Atmos. Meas. Tech., 11, 5643–5655, 2018
https://doi.org/10.5194/amt-11-5643-2018

Atmospheric Measurement Techniques
Open Access

An in situ flow tube system for direct measurement of N_2O_5 heterogeneous uptake coefficients in polluted environments

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Received: 5 June 2018 – Discussion started: 21 June 2018
Revised: 17 September 2018 – Accepted: 27 September 2018 – Published: 16 October 2018

Abstract. The heterogeneous reactivity of dinitrogen pentoxide (N_2O_5) on ambient aerosols plays a key role in the atmospheric fate of NO_x and formation of secondary pollutants. To better understand the reactive uptake of N_2O_5 on complex ambient aerosols, an in situ experimental approach to direct measurement of N_2O_5 uptake coefficient (γN_2O_5) was developed for application in environments with high, variable ambient precursors. The method utilizes an aerosol flow tube reactor coupled with an iterative chemical box model to derive γN_2O_5 from the depletion of synthetically generated N_2O_5 when mixed with ambient aerosols. Laboratory tests and model simulations were performed to characterize the system and the factors affecting γN_2O_5, including mean residence time, wall loss variability with relative humidity (RH), and N_2O_5 formation and titration with high levels of NO, NO_x, and O_3. The overall uncertainty was estimated to be 37 %–40 % at γN_2O_5 of 0.03 for RH varying from 20 % to 70 %. The results indicate that this flow tube coupled with the iterative model method could be buffered to NO concentrations below 8 ppbv and against air mass fluctuations switching between aerosol and non-aerosol modes. The system was then deployed in the field to test its applicability under conditions of high ambient NO_2 and O_3 and fresh NO emission. The results demonstrate that the iterative model improved the accuracy of γN_2O_5 calculations in polluted environments and thus support the further field deployment of the system to study the impacts of heterogeneous N_2O_5 reactivity on photochemistry and aerosol formation.

1 Introduction

Dinitrogen pentoxide (N_2O_5) is a nocturnal reactive intermediate in the atmospheric oxidation of nitrogen oxides (NO_x), which plays an important role in atmospheric photochemistry and the production of secondary pollutants (e.g., Chang et al., 2011). N_2O_5 is formed from the reaction of nitrogen dioxide (NO_2) and nitrate radical (NO_3). Because NO_3 is photolytically unstable, it (and therefore N_2O_5) only accumulates under dark conditions (i.e., at night). The heterogeneous reactions of N_2O_5 on aerosols have been recognized as a major sink for NO_x, affecting the atmospheric lifetime of NO_x and the formation of ozone and other secondary pollutants (e.g., Brown et al., 2007; Wang et al., 2016). The heterogeneous N_2O_5 loss rate on aerosols (k_{aerosols}) depends on the uptake coefficient of N_2O_5 (γN_2O_5) and the available aerosol surface area, and can be expressed using Eq. (1) when the gas-phase diffusion effect is negligible (Fuchs and Sutugin, 1971; Tang et al., 2014).

$$k_{\text{aerosols}} = \frac{1}{4} c_{N_2O_5} S_a \gamma N_2O_5, \tag{1}$$

where $c_{N_2O_5}$ ($\mathrm{m\,s^{-1}}$) is the mean molecular speed of N_2O_5 and S_a ($\mathrm{m^2\,m^{-3}}$) is the aerosol surface area concentration. γN_2O_5 is the reaction probability of a N_2O_5 molecule colliding with the aerosol surface, resulting in net removal via reactions on aerosols. Because γN_2O_5 is a critical parameter for determining N_2O_5 uptake on aerosols, it is necessary to develop reliable methods to measure it.

γN_2O_5 has typically been determined in the laboratory using different types of flow tubes and reactors to measure the decay rate of N_2O_5 in the presence of pure inorganic and organic aerosols or mixed aerosols under different conditions (e.g., Thornton et al., 2003; Tang et al., 2017, and references cited therein). The γN_2O_5 has been shown to be highly dependent on aerosol composition, temperature, and relative humidity; different parameterizations of varying degrees of complexity have thus been proposed to relate γN_2O_5 to aerosol composition (Anttila et al., 2006; Bertram and Thornton, 2009; Davis et al., 2008; Evans and Jacob, 2005; Riemer et al., 2009). In ambient conditions, several methods have been developed to derive γN_2O_5 directly from atmospheric concentrations of N_2O_5. Brown et al. (2007) utilized steady-state approximation of NO_3 and N_2O_5 to derive γN_2O_5 based on the correlation of inverse N_2O_5 steady-state lifetime with NO_2 concentration and aerosol surface area; Phillips et al. (2016) assumed a conserved air mass and used the production rates of NO_3^- and $ClNO_2$ to derive γN_2O_5; and Wagner et al. (2013) applied an iterative chemical box model to derive the appropriate γN_2O_5 to match the predicted N_2O_5 concentration to the measured values with the assumption of the reaction time starting at sunset and with no interception of other NO_x emissions.

Bertram et al. (2009a) introduced an approach to directly measure γN_2O_5 on ambient aerosols by utilizing an entrained aerosol flow reactor coupled with a chemical ionization mass spectrometer (CIMS). By switching sampling between filtered and unfiltered ambient air, the reactivity of N_2O_5 was determined based on a comparison of the pseudo-first-order loss rate of N_2O_5 in ambient air with and without aerosols. The loss rate of N_2O_5 to aerosols (k_{aerosols}) could be derived from the concentration ratio at the exit of the flow reactor, with the assumption that the wall loss of N_2O_5 is constant in the successive two measurements and that all losses are first order (Bertram et al., 2009a):

$$k_{\mathrm{aerosols}} = -\frac{1}{\Delta t}\ln\left(\frac{[N_2O_5]_{\Delta t}^{\mathrm{w/aerosols}}}{[N_2O_5]_{\Delta t}^{\mathrm{wo/aerosols}}}\right), \qquad (2)$$

where Δt is the mean residence time in the flow tube reactor and $[N_2O_5]_{\Delta t}$ is the N_2O_5 concentration measured at the exit of the flow reactor in the two modes (i.e., the presence and absence of aerosols). This flow tube apparatus was deployed at two urban sites in Boulder and one coastal site in La Jolla to measure γN_2O_5 on ambient aerosols (Bertram et al., 2009b; Riedel et al., 2012). They found that the fluctuation of relative humidity (RH) and NO_3 reactivity (mainly dominated by NO) could lead to great uncertainty in measured γN_2O_5, and they therefore applied some screening criteria, including only data with a RH fluctuation of less than 2 % and NO concentration lower than 750 pptv. This constraint resulted in about 20 % of the data being used for further analysis. It was necessary to adopt these criteria because only first-order loss is considered in the flow tube reactor and other reactions involving ambient NO, NO_2, and O_3 are not. The latter treatment is suitable when ambient concentrations are low and the air mass is relatively stable, but it may be problematic in polluted environments with high fresh NO_x emissions, high O_3 concentrations, and rapidly changing air mass.

Several recent studies have revealed active N_2O_5 heterogeneous processes on aerosols at polluted sites and its significant impacts on photochemistry and secondary aerosol formation due to abundant NO_x, O_3, and aerosols (e.g., Li et al., 2016; Tham et al., 2016; Wang et al., 2016; X. Wang et al., 2017; Z. Wang et al., 2017; Yun et al., 2018). The γN_2O_5 derived from ambient concentration measurements showed different characteristics and dependence compared to previous measurements in relatively clean environments (Morgan et al., 2015; Z. Wang et al., 2017). To better understand the reactive uptake of N_2O_5 on complex ambient aerosols, a flow tube reactor approach was developed for direct N_2O_5 reactivity measurement under highly polluted conditions. In the following sections, we describe in detail the method used for determining the N_2O_5 uptake coefficient with an iterative box model and discuss the factors affecting the system's performance and uncertainty. Laboratory tests and field deployment of the method are presented to demonstrate its application under conditions with high ambient concentrations of NO_2 and O_3 and fresh NO emission.

2 Methodology

2.1 Flow tube reactor

The flow tube system consists of an N_2O_5 generation part, a sample inlet with aerosol filter manifold, a flow tube reactor, and detection instruments. A schematic diagram of the experimental apparatus is given in Fig. 1. The sample inlet with an aerosol filter manifold is made of 1/4 in. outer diameter (OD) stainless-steel tubing. By switching two stainless-steel ball valves, ambient air can be introduced directly into the flow tube or through a PTFE membrane (Pall Life Sciences) to remove aerosols. The flow tube is a Teflon-coated stainless-steel tube, 120 cm in length with an internal diameter of 12.5 cm. The ambient or filtered air enters and exits the flow tube via 10 cm deep 60° tapered end caps. The total flow rate through the flow tube is 4.6 standard liter per minute (SLPM) and includes 120 standard cubic centimeter per minute (SCCM) of N_2O_5 flow, which is introduced through an orthogonal entry to minimize the entrance length of the injected flow. The air pressure in the flow tube reactor is around 730 torr. The adopted flow rate and pressure give a Reynolds number of 55 (i.e., laminar flow) in the flow tube reactor. At the exit of the flow tube reactor, several detection instruments are used to measure the concentrations of N_2O_5, O_3, NO_x, and aerosol surface area.

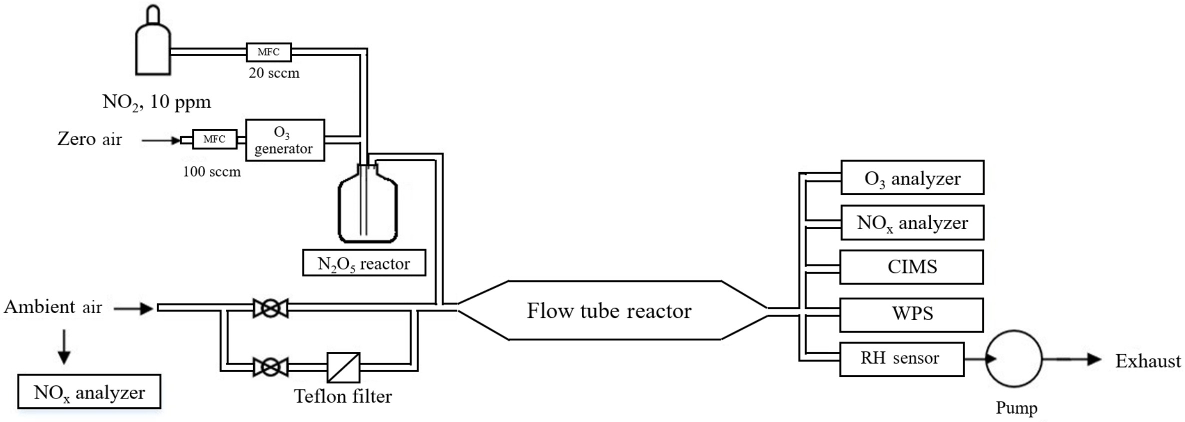

Figure 1. Schematic diagram of the aerosol flow tube system.

2.2 Generation of N_2O_5

N_2O_5 is generated in situ from the reaction of O_3 with excess NO_2 at room temperature via Reactions (R1) and (R2), which has been used in many previous lab and field measurements (e.g., Bertram et al., 2009a).

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad \text{(R2)}$$

In this study, ozone was generated from O_2 photolysis with a mercury lamp in a commercial calibrator (model 4010, Sabio Instrument Inc.). One hundred SCCM of produced O_3 flow was mixed with 20 SCCM of NO_2 (10 ppmv balanced in N_2; Arkonic, USA) in a Teflon reaction chamber (volume = 68 cm^3) for about 28 s prior to injection into the flow tube reactor. Under conditions of excessive NO_2, the system was expected to shift the R2 equilibrium towards N_2O_5. Concentrations of synthesized N_2O_5 were calculated from observed changes in NO_2 (before and after addition of O_3), and the N_2O_5 content had also been inter-validated with a cavity ring-down spectrometer (CRDS) in our previous studies (Wang et al., 2016). Prior to the N_2O_5 generation, the system was purged with dry zero air and NO_2 for at least 2 h, to minimize the water content level and stabilize the NO_2 source. This system was shown to be able to produce N_2O_5 concentrations from 1 to 10 ppbv (after dilution in the flow tube). In a typical experiment used in the present study, the input of the N_2O_5 source to the top of the flow tube contained 4.3 ppbv of N_2O_5, together with 106 ppbv of O_3 and 57 ppbv of NO_2. The stability of the synthetic-N_2O_5 source was tested continuously for 8 h, and the variation of the signal was within ±2 % in each hour. More detailed description of the N_2O_5 generation can be found in Wang et al. (2016).

2.3 Detection instruments

At the exit of the flow tube reactor, O_3 was measured by a UV photometric analyzer (Thermo, Model 49i) and NO_2 was measured by a chemiluminescence NO_x analyzer (Thermo, Model 42i) equipped with a blue-light photolytic converter (BLC). The aerosol number concentration and size distribution (10 nm to 10 µm) were measured by a wide-range particle spectrometer (WPS, model 1000XP, MSP Corporation, USA) to determine the aerosol surface area. The uncertainty of the aerosol surface area measurement was 20 %–30 % (Z. Wang et al., 2017; Tham et al., 2018). The transmission of aerosols in the flow tube was evaluated using laboratory-generated $(NH_4)_2SO_4$ particles. The passing efficiency was around 50 % for particles with a size of 20 nm and more than 90 % for particles larger than 100 nm. The total surface area loss in the flow tube was around 10 %–25 %. The N_2O_5 and $ClNO_2$ concentrations were quantified by an iodide-adduct chemical ionization mass spectrometer (CIMS; THS Instrument, Atlanta). The CIMS has been deployed in several field campaigns, and the setup and operation have been previously described (Tham et al., 2016; Wang et al., 2016; X. Wang et al., 2017; Z. Wang et al., 2017). Briefly, the primary ion I^- was generated from ionization of CH_3I diluted in N_2 flow through a ^{210}Po source. The N_2O_5 and $ClNO_2$ were detected as ion clusters of $I(N_2O_5)^-$ and $I(ClNO_2)^-$ at 235 and 208 m/z by the quadrupole mass spectrometer. Because of the higher pipeline resistance in the flow tube reactor compared to ambient measurement, a smaller orifice with a 0.0135 in diameter was utilized in the CIMS inlet to reduce the sample flow, and another orifice was added before the scroll pump to keep the pressure in the ionization reaction chamber at 50 torr. The corresponding sample flow was 0.4 SLPM. The detection limit of the instrument was estimated to be 2 pptv (1 min averaged data), and the uncertainty of the CIMS measurement was estimated as ±25 % (Tham et al., 2016). The ambient volatile organic compounds (VOCs) were determined using an online gas chromatograph (GC) coupled with a flame ionization detector (FID) and a mass spectrometer (MS). The VOC concentrations were used to determine the $k_{NO_3\text{-}VOC}$ in the aerosol flow tube system, which was treated as constant during the short time period of flow tube measurement. The ambient NO level was measured by another chemiluminescence NO_x analyzer (Thermo, Model 42i) equipped with a molybdenum converter.

3 Determination of residence time

The mean residence time that represents the average reaction time of the gases in the flow tube reactor is an essential parameter in calculation of the reactive uptake coefficient. In a previous flow reactor studies (e.g., Thornton et al., 2003), the average residence time has usually been calculated from the flow rate and flow tube volume assuming an ideal laminar flow. To determine the mean residence time for non-ideal flow more accurately, the residence time distribution (RTD) method introduced by Danckwerts (1953) was used in the present study. The RTD method involves introduction of an inert tracer species into the reactor and detection of its transient concentration leaving the reactor outlet, and it has been widely used in previous lab studies to characterize the mixing and flow behavior of non-ideal aerosol flow reactors (e.g., Lambe et al., 2011).

Pulse injection of highly concentrated $ClNO_2$ was used in the present study to measure the RTD and hence determine the mean residence time. $ClNO_2$ is an inert gas within the dark Teflon-coated flow tube reactor and can be measured by CIMS with high time resolution (> 1 Hz). $ClNO_2$ was synthesized in situ via passing the N_2O_5 through a NaCl slurry in the Teflon tubing reactor (Wang et al., 2016). The pulse injection was controlled by a solenoid valve. At $t = 0$ s, 120 SCCM (the same flow as N_2O_5 injection during the uptake measurement) of $ClNO_2$ was directly injected into the flow tube reactor; at $t = 2$ s, the solenoid valve switched and the $ClNO_2$ flow was passed through a charcoal filter to provide zero gas into the flow tube reactor. The RTD function $E(t)$ is defined by the following equation:

$$E(t) = \frac{C_{(t)}}{\int_0^\infty C_{(t)}\,\mathrm{d}t}, \tag{3}$$

where $C_{(t)}$ represents the $ClNO_2$ concentration measured at time t. Then the mean residence time can be calculated as follows:

$$\Delta t = \int\limits_0^\infty t E(t)\,\mathrm{d}t. \tag{4}$$

The measurement result of the residence time test is shown in Fig. 2. With a flow rate of 4.6 SLPM in the flow tube reactor, the mean residence time determined from the RTD method was 149 ± 2 s. In comparison, the residence time calculated using the flow rate and reactor volume gives a value of 159 ± 5 s, which is 6.7 % higher than that given by the RTD method, and could lead to underestimation of the rate constant. The RTD function in Fig. 2 is clearly different from the ideal laminar flow reactor. Bertram et al. (2009a) have suggested that the determined rate constant would be underestimated by up to 25 % due to non-ideal plug flow conditions. More discussion of the uncertainty in γN_2O_5 calculation associated with residence time distribution is presented in Sect. 5.

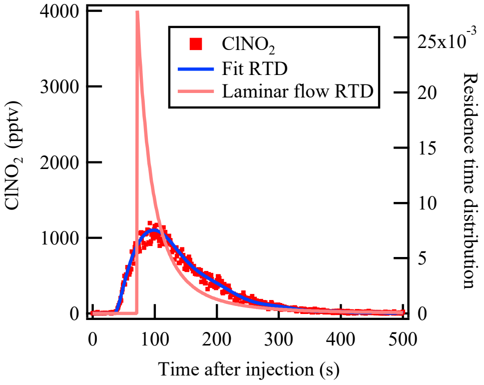

Figure 2. The measured residence time distribution of the injected $ClNO_2$ in the flow tube reactor. The blue line represents the fitted residence time distribution of the $ClNO_2$ pulse injection experiment. The pink line represents the expected residence time distribution of an ideal laminar flow reactor without diffusion.

4 Iterative box model for determination of loss rate and uptake coefficient

As described previously, the reactivity of N_2O_5 can be investigated using the aerosol modulation by comparing the loss rate of generated N_2O_5 in the flow tube reactor with and without ambient aerosols. Previous studies (e.g., Bertram et al., 2009a) utilized the exit-concentration ratio of N_2O_5 to obtain the N_2O_5 loss rate on aerosols. However, air mass changes lead to different NO_3 loss rates and production rates over a short time period (i.e., a typical sampling cycle for about 1 h), and high background NO_2 and O_3 in the ambient air would affect the exit N_2O_5 concentration and hence bias the measurement of loss rate and uptake coefficient from the flow tube experiments. To minimize the potential influences of high levels of ambient pollutants and rapidly changing air mass, a time-dependent box model constrained by the real measurement data was used in the present study to directly calculate the N_2O_5 loss rate in both aerosol and non-aerosol mode, considering multiple reactions describing the production and loss of NO_3 and N_2O_5 (Reactions R1–R6) under ambient conditions.

$$O_3 + NO \rightarrow NO_2 + O_2; \quad k_3 \tag{R3}$$

$$NO_3 + NO \rightarrow 2NO_2; \quad k_{NO_3\text{-}NO} \tag{R4}$$

$$NO_3 + VOC \rightarrow \text{products}; \quad k_{NO_3\text{-}VOC} \tag{R5}$$

$$N_2O_5 + \text{aerosols/wall} \rightarrow \text{products}; \quad k_{het} = k_{wall} + k_{aerosols} \tag{R6}$$

The rate constants for Reactions (R1) to (R4) recommended by the National Aeronautics and Space Administration–Jet Propulsion Laboratory (Sander et al., 2009) were used. The loss rate coefficient $k_{NO_3\text{-}VOC}$ from NO_3 reactions with VOCs (Reaction R5) was determined by ambient measured VOC concentrations and rate coefficients from Atkinson and Arey (2003). The N_2O_5 heterogeneous loss rate coefficient k_{het} (Reaction R6) including heterogeneous loss on both aerosol and reactor surfaces was the only adjustable parameter, while other parameters such as N_2O_5, NO, NO_2, and O_3 concentration were constrained by concurrent measurements. The model simulated the reactions starting from the entrance of the reactor after mixing the ambient air sample and synthetic-N_2O_5 source. The initial concentrations of $[NO_2]_{t=0}$ and $[O_3]_{t=0}$ were calculated from the ambient measured levels of NO_2 and O_3 and those from the N_2O_5 source. Given the constraint of measured parameters at the entrance of the flow tube reactor – including $[NO]_{t=0}$, $[NO_2]_{t=0}$, $[O_3]_{t=0}$, $[N_2O_5]_{t=0}$, $[VOCs]_{t=0}$, temperature, and pressure – these reactions could be integrated in time (performed in Matlab with the Kinetic PreProcessor using a Radau5.integrator) (Damian et al., 2002) to obtain the exit concentrations of NO_2, O_3, and N_2O_5. The calculated concentrations were then compared with the measured concentrations at the exit of the flow tube reactor, and the N_2O_5 loss rate coefficient was tuned until the N_2O_5 concentration predicted by the box model agreed with the measured N_2O_5 concentration, $[N_2O_5]_{\Delta t}$. Assuming that k_{wall} are constant between successive flow tube experiments with and without aerosols, the loss rate coefficient on aerosols surfaces can be determined from the differences between two modes: $k_{aerosols} = k_{het}^{w/aerosols} - k_{het}^{wo/aerosols}$. Then the uptake coefficient of N_2O_5 on aerosol surfaces (γN_2O_5) can be calculated by the following equation:

$$\gamma N_2O_5 = 4\left(k_{het}^{w/aerosols} - k_{het}^{wo/aerosols}\right)/(cS_a). \tag{5}$$

In circumstances without concurrent ambient measurement of NO_2 and O_3 and when accurate measurements are only available at the flow tube outlet, as in the present study, an iterative box model including both backward and forward simulation is needed. Following the method suggested by Wagner et al. (2013), the relevant reactions can be integrated backward starting with the measured concentrations at the exit of the reactor ($t = \Delta t$) to obtain the initial concentrations. As the cycle between NO_3 and N_2O_5 is fast and quickly established in high-NO_x conditions, the NO_3 and N_2O_5 are considered as one singular N_2O_5* species by assuming NO_3 and N_2O_5 are in equilibrium (Brown et al., 2003). Doing this also makes backward reaction simulation possible by avoiding unstable equilibrium in the box model. The NO at the entrance of the flow tube could react quickly with O_3 and NO_3, with a short lifetime of a few seconds, resulting in near-zero concentration at the exit of the flow tube. To initialize the simulation, a time-dependent NO concentration in the flow tube must be derived. An approximate [NO] profile can be estimated from a forward simulation with inputs of measured initial NO, N_2O_5, guessed k_{het}, and estimated initial NO_2 and O_3 concentrations from the following equations. The measured initial NO data used 3 min earlier data as input data considering the mean residence time of 150 s.

$$[NO_2]_0 = [NO_2]_{\Delta t} \times e^{\Delta t\, k_1 [O_3]_{\Delta t}} [NO]_0 \tag{6}$$

$$[O_3]_0 = [O_3]_{\Delta t} \times e^{\Delta t\, k_1 [NO_2]_{\Delta t}} + [NO]_0 \tag{7}$$

$$[NO]_t = [NO]_0 \times e^{-t\left(k_3[O_3]_0 + \frac{k_4[N_2O_5]_0}{K_{eq}[NO_2]_0}\right)} \tag{8}$$

The estimated [NO] profile was then constrained in the backward model simulation – together with inputs of measured concentrations of N_2O_5, NO_2, and O_3 at the exit of the flow tube reactor and the initially guessed k_{het} – to derive the initial mixing ratios. The box model was run forward and backward iteratively with updated values and adjusted k_{het} until simulated N_2O_5 concentration matched the measurement at the exit of the flow tube reactor. The agreement of simulated NO_2 and O_3 concentrations with measurements was also used as a check to validate the model calculation. Thus, the uptake coefficient of N_2O_5 was determined from Eq. (5). An example of the iterative box model calculation is shown in Fig. 3.

For some conditions, the iterative box model returns a negative N_2O_5 loss rate coefficient. This non-physical result might result from much larger fluctuations of k_{NO_3} or k_{wall} in the system during each measurement cycle. When $k_{aerosol}$ is small due to the low S_a or insignificant uptake, the k_{NO_3} or k_{wall} may dominate the N_2O_5 loss in flow tube reactor, and the fluctuations of k_{NO_3} or k_{wall} due to the air mass or temperature/RH changes would bias the $k_{aerosol}$ determination and lead to large uncertainty or negative values. This situation often occurred under conditions of fresh NO emission; more discussion of the influence of NO is presented in Sect. 6.

5 Laboratory test and overall uncertainty

Laboratory tests of N_2O_5 uptake on $(NH_4)_2SO_4$ aerosols were also performed with different NO, NO_2, and O_3 conditions, and the uptake coefficients were determined from the iterative box model analysis described above with input of measured concentrations. The determined uptake coefficient

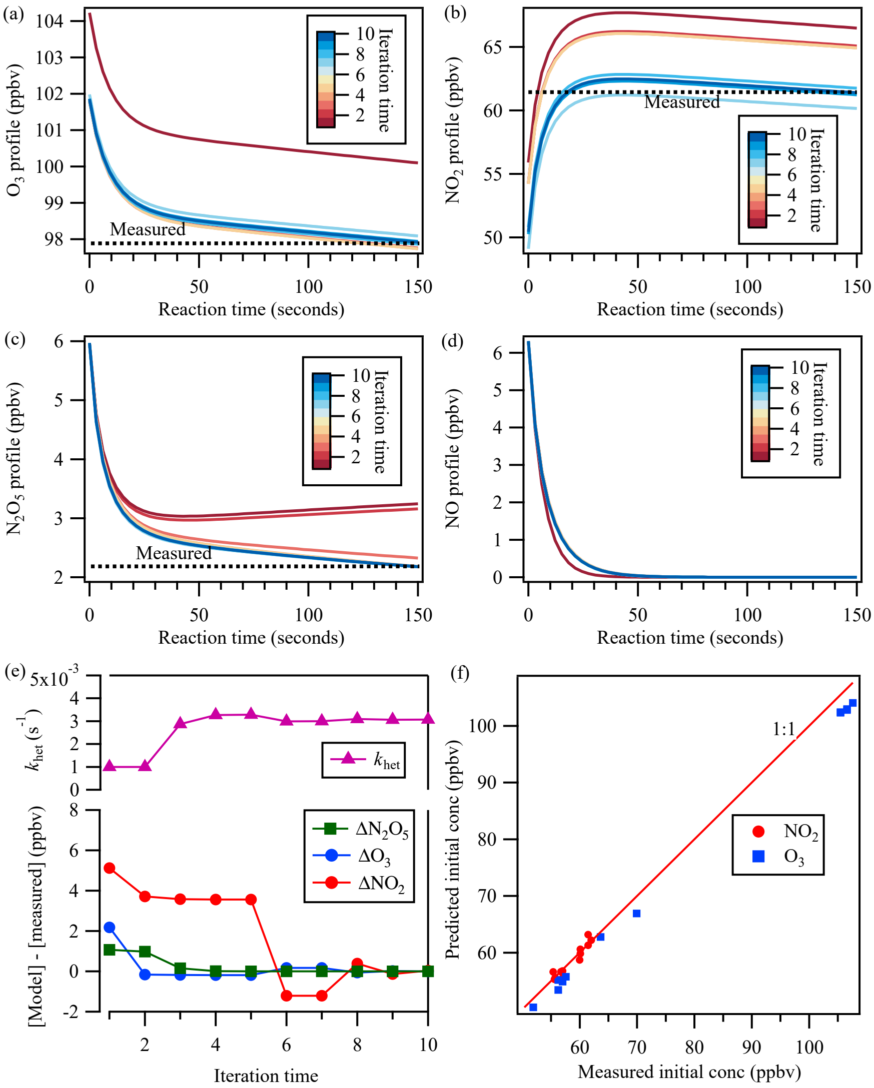

Figure 3. An example of the iterative box model simulation to derive k_{het} from the measured concentrations of NO_2, O_3, and N_2O_5 at the exit of the flow tube reactor. The concentration profiles obtained from the simulation in 10 iterations are shown for **(a)** O_3, **(b)** NO_2, **(c)** N_2O_5, and **(d)** NO. In the upper part of **(e)**, the adjusted N_2O_5 loss rate is shown for each iteration. The lower part of **(e)** shows the concentration differences between the model simulation and measurements of N_2O_5, O_3, and NO_2 at the exit of the reactor for each iteration. **(f)** shows the comparison between measured initial concentrations from laboratory test and predicted initial concentrations from the iterative model.

ranged from 0.018 to 0.026 (Table S1 in the Supplement), which are similar to previous laboratory study results with $(NH_4)_2SO_4$ aerosols (Davis et al., 2008). The consistency also can serve as a validation of the applicability of the introduced system and method. In addition, we also compared the measured initial concentration of NO_2 and O_3 during the lab tests with that predicted from the iterative model (Fig. 3f). The NO_2 concentration matched well between model prediction and measurement, while O_3 was a little lower from the model simulation, which might be due to the wall loss or other loss ways of O_3 in the flow tube reactor.

In the present work, the determination of $k_{aerosols}$ is independent of the magnitude of k_{wall}, but the stability of k_{wall} is critical for the accurate retrieval of $k_{aerosols}$. k_{wall} depends on RH, and the variability in RH on the timescale of the measurement can introduce additional uncertainty (Bertram et al., 2009a). Laboratory experimental tests have been conducted to investigate the variability of k_{wall} with RH in the current flow tube system. k_{wall} can be determined from the previously described iterative model with the measurement of N_2O_5 loss through the flow tube in a zero air flow in the absence of aerosols. As shown in Fig. 4, k_{wall} has a strong positive relationship with RH and increases with RH, espe-

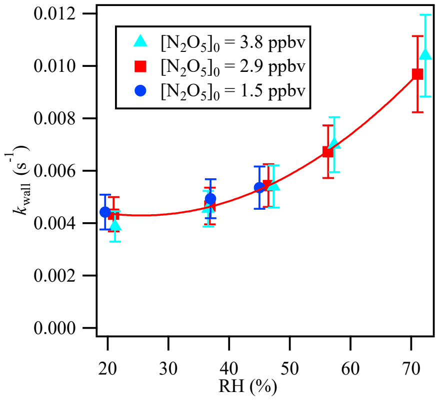

Figure 4. Relative humidity dependence of the wall loss rate coefficient (k_{wall}) of N_2O_5 in the flow reactor.

cially when RH is higher than 50 %. The consistent k_{wall} at each RH condition with different initial N_2O_5 concentrations suggests that k_{wall} in the current system is relatively stable under different chemical conditions but varies as a function of RH.

The sample air exiting the flow reactor was continuously measured by a RH probe, and the results showed that the RH variation between the aerosol presence and absence modes was within 1 % more than 80 % of the time during the ambient measurement cases. This result would translate into an uncertainty of ($\pm 0.15 \times 10^{-3}$) to ($\pm 2.4 \times 10^{-3}$) in γN_2O_5 with RH of 20 % to 70 %, respectively, and a S_a of 1000 µm^2 cm^{-3}. To minimize the magnitude of the variability in k_{wall}, the wall of the reactor was coated with Teflon PFA, and the flow tube reactor was cleaned daily with distilled water. Ultrasonic baths were also utilized after a 1-week period of ambient measurement to remove aerosol buildup from the wall of the flow tube reactor.

In addition to k_{wall} being affected by RH, uncertainty in $k_{aerosols}$ determination can also result from N_2O_5 source variability, NO_3 reactivity with VOCs, and precision as well as accuracy associated with the measurement of all parameters. The long measurement cycle may also bring about uncertainty due to variation in concentrations in two operation modes. As described in Sect. 2.2, the stability of the N_2O_5 generation source was within ±2 % over an hour. In the present study, online VOCs were measured with a time resolution of 1 h. A ± 0.01 s^{-1} variation of $k_{NO_3\text{-VOC}}$ would lead to a single-point uncertainty in γN_2O_5 of $\pm 0.4 \times 10^{-3}$ for $S_a = 1000$ µm^2 cm^{-3}. NO reacts at a faster rate with NO_3, having a larger impact on the γN_2O_5 calculation compared to VOCs. With a constrained real-time NO concentration, the iterative model can buffer against small NO changes. Stability of NO, NO_2, O_3, and N_2O_5 for a period of at least 5 min for each mode is required to ensure that the flow tube reactor measurement and iterative model yield reasonable results. The measurement precision and variation of these species during each cycle might also introduce uncertainty in the iterative model calculation.

The uncertainty in the γN_2O_5 determination associated with k_{wall} changes, VOC variation, and the variation of the different parameters during the measurement cycles was estimated with a Monte Carlo approach, as described in Groß et al. (2014), by assessing the uncertainty from individual key parameters (shown in Table 1) in the calculation model. γN_2O_5 was found to be most sensitive to RH, which was closely related to k_{wall} as discussed before. Figure 5a shows the partial uncertainty of γN_2O_5 derived from Monte Carlo simulations with RH at 40 %. The single-point uncertainty in γN_2O_5 was estimated to be $\pm 4.1 \times 10^{-3}$ for γN_2O_5 around 0.03 and $\pm 3.6 \times 10^{-3}$ for γN_2O_5 around 0.01, with RH of 40 %. The uncertainty increased with RH and would be 9 % to 17 % at γN_2O_5 around 0.03 for RH ranging from 20 % to 70 % (Fig. 5b).

Sensitivity tests with the iterative model calculation were performed to evaluate the uncertainty associated with measurement accuracy of N_2O_5 and VOCs, by varying the input N_2O_5 concentrations and $k_{NO_3\text{-VOC}}$ in both modes. It is found that the N_2O_5 measurement uncertainty of 25 % (Tham et al., 2016; Z. Wang et al., 2017) would translate into an uncertainty of 12 % in the γN_2O_5 (shown in the Supplement). The VOC measurement uncertainty, however, has negligible influence on γN_2O_5 calculation. In a previous flow tube method introduced by Bertram et al. (2009a), the homogeneous reaction was expected to be independent of the aerosol and non-aerosol modes and was thus able to be canceled out in the calculation. Only strong atmospheric variation in VOC in a short time period would influence the N_2O_5 uptake measurement. The uncertainty introduced by the aerosol surface area measurement including aerosol loss influence would be propagated to an uncertainty in the γN_2O_5 calculation of 30 %.

As mentioned in Sect. 3, the use of mean residence time rather than RTD function by assuming an ideal reactor and ignoring diffusion and dispersion processes would also introduce uncertainties. In order to evaluate the magnitude of this bias, we performed a simplified test by comparing a first-order loss rate from mean residence time with a residence time distribution range. Briefly, the mean concentration of N_2O_5 at the exit of the reactor could be expressed by

$$\overline{[N_2O_5]} = \int_0^\infty [N_2O_5]_t E_t \mathrm{d}t = \int_0^\infty [N_2O_5]_0 e^{-kt} E_t \mathrm{d}t, \qquad (9)$$

where $[N_2O_5]_t$ is the average concentration exit from the reactor between t and $t + \mathrm{d}t$, $E(t)$ is the residence time distribution function, and k is the first-order loss rate coefficient of N_2O_5. The results showed that the first-order loss rate calculated from the distribution function was higher than that with a mean residence time and was about 5 % or 16 % higher when the ratio of $\frac{[N_2O_5]_t}{[N_2O_5]_0}$ was 0.6 or 0.2 in the flow tube system, respectively. When all of these factors are incorporated,

Table 1. Parameters varied in the Monte Carlo simulations.

Parameter	Fixed value	Variation[a]	Parameter	Fixed value	Variation[a]
$[NO_2]_t$	53.5 ppbv	0.3 ppbv	$[N_2O_5]_0$	5.0 ppbv	0.1 ppbv
$[NO]_0$	2 ppbv	0.1 ppbv	$[N_2O_5]_t$	1.8 ppbv	0.1 ppbv
$[O_3]_t$	78.8 ppbv	0.6 ppbv	$k_{NO_3\text{-VOC}}$	$0.01\ s^{-1}$	$0.01\ s^{-1}$
Temperature	25 °C	0.1 °C	RH	20 %–70 %	1 %
Residence time	150 s	2 s	k_{wall}	[b]	[c]

[a] 1σ standard deviation for the varied parameters. [b] The k_{wall} is calculated from RH, using the relation fitting equation in Fig. 4. [c] The variation of k_{wall} is calculated as RH varied 1 %.

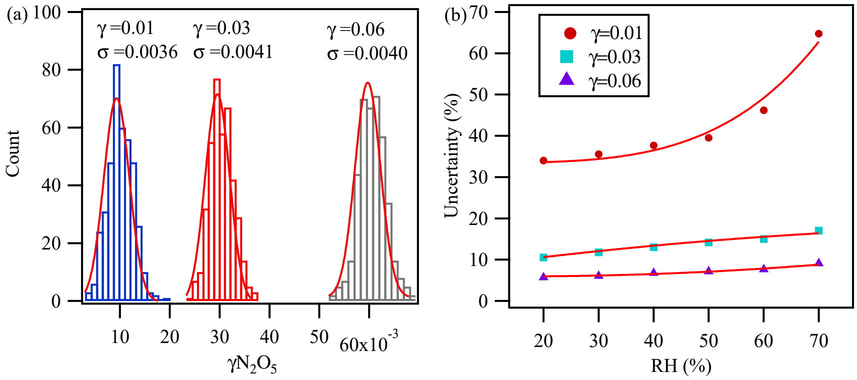

Figure 5. The partial uncertainty in γN_2O_5 determination associated with k_{wall} changes, VOC variation, and the variation of different parameters during the measurement cycles derived from Monte Carlo simulations for three individual sets with 400 simulations at **(a)** RH = 40 % and **(b)** different RH values. In these three data sets, the condition was set as follows: surface area = $1000\ \mu m^2\ cm^{-3}$, reaction time = 150 s, initial O_3 = 80 ppbv, initial NO_2 = 50 ppbv, initial NO = 2 ppbv, initial N_2O_5 = 5 ppbv, temp = 25 °C, and $k_{NO_3\text{-VOC}} = 0.01\ s^{-1}$.

the estimated total uncertainty is propagated to be 37 % to 40 % at γN_2O_5 around 0.03 with $1000\ \mu m^2\ cm^{-3}$ S_a for RH ranging from 20 % to 70 %.

6 Demonstration of γN_2O_5 measurements under polluted conditions

In polluted environments, high concentrations of NO_2, O_3, or NO in ambient air would affect the determination of the N_2O_5 loss rate and uptake coefficient in the flow tube experiments. To investigate the effect of multiple reactions of these species in polluted conditions, a series of tests with different conditions were simulated to compare the derived loss rate and uptake coefficient with and without consideration of N_2O_5 regeneration and NO titration in the flow tube system. Using the forward box model described in Sect. 4, the process in the flow tube reactor was simulated with an assumed fixed S_a of $1000\ \mu m^2\ cm^{-3}$, γN_2O_5 of 0.03, k_{wall} of $0.004\ s^{-1}$, and $k_{NO_3\text{-VOC}}$ of $0.01\ s^{-1}$. Various conditions were simulated with different O_3, NO_2, and NO levels introduced into the flow tube, and the resulting concentrations of N_2O_5, NO_2, and O_3 at the exit of the reactors with and without aerosols modes were obtained. The loss rate and uptake coefficients of N_2O_5 were then calculated using the simple exit-concentration ratio approach (Eq. 2) and time-dependent iterative box model, respectively. The difference in γN_2O_5 obtained from these two methods reflects the effect of N_2O_5 regeneration and NO titration on uptake coefficient determination.

Figure 6 shows the simulation results for the derived uptake coefficients regarding the effect of N_2O_5 formation in the flow tube reactor, with O_3 varying in the range of 0–100 ppbv and NO_2 in the range of 0–40 ppbv without NO presence in the ambient air. The N_2O_5 source input was fixed at 4.3 ppbv, as measured in the laboratory, together with 106 ppbv of O_3 and 57 ppbv of NO_2 from the N_2O_5 source. The N_2O_5 regeneration effect on γN_2O_5 calculation was significant when O_3 and NO_x levels in the ambient air were high. For example, at NO_2 = 40 ppbv and O_3 = 100 ppbv, which may frequently be encountered in city cluster regions in China, neglecting N_2O_5 formation in the flow tube would result in underestimating γN_2O_5 by 42 %.

To demonstrate the influence of NO titration, simulation tests were performed with NO varying from 0 to 8 ppbv. Because the reaction rate of NO with NO_3 is 2 orders of magnitude faster than that of NO with O_3, the initial N_2O_5 level would affect the NO titration process. We performed the simulation with different initial N_2O_5 concentrations injected

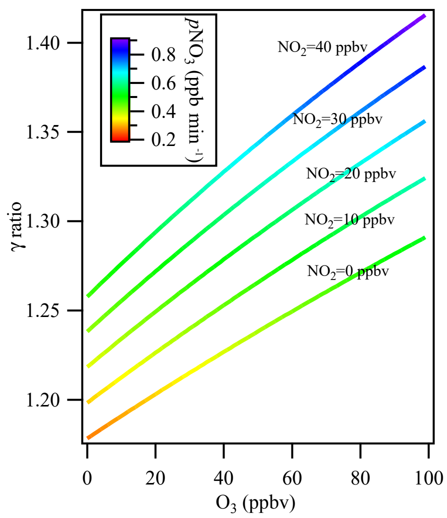

Figure 6. The influence of multiple reactions resulting from high ambient NO_2 and O_3 levels under different ambient NO_2 levels from 0 to 40 ppbv. The colors indicate the NO_3 production rate (pNO_3) at the entrance of the flow tube reactor after mixing with 106 ppbv of O_3 and 57 ppbv of NO_2 from the N_2O_5 source.

into the flow tube reactor. As the green line in Fig. 7a indicates, the calculated γN_2O_5 will be greatly underestimated when NO concentration increases, up to 55 % at a NO level of 8 ppbv with an initial N_2O_5 level of 3 ppbv compared to a NO level of 0. During the laboratory experiments, two initial N_2O_5 conditions with the input of an additional 5 ppbv of NO were also tested. The determined γN_2O_5 from the iterative model simulation and exit-concentration method was compared and is shown as cubes in Fig. 7a. The model results lie within the uncertainty range of the measurements, further cross-validating the NO influences and the model simulation. Figure 7a also shows that a lower initial N_2O_5 leads to a larger underestimation of γN_2O_5 in the presence of NO. It is not desirable to use N_2O_5 concentrations above 5 ppbv to minimize the NO effect, because of other potential artifacts associated with working at high concentration (Thornton et al., 2003).

To explore which NO level would leave an extremely low N_2O_5 concentration in the exit of the reactor and make N_2O_5 loss rate measurement impossible, a series of experiments in clean air with additional NO was conducted in the laboratory to investigate NO titration effects and the performance of the iterative model in buffering against high NO. As shown in Fig. 7b, the derived k_{het} showed consistent results for zero NO and NO < 6 ppbv conditions when RH and other parameters were unchanged. With higher NO addition and a lower initial N_2O_5 level, the calculated k_{het}, however, could be underestimated due to greater uncertainty when NO_3 and N_2O_5 were insufficient to titrate with NO. Figure 7b also shows that the introduced box model method could buffer against NO below 8 ppbv with an initial N_2O_5 level of 4.3 ppbv. For future development, an activated-carbon scrubber in the inlet to reduce the gas-phase interferers (NO, NO_2, O_3, VOCs) but transmit aerosols could be a complementary approach to apply the flow tube system coupled with iterative box model analysis to even more polluted conditions.

In summary, the simulation and laboratory results demonstrate that neglecting the formation and titration reactions in a flow tube reactor will result in underestimating γN_2O_5. To reduce the NO titration effect, a relatively high level of N_2O_5 (but less than 5 ppbv) should be introduced to the flow tube reactor. Consideration of the multiple reactions in the iterative model is sufficiently robust to encourage further development to improve the accuracy of γN_2O_5 calculations.

7 Ambient measurement

During winter 2017, the flow tube system was deployed to measure the N_2O_5 uptake coefficient at a sub-urban site in Heshan, Guangdong, in southern China. The sampling time for each mode with and without ambient aerosols lasted for at least 15 min to ensure 5 min stable data at the exit for subsequent modeling analysis. The measured 5 min average concentrations of initial NO and exit N_2O_5, NO_2, and O_3 were used as the inputs in the iterative box model to derive k_{het} and γN_2O_5. Most measurements were conducted during the daytime to avoid interruption of nighttime ambient N_2O_5, and daytime N_2O_5 levels could be neglected. The average ambient temperature, RH, NO, NO_2, and O_3 during the field campaign were 23 °C, 51 %, 3.2 ppbv, 23 ppbv, and 32 ppbv, respectively. As discussed previously, changes in RH and temperature can influence the stability of k_{wall} and N_2O_5–NO_3 equilibrium, and thus upset γN_2O_5 measurement. In the cases where γN_2O_5 measurement was affected by extreme fluctuations in NO (above 8 ppbv), temperature and RH (fluctuation > 2 %) were discarded from the analysis.

In addition to the iterative box model approach, we also used the exit-concentration ratio approach (cf. Eq. 2) to calculate the γN_2O_5. Figure 8 exhibits the comparison of γN_2O_5 obtained using these two methods. Fifteen out of 51 measurements occurred under relatively "clean and stable" conditions (defined as ambient NO < 1 ppbv, fluctuation of NO < 0.3 ppbv, NO_3 production rate < 0.8 ppbv min^{-1}, and fluctuation of NO_2 and O_3 < 4 ppbv), and the corresponding values of γN_2O_5 from the two methods show good correlation, with an average ratio of 1.34, which is consistent with our previous simulation results that the exit-concentration ratio approach could underestimate γN_2O_5 mainly due to N_2O_5 regeneration reaction. For conditions with higher precursor concentrations and fluctuations, a larger discrepancy between γN_2O_5 from two methods was found (see Fig. 8). As described previously, greater uncertainty in the exit-concentration ratio approach could result from multiple reactions and air mass changes. The fluctu-

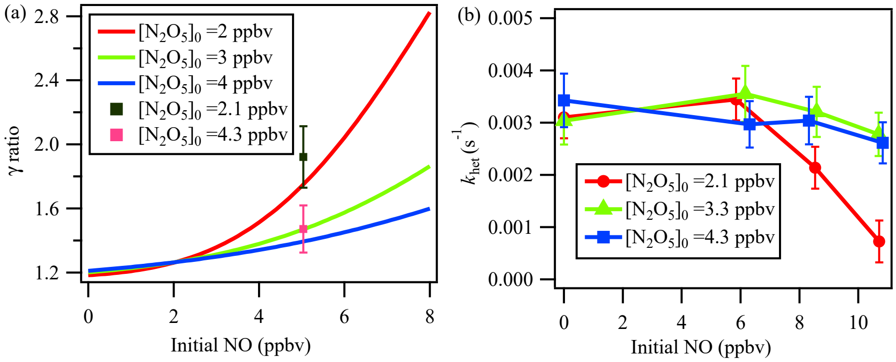

Figure 7. (a) Simulation results of NO titration effect on γN_2O_5. The γN_2O_5 ratio represents (γN_2O_5 from the iterative model) / (γN_2O_5 from the method of ignoring multiple reactions). Initial NO and initial N_2O_5 represent the respective initial concentrations of NO and N_2O_5 in the flow tube reactor. The lines represent the simulation result, and the cubes represent the lab test result. **(b)** k_{het} calculated via the iterative model in laboratory experiments with constant RH of 21 %, different initial N_2O_5, and varied NO additions.

ations of NO, NO_2, and O_3 could greatly affect the exit N_2O_5 concentration ratio. For example, a lower NO level and higher NO_2 and O_3 levels in the aerosol mode relative to the non-aerosol mode would result in a higher exit N_2O_5 concentration ratio, which would lead to underestimation of γN_2O_5 and even negative values (see Fig. 8 and Supplement). As even a 1 ppbv fluctuation of NO concentration could largely affect the exit N_2O_5 concentration, it would result in significant uncertainty for the exit-concentration ratio approach. When NO concentration is much higher, for example in the aerosol-existing mode, the measured N_2O_5 concentration is lower due to NO titration; thus the uptake coefficient is overestimated when only the end concentration ratio of N_2O_5 in two modes is compared.

Two example cases with large air mass changes are shown in Fig. 9. In Fig. 9a, a case with high and fluctuating NO emission was observed on the night of 21 March 2017, with average ambient concentrations of NO of 6 ppbv, NO_2 of 27 ppbv, O_3 of 2 ppbv, and S_a of 1880 $\mu m^2\,cm^{-3}$. γN_2O_5 was determined to be 0.028 from the iterative model approach, and a higher γN_2O_5 value of 0.036 was obtained from the exit-concentration ratio approach. The overestimated γN_2O_5 from the exit-concentration ratio approach could be explained by the increased NO level (∼ 1.5 ppbv) in the aerosol mode. For comparison, another two periods of data points in the 21 March case (Fig. 9a) with different NO levels were also selected to derive the k_{het}, and the results showed good consistency (0.0136–0.0140 s^{-1}) (Fig. S2 in the Supplement), also demonstrating the applicability of the iterative model in buffering against fluctuating NO. In Fig. 9b, another case with fluctuating NO_2 and O_3 levels was observed on 26 March 2017, and the NO_2 level was about 5 ppbv higher, but the O_3 level was about 11 ppbv lower in aerosol mode. With S_a of 681 $\mu m^2\,cm^{-3}$, γN_2O_5 was determined to be 0.020 from the iterative model approach and a much lower value of 0.008 from the exit-concentration ratio approach. The consideration of multiple reactions in the iterative model approach was able to buffer against small fluctuations of precursors in switching between aerosol and non-aerosol modes. The results demonstrated the applicability of the iterative model approach to directly measuring the N_2O_5 heterogeneous uptake coefficient under conditions of high NO_2 and O_3 and fresh NO emission.

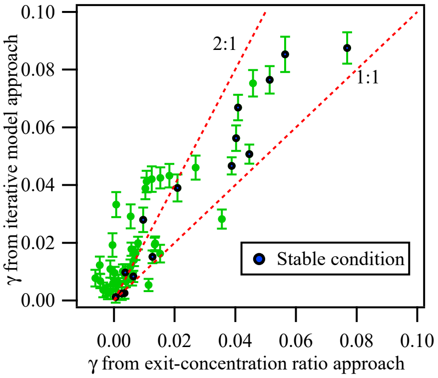

Figure 8. Comparison of γN_2O_5 determined from the exit-concentration ratio approach and the iterative model approach for all available data measured in the Heshan campaign. The blue points represent the data obtained under "clean and stable condition", while green points are data obtained from other condition. The "clean and stable condition" is defined as follows: ambient NO < 1 ppbv, the change of NO < 0.3 ppbv, the NO_3 production rate < 0.8 ppbv min^{-1}, and the change of NO_2 and O_3 < 4 ppbv. The error bar represents the uncertainty calculated by the Monte Carlo approach under the measurement condition.

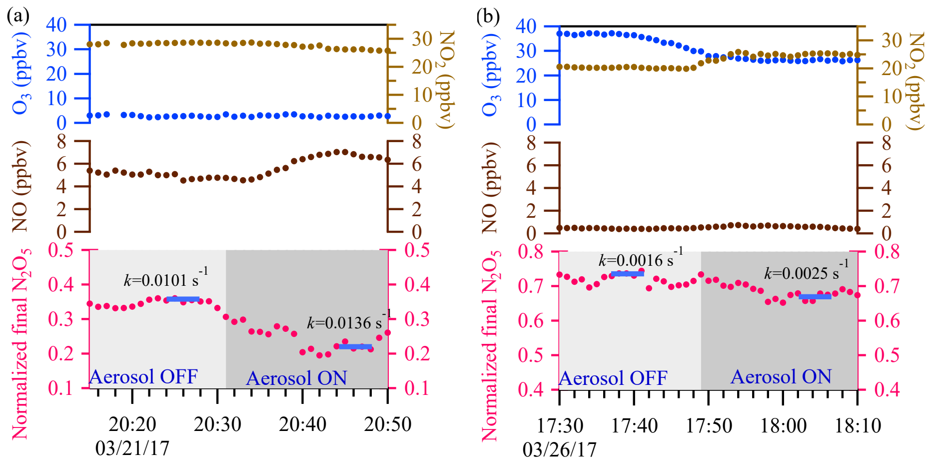

Figure 9. Two sample cases are shown. In the upper panel, the blue and light brown dots represent 1 min ambient O_3 and NO_2 data, respectively. In the middle panel, the brown dots represent 1 min ambient NO data. In the lower panel, the pink dots represent 1 min average of N_2O_5 concentration normalized to the initial N_2O_5 concentration in the flow tube reactor. The calculated total N_2O_5 loss rate derived from the iterative model with 5 min average input data (the blue bar) is also shown for each cycle.

8 Summary and conclusion

An in situ experimental approach for direct measurement of N_2O_5 heterogeneous reactivity in a polluted environment was developed and introduced in the present study. The method uses an aerosol flow tube reactor combined with an iterative box model, to determine the heterogeneous loss rate of synthesized N_2O_5 on ambient aerosols with consideration of multiple reactions affecting N_2O_5 in the flow tube. A series of laboratory and model simulations were conducted to test the applicability of the system under different conditions. The overall γN_2O_5 uncertainty from the variations of parameters during two operation modes and uncertainties associated with measurements of gaseous and aerosol species was propagated to be 37 %–40 % at γN_2O_5 around 0.03 with S_a of 1000 µm^2 cm^{-3} and RH ranging from 20 % to 70 %. Field deployment of this system at a polluted suburban site in southern China demonstrated the applicability of the introduced method in measuring N_2O_5 uptake coefficients in polluted environments with high ambient levels of O_3, NO, and NO_2 and rapid air mass changes. Both field results and simulation tests demonstrate that neglecting multiple reactions within the flow tube reactor leads to underestimating γN_2O_5 values. The introduced approach could also be used to investigate the heterogeneous reactivity of other trace gases on ambient aerosols in polluted environments.

Data availability. The data used in this study are available upon request from the corresponding author (z.wang@polyu.edu.hk or cetwang@polyu.edu.hk).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/amt-11-5643-2018-supplement.

Author contributions. TW and ZW designed the research in this study; WW and ZW developed the method; WW and XP carried out the lab testing; WW, CY, and MX conducted the filed measurement and analyzed the data; YZ, DY, and YO contributed to the field measurement and data analysis; and WW, ZW, and TW wrote the manuscript. All authors contributed to discussion and commented on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This work was funded by the National Natural Science Foundation of China (grant nos. 91544213 and 41505103); the Research Grants Council of Hong Kong Special Administrative Region, China (grant nos. C5022-14G and 15265516); and the National Key R&D Program of China (grant no. 2016YFC0200500). The authors also acknowledge the support of the Research Institute for Sustainable Urban Development (RISUD).

Edited by: Lisa Whalley
Reviewed by: two anonymous referees

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