{k_{2b}[NO_3^-]}\right) + 1 + \left(\frac{k_4[Cl^-]}{k_{2b}[NO_3^-]}\right)}\right)$$ Eq. (2)

$$k'_{2f} = \beta - \beta e^{(-\delta[H_2O])}$$ Eq. (3)

where V_a/S_a is the aerosol volume to surface area ratio; K_H is Henry's law coefficient; $\beta = 1.15\times10^6$; $\delta = -0.13$. k_3/k_{2b} (= 0.06)

180 and k_4/k_{2b} (= 29) represent the relative rates of competing reactions of intermediate $H_2ONO_2^+(aq)$ with H_2O (R3) and Cl^- (R4) over NO_3^- (R2), respectively. $[H_2O]$, $[NO_3^-]$ and $[Cl^-]$ are the aerosol water content, aerosol nitrate and chloride molarity, respectively, calculated by the E-AIM model with the measured ionic compositions of $PM_{2.5}$ and RH (http://www.aim.env.uea.ac.uk/aim/aim.php) (Wexler and Clegg, 2002).

We calculate the γ_{N2O5} values from BT09 with the measured aerosol composition at the five sites. The parameterized γ_{N2O5}

185 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 γ_{N2O5} 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

γ_{N2O5} at five sites in China and in different parts of the world. The BT09 parameterization (blue markers in Fig. 3) generally overestimates the observed γ_{N2O5} values in the range of 0.001 to 0.03, but is closer (within a factor of 1.5) to the observed value

190 for γ_{N2O5} 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 γ_{N2O5} 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

195 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

200 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

205 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 γ_{N2O5}

Based on the above discussion and comparison, we attempt to derive a new empirical parameterization of γ_{N2O5} 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

210 China. The derived empirical parameterization of γ_{N2O5} is shown as Eq. (4) and the fitted γ_{N2O5} are summarized in Table 1.

$$\gamma_{N2O5} = \frac{4}{c}\frac{V_a}{S_a}K_H \times 3.0 \times 10^4 \times [H_2O]\left(1 - \frac{1}{\left(0.033 \times \frac{[H_2O]}{[NO_3^-]}\right) + 1 + \left(3.4 \times \frac{[Cl^-]}{[NO_3^-]}\right)}\right) \qquad \text{Eq. (4)}$$

In view of the linear dependence of γ_{N2O5} on the aerosol water content in this study and reaction mechanism (Bertram & Thornton, 2009), the reaction coefficient with water (refer to k'$_{2f}$ in Eq. (2) and Eq. (3)) was fitted as a linear function of $[H_2O]$, as $(3.0 \pm 0.4) \times 10^4 \times [H_2O]$. Compared to original BT09 (Eq. (3)), the newly fitted k'$_{2f}$ is smaller for $[H_2O] < 38$ M, but become

215 higher with the increasing of aerosol water content (Fig. S2). 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 with a factor of 1.8 and 8.5, respectively. The smaller ratios of the reaction rates indicate a smaller enhancement effect of chloride but a larger

suppression effect by nitrate, which is consistent with the above-observed relationship of γ_{N2O5} with the aerosol composition. Other suppression effects such as organic coating and mixing state that was not specified in the parameterization also may

220   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 value and the large variability of the observed γ_{N2O5} than the original BT09 both with and without considering Cl⁻ effects.

As suggested by previous studies, the production yield of $ClNO_2$ (Φ_{ClNO2}) 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 $\Phi_{ClNO2} = 1/(1+k_3/k_4\times[H_2O]/[Cl^-])$ (Bertram & Thornton,

225   2009). Based on the above-fitted results for γ_{N2O5}, 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_{ClNO2} in different campaigns still cannot be well captured. As shown in Fig. 5, the new

230   fits can better catch the Φ_{ClNO2} trend at $[H_2O]/[Cl^-] > 750$, but discrepancy is still obvious at $[H_2O]/[Cl^-] < 750$. 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_{ClNO2} 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

235   for better parameterizing the heterogeneous $ClNO_2$ production.

3.4 Evaluation of the empirical parameterization

To further evaluate the representativeness and validity of the newly fitted empirical parameterization of γ_{N2O5} 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

240   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 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±18.77 µg m⁻³ vs 20.94±17.16 µg m⁻³), reducing the normalized mean

245   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 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 γ_{N2O5} and Φ_{ClNO2}, would therefore also reduce the discrepancies from the observation and improve the model performance in southern China.

4 Conclusion

Nitrate is becoming the predominant component of PM$_{2.5}$ during severe haze events in China 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$_2$O$_5$ 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$_2$O$_5$ uptake processes and derived an observation-based empirical parameterization of N$_2$O$_5$ uptake. While further research is still needed on the additional factors affecting γ_{N2O5} and Φ_{ClNO2}, the empirical parameterization derived here can be used in air quality models to improve the prediction of PM$_{2.5}$ and photochemical pollution in China and similar polluted regions of the world.

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.

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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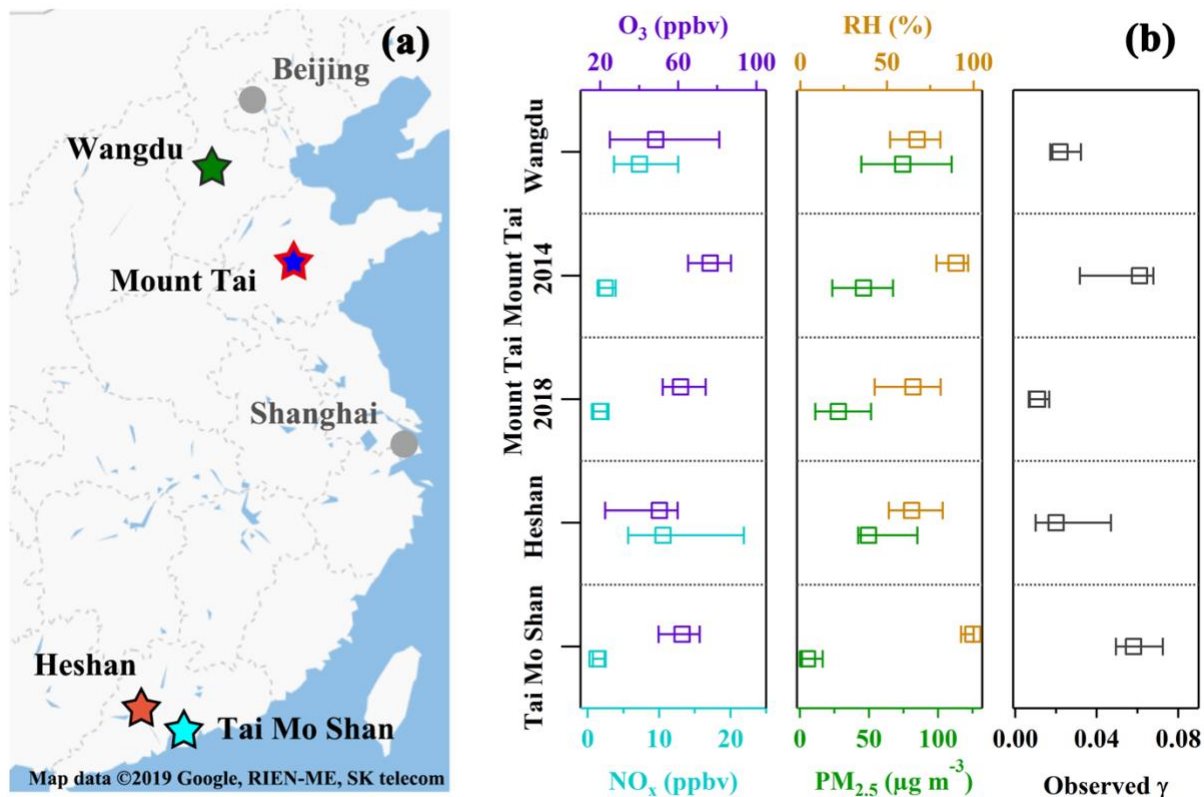
Figure 1. (a) The locations of the four field measurement sites (pentagram markers) in China. (b) Comparisons of the concentrations of O₃, NOₓ, PM₂.₅, and observed RH and γN2O5 during the five campaigns in China. Squares represent the median values and bars represent the interquartile ranges of the values 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 γN2O5 was determined only during non-cloudy periods in these two campaigns.

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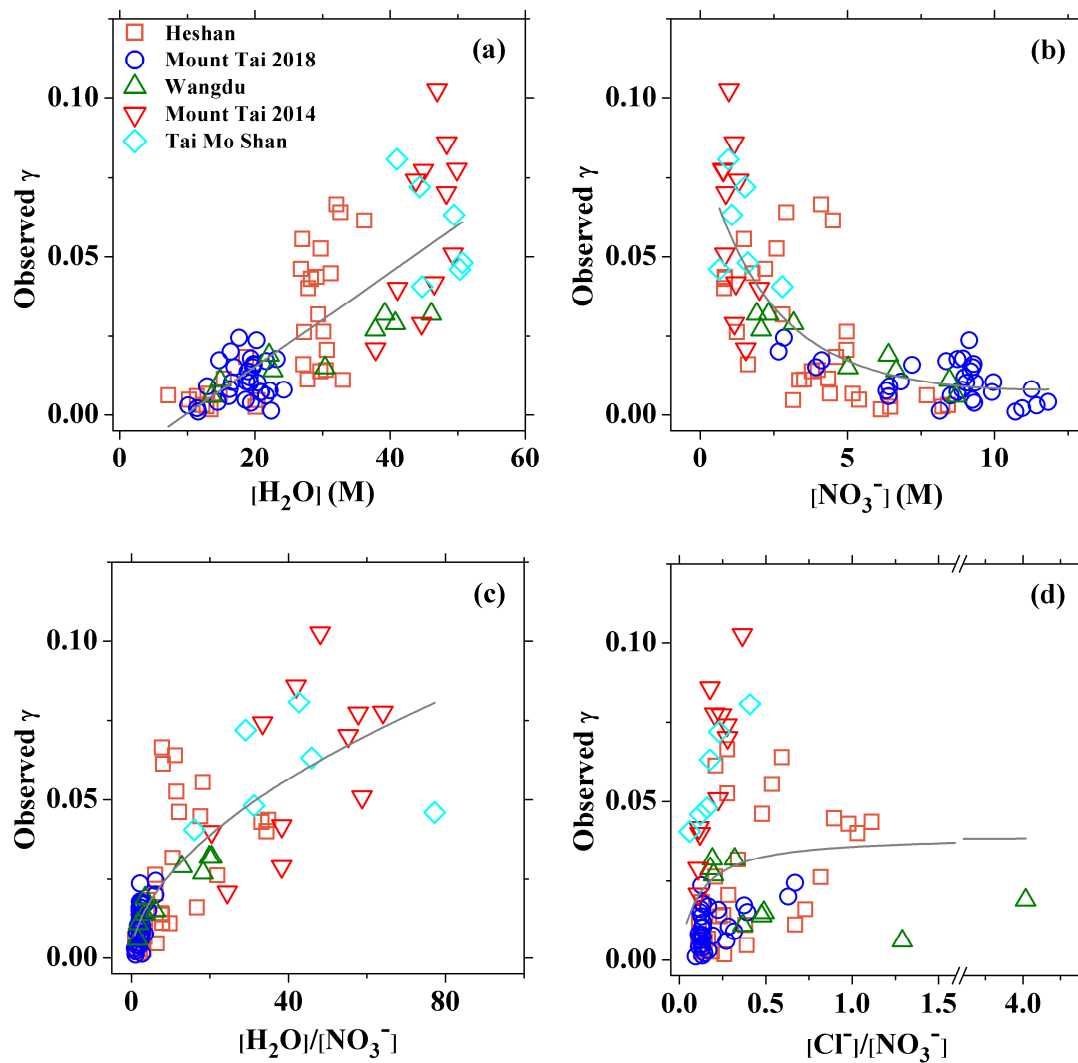
Figure 2. Relationship between the field measured/derived N₂O₅ uptake coefficient γ$_{N2O5}$ and (a) aerosol water content, (b) particle nitrate, (c) H₂O to NO₃⁻ molarity ratio, and (d) Cl⁻ to NO₃⁻ molarity ratio. Green triangles, red triangles, cyan squares, yellow squares and blue circles represent 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.
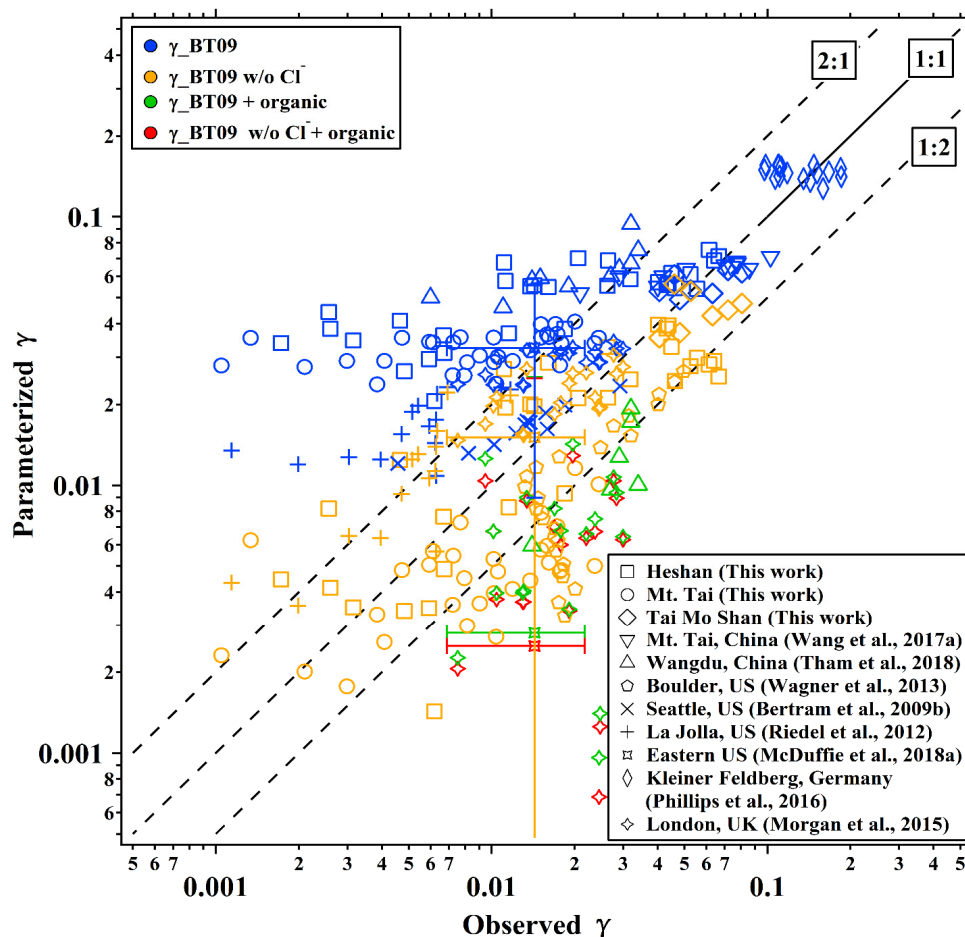
Figure 3. Summary of the comparisons of field measured/derived γ_{N2O5} **and values estimated from parameterizations from the literature. Blue, yellow, green and purple markers represent the results calculated from parameterizations of original BT09, BT09 excluding chloride effect, BT09 plus organic effect, and BT09 excluding chloride but with organic effect, respectively.**

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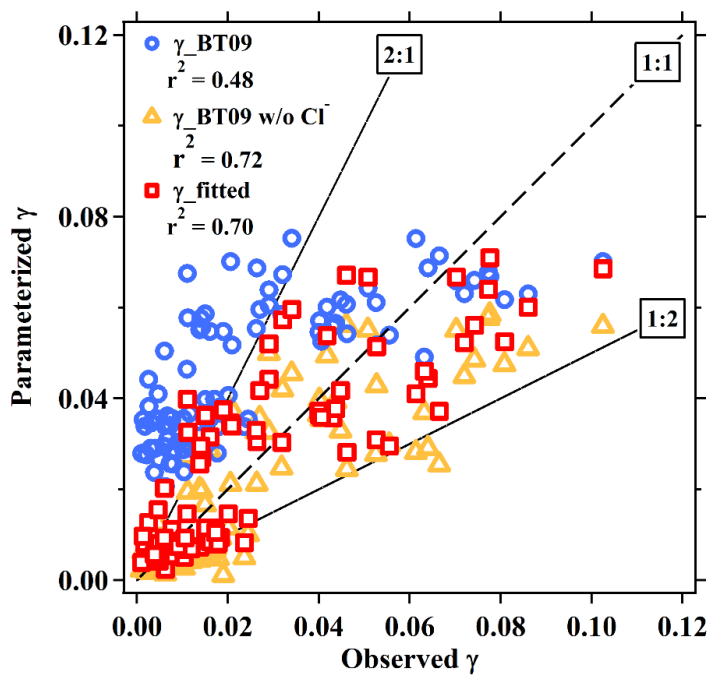
Figure 4. Comparison of the field measured/derived γ_{N2O5} with the values estimated from parameterizations for the five sites in the present study. The dashed line represents the 1:1 line. Blue circles, yellow triangles, and red squares are results estimated by BT09 parameterization, BT09 excluding chloride effect and the derived observation-based empirical parameterization, respectively.
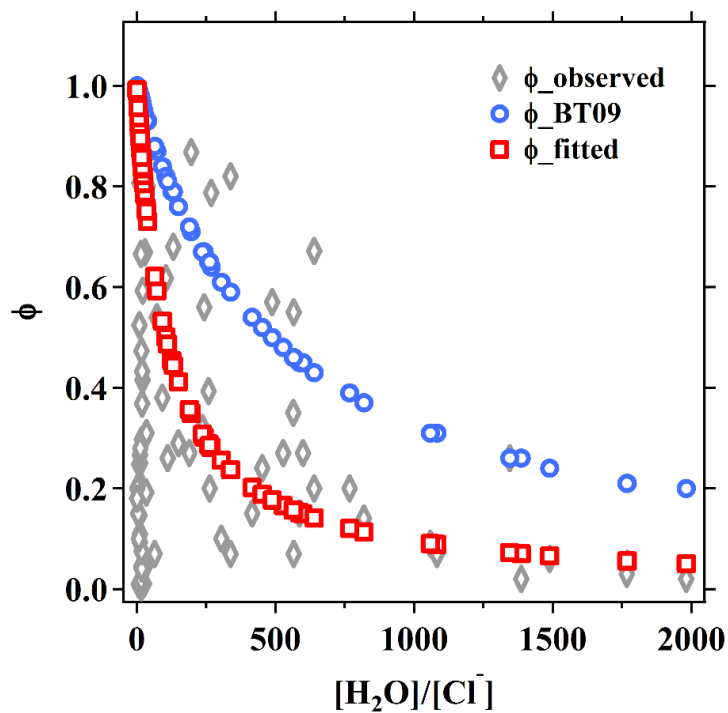
Figure 5. Relationship between the ClNO₂ yield, Φ_{ClNO_2}, and the molarity ratio of H₂O to Cl⁻. Grey rhombi, blue circles, and red squares represent the observed Φ_{ClNO_2}, values from BT09 parameterization and fitted from the empirical parameters derived in the present study, respectively.

Table 1. Statistical summary and comparison of the observed parameters (N_2O_5 uptake coefficient, γ_{N2O5}; $ClNO_2$ yield, Φ_{ClNO2}) with values predicted from different parameterizations.

Parameters		Average ± SD	Maximum	Minimum	r^2
γ_{N2O5}	Observed	0.026 ± 0.024	0.10	0.001	-
	BT09	0.047 ± 0.015	0.075	0.021	0.54
	BT09 w/o Cl$^-$	0.020 ± 0.018	0.058	0.001	0.72
	Fitted	0.026 ± 0.020	0.071	0.002	0.70
Φ_{ClNO2}	Observed	0.31 ± 0.27	1.04	0.004	-
	BT09	0.74 ± 0.26	1.00	0.20	0.025
	Fitted	0.57 ± 0.33	0.99	0.05	0.003

Table 2. Statistical summary and comparison of the observed species (nitrate and NO_2 concentrations) with values predicted from different parameterization. NMB represents the normalized mean bias.

Species		Observed average ± SD ($\mu g\ m^{-3}$)	Simulated average ± SD ($\mu g\ m^{-3}$)	NMB (%)	r^2
NO_3^-	CAMQ default (BT09)	20.94 ± 17.16	24.86 ± 20.48	18.72	0.56
	CAMQ revised (Fitted)		20.98 ± 18.77	0.19	0.56
NO_2	CAMQ default (BT09)	52.09 ± 27.25	45.71 ± 31.21	-12.25	0.31
	CAMQ revised (Fitted)		47.89 ± 32.10	-8.06	0.34