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 models 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

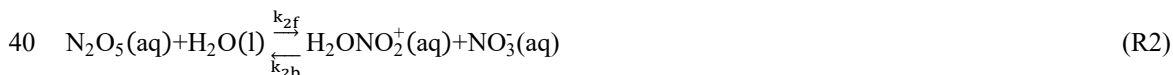
Heterogeneous reaction of dinitrogen pentoxide (N_2O_5) on aerosol surfaces plays an important role in the nocturnal removal of nitrogen oxides (NO_x), secondary nitrate formation, and chlorine activation through nitryl chloride ($ClNO_2$) production on chloride-containing aerosols (Brown et al., 2006; 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 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).

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

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

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

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

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 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 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 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; 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 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, which revealed significant discrepancies between them and large variations 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 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.

To further investigate the active N_2O_5 heterogeneous process revealed in previously studies 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} were conducted at two rural sites in northern and southern China 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 the γ_{N2O5} and compare them with laboratory-derived parameterizations. Then we propose improved parameters for γ_{N2O5} 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 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 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. 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 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 and 60 km to the south and north, respectively. N_2O_5 and $ClNO_2$ were 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 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 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). 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 Teflon to reduce the wall loss of N_2O_5. The inlet was equipped with parallel sampling pass ways with one having a filter to remove aerosols. 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 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, 2018).

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{R5}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{R6}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{R7}$$

$$NO_3 + NO \rightarrow 2NO_2 \tag{R8}$$

$$NO_3 + VOC \rightarrow products \tag{R9}$$

$$N_2O_5 + aerosol/wall \rightarrow products \tag{R10}$$

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

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

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 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 γ_{N2O5}. 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 γ_{N2O5} around 0.03 and from 34% to 65% at γ_{N2O5} around 0.01 with $S_a = 1000$ μm^2 cm^{-3} when RH varied from 20% to 70 %, and could be higher at RH>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 the 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 γ_{N2O5} 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, NOx 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.

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 $ClNO_2$ 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). 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 simulation period was from 1 to 31 December 2017, with five days before as a spin-up time.

3 Results and discussion

3.1 Field measured γ_{N2O5} and influencing 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 $\mu g\ m^{-3}$ 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 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). The field measured γ_{N2O5} 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
160   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 the positive correlation of γ_{N2O5} with the humidity or aerosol water has been observed in the low range in previous laboratory
165   studies, the γ_{N2O5} reached plateaus at a value around 0.036 at RH> 50% or $[H_2O] > 15$ M (Hallquist et al., 2003; Thornton et al., 2003; Bertram & Thornton, 2009). In contrast, other laboratory studies also measured higher γ_{N2O5} values on NH_4HSO_4 particles. For example, Mozurkewich and Calvert (1988) reported an upper limit of γ_{N2O5} 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 γ_{N2O5}, 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
170   measurements also observed γ_{N2O5} 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 γ_{N2O5} 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 γ_{N2O5} with $[H_2O]$ 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
175   always limited by aerosol water content under all the encountered ambient conditions. Since limited measurement data of γ_{N2O5} 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. For nitrate, a clear suppression effect can be
180   found at the Chinese sites (Fig. 2b), which is similar to most of the previous field and laboratory studies. The decrease of γ_{N2O5} with increasing nitrate concentration seems to be better captured by an 'exponential-decay' curve, with almost linear 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.

The γ_{N2O5} variation was affected by the additive effects from both $[NO_3^-]$ and $[H_2O]$, which could not be easily isolated because
185   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 plateauing 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 that the variation of γ_{N2O5} become more sensitive to other factors in the diluted aqueous aerosols. Although the γ_{N2O5} measured
190   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 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 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 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); $\beta = 1.15\times10^6$; $\delta = -0.13$. k_3/k_{2b} (= 0.06) and k_4/k_{2b} (= 29) represent the relative rates of competing reactions of intermediate $H_2ONO_2^+$(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} 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 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 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 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 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 second-order reaction rate coefficient with water (refer to k'_{2f} in Eq. (2) and Eq. (3)) was fitted as a linear function of $[H_2O]$, as $(3.0 \pm 0.4) \times 10^4 \times [H_2O]$. This value is in reasonable agreement with the values of $(2.7-3.8) \times 10^4$, $\sim 3.9 \times 10^4$, and 2.6×10^4 M^{-1} 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 $[H_2O] < 38$ 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 γ_{N2O5} in the parameterization is linearly dependent on the K_H, an increase of K_H value would proportionally increase the γ_{N2O5} value but cannot account for the large variability of measured γ_{N2O5} 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 a factor of 1.8 and 8.5, respectively. The smaller ratios of the reaction rates indicate a smaller enhancement effect of chloride or 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 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 γ_{N2O5} than the original BT09 both with and without considering Cl^- effects.

As suggested by the 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, 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 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 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_{ClNO2} 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 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 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% 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 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 Herbei 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.

4 Conclusion

Nitrate is becoming the predominant component of $PM_{2.5}$ during severe haze events in China in 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 γ_{N2O5} and $\Phi_{ClNO2,}$ 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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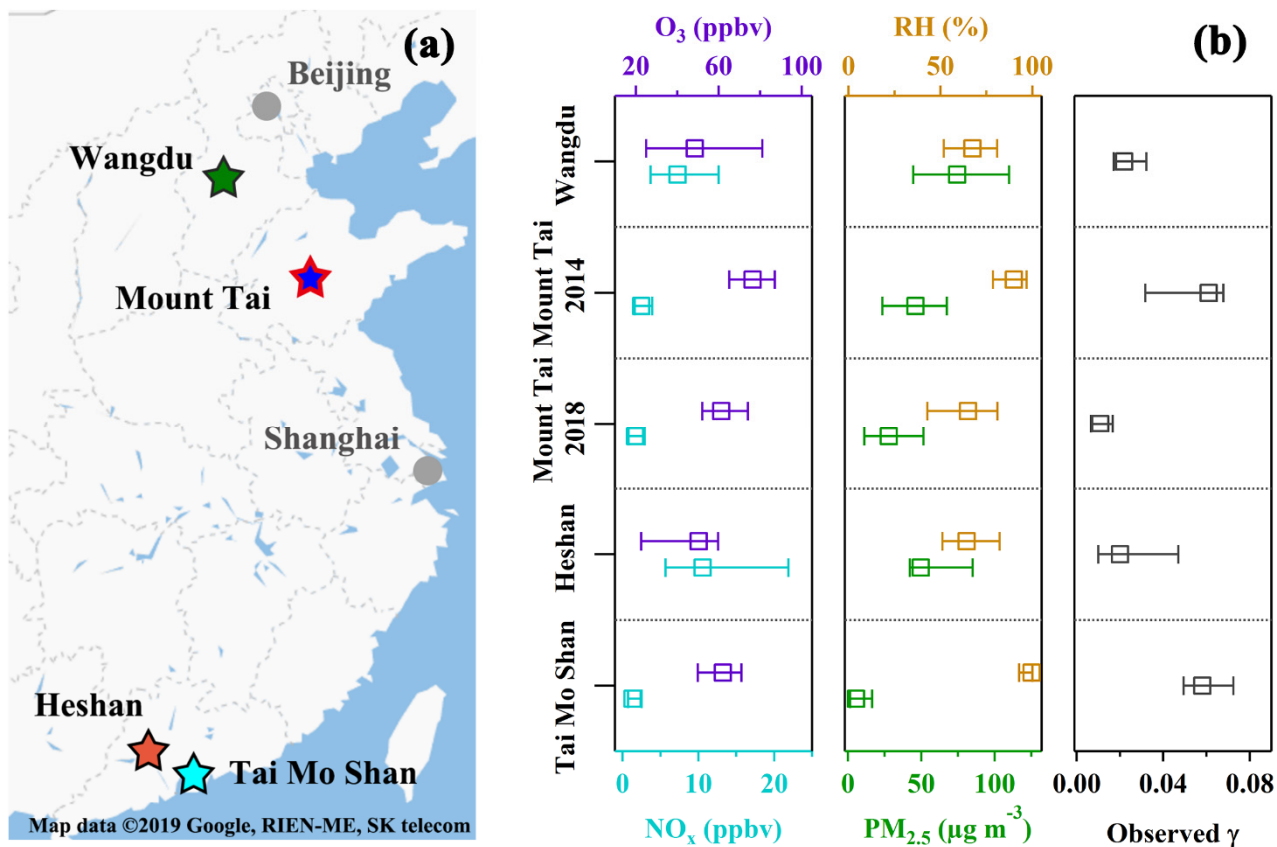
Figure 1. (a) The locations of the four field measurement sites (pentagram markers) in China. (b) Comparisons of the concentrations of O₃, NOₓ, PM₂.₅, and observed RH and γ_N2O5 during the five campaigns in China. Squares represent the median values and bars represent the interquartile ranges of the values in the five measurements. It should be noted that the high RH in 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.
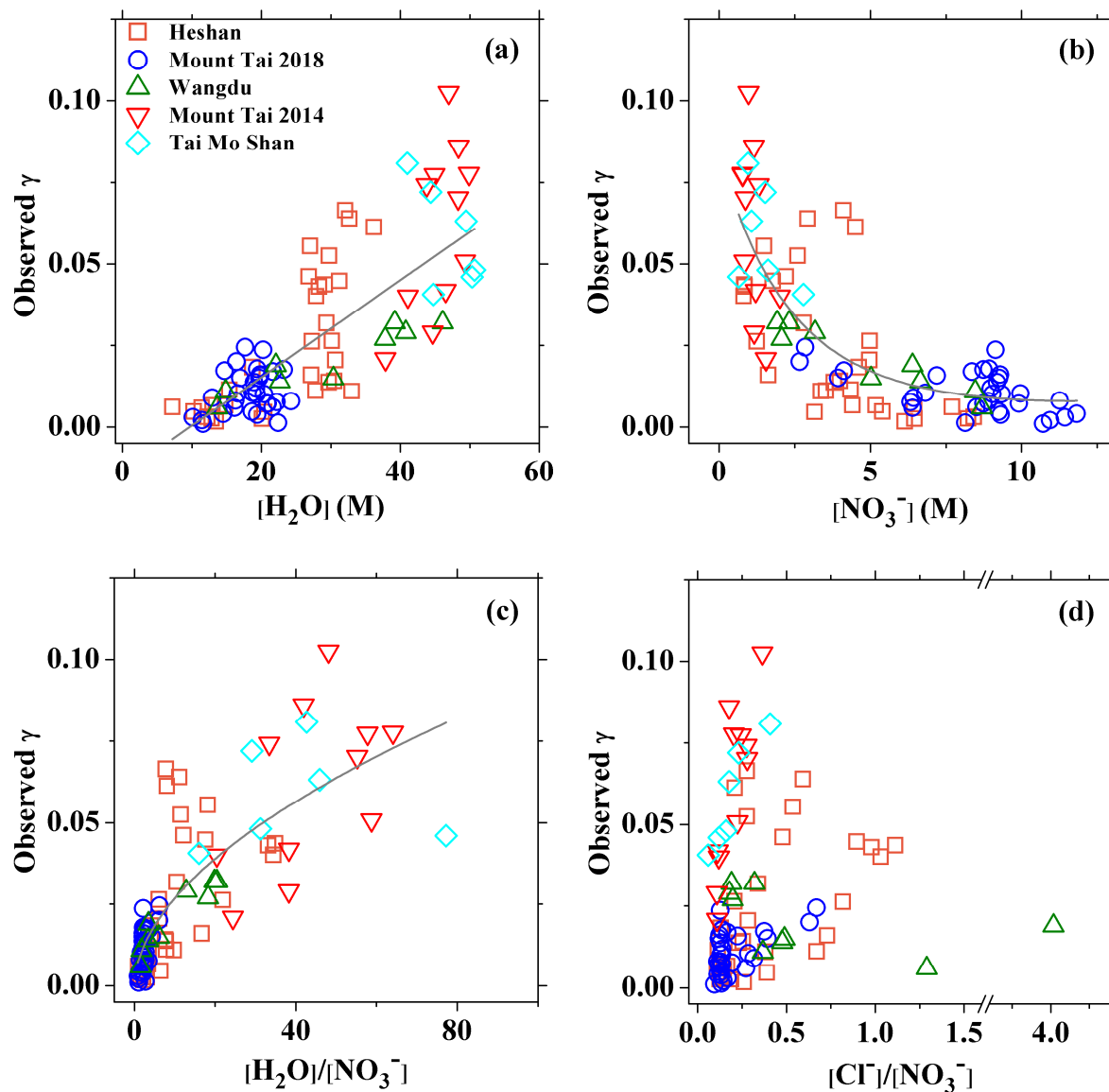
Figure 2. Relationship between the field measured/derived N₂O₅ uptake coefficient γ_{N2O5} and (a) aerosol water content, (b) particle nitrate, (c) H₂O to NO₃⁻ molarity ratio, and (d) Cl⁻ to NO₃⁻ molarity ratio. Green triangles, red triangles, cyan squares, yellow squares and blue circles represent the 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.
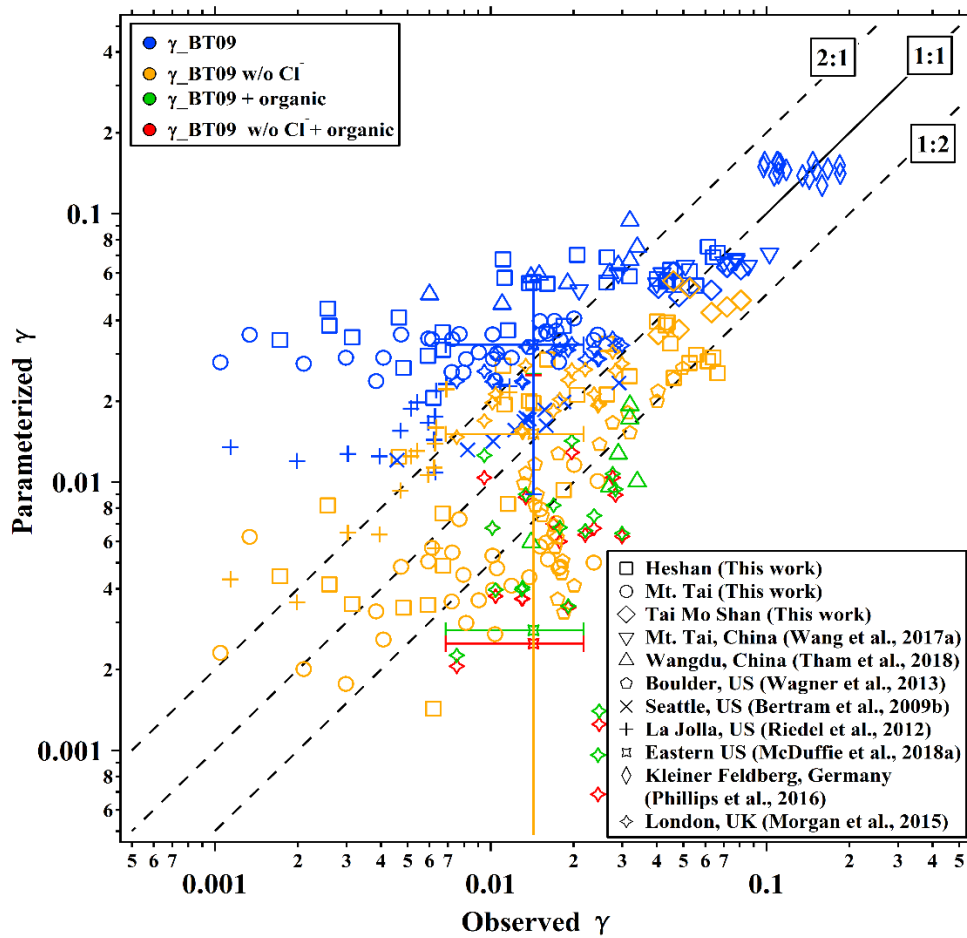
Figure 3. Summary of the comparisons of field measured/derived γ_{N2O5} and values estimated from parameterizations from the literature. Blue, yellow, green and purple markers represent the results calculated from parameterizations of original BT09, BT09 excluding chloride effect, BT09 plus organic effect, and BT09 excluding chloride but with organic effect, respectively.

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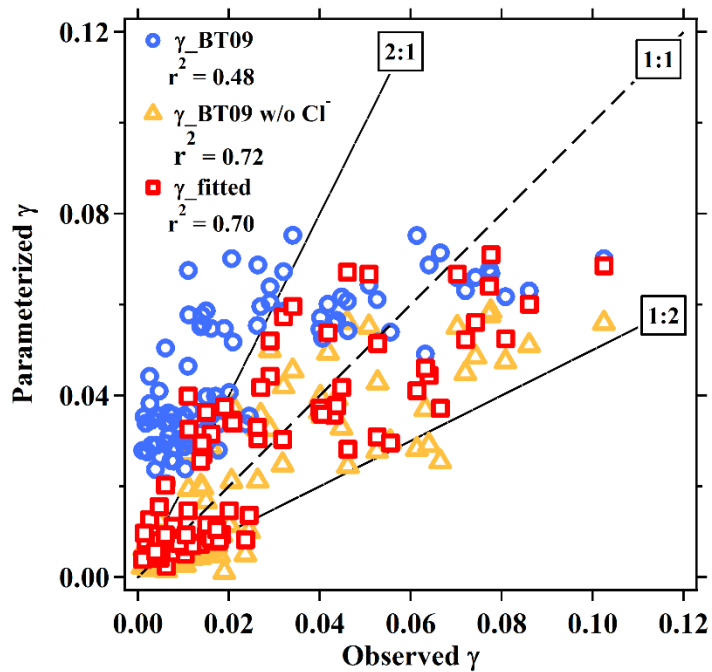
505 **Figure 4. Comparison of the field measured/derived γ_{N2O5} with the values estimated from parameterizations for the five sites in the present study. The dashed line represents the 1:1 line. Blue circles, yellow triangles, and red squares are results estimated by BT09 parameterization, BT09 excluding chloride effect and the derived observation-based empirical parameterization, respectively.**
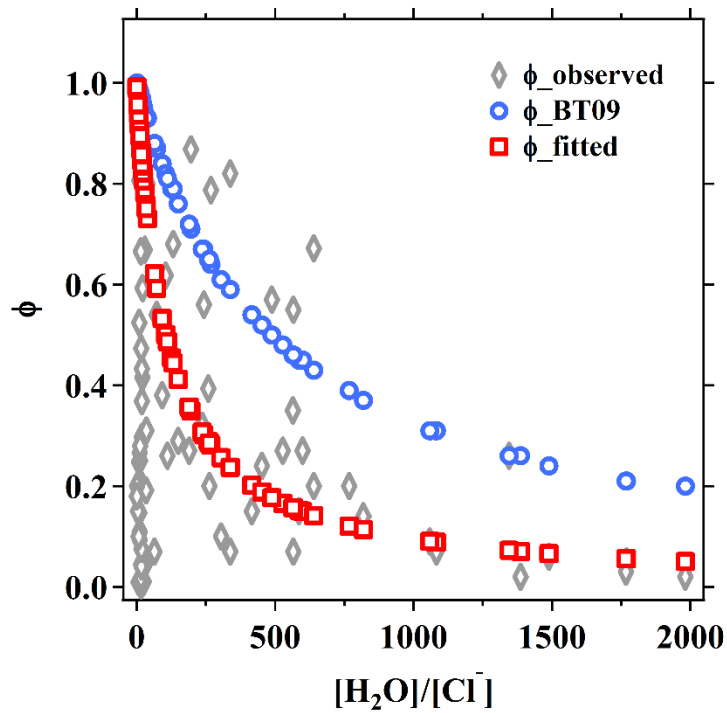
Figure 5. Relationship between the ClNO2 yield, Φ_{ClNO2}, and the molarity ratio of H2O to Cl-. Grey rhombi, blue circles, and red squares represent the observed Φ_{ClNO2}, values from BT09 parameterization and fitted from the empirical parameters derived in the present study, respectively.
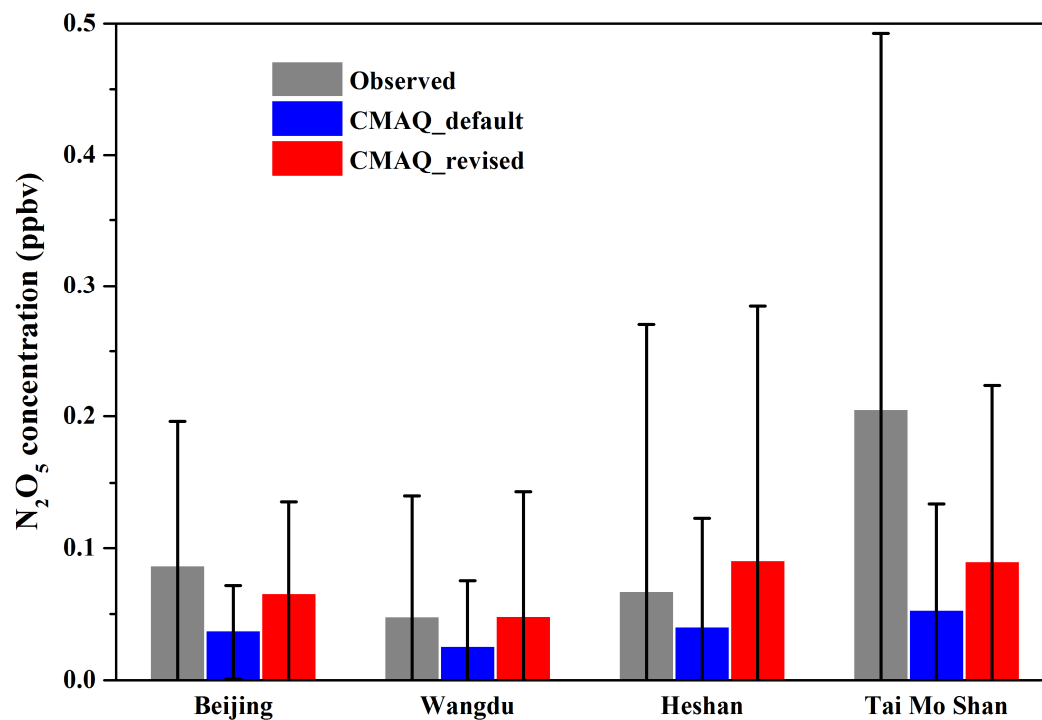
Figure 6. Comparison of simulated N_2O_5 concentrations by the CMAQ model for December 2017 with the wintertime observation results from four sites in China. The field observations were conducted in Wangdu (Hebei Province) in December 2017, Beijing in January 2018, Heshan (Guangdong Province) in January 2017 and Tai Mao Shan (Hong Kong) in November 2013. The columns and error bars represent the average value and standard deviation, respectively.

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

Parameters		Average $\pm$ 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 NO₂ concentrations) with values predicted from different parameterization. NMB represents the normalized mean bias.

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