An in-situ flow-tube system for direct measurement of N₂O₅ heterogeneous uptake coefficients in polluted environments

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Abstract. The heterogeneous reactivity of dinitrogen pentoxide (N₂O₅) on ambient aerosols plays a key role in atmospheric fate of NO_x and formation of secondary pollutants. To better understand the reactive uptake of N₂O₅ on complex ambient aerosols, an in-situ experimental approach to direct measurement of N₂O₅ uptake coefficient (γN₂O₅) 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 γN₂O₅ from the depletion of synthetically generated N₂O₅ when mixed with ambient aerosols. Laboratory tests and model simulations were performed to characterize the system and the factors affecting γN₂O₅, including mean residence time, wall loss variability with RH, and N₂O₅ formation and titration with high levels of $NO/NO_x/O_3$. The overall uncertainty was estimated to be 9%-17% at γN₂O₅ 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/O_3 and fresh NO emission. The results demonstrate that the iterative model improved the accuracy of γN₂O₅ calculations under polluted environments, and thus support the further field deployment of the system to study the impacts of heterogeneous N₂O₅ reactivity on photochemistry and aerosol formation.

1 Introduction

Dinitrogen pentoxide (N₂O₅) 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). N₂O₅ is formed from the reaction of nitrogen dioxide (NO₂) and nitrate radical (NO₃). Because NO₃ is photolytically unstable, it (and therefore N₂O₅) only accumulates under dark conditions (i.e., at night). The heterogeneous reactions of N₂O₅ 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 N₂O₅ 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).

$$k_{aerosols} = \tfrac{1}{4}\, c_{N2O5}\, Sa\, \gamma N_2O_5 \qquad\qquad (1)$$

where c_{N2O5} (m/s) is the mean molecular speed of N_2O_5 and Sa ($\mu m^2/cm^3$) is the aerosol surface area concentration. γN_2O_5 is

5 the reaction probability that a N_2O_5 molecule collides with the aerosol surface resulting in net removal via reactions on aerosols. Because γN_2O_5 is a critical parameter to determine N_2O_5 uptake on aerosols, it is necessary to develop reliable methods to measure it.

γN_2O_5 has typically been determined in laboratory using different types of flow tube and reactors to measure the decay rate of N_2O_5 in the presence of pure or synthetic aerosols under different conditions (e.g., Thornton et al., 2003; Tang et al., 2017 and

10 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

15 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; 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

20 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):

25 $$k_{aerosols} = -\frac{1}{\Delta t}\ln\left(\frac{[N_2O_5]_{\Delta t}^{w/aerosols}}{[N_2O_5]_{\Delta t}^{wo/aerosols}}\right), \qquad\qquad (2)$$

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 rural 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 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

5   concentrations are low and the air mass is relatively stable, but 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 process 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; Wang et al., 2017a; Wang et al., 2017b; Yun et al., 2018). The γN_2O_5 derived from ambient

10   concentration measurements showed different characteristics and dependence compared to previous measurements in relatively clean environments (Wang et al., 2017b). 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

15   of the method are presented to demonstrate its application under conditions with high ambient concentrations of NO_2/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

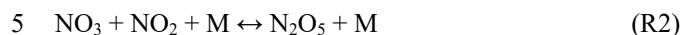
20   detection instruments. A schematic diagram of the experimental apparatus is given in Fig. 1. The sample inlet with an aerosol filter manifold is made of ¼-inch outer diameter (OD) stainless-steel tubing. By switching two stainless-steel ball valves, ambient air can be introduced directly into the 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

25   SLPM and includes 120 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.

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).

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \hspace{3cm} \text{(R1)}$$

5    $$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \hspace{2cm} \text{(R2)}$$

In this study, ozone was generated from O_2 photolysis with a mercury lamp in a commercial calibrator (Model 4010, Sabio Instrument Inc.). A 100 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 the excessive NO_2 condition, the system was expected to shift the R2 equilibrium towards N_2O_5. Concentrations of synthesized

10   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 two hours, 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). The stability of synthetic N_2O_5 source was tested continuously for eight hours, and the variation of the signal

15   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 10μm) were measured by a wide-range particle spectrometer

20   (WPS, model 1000XP, MSP Corporation, USA) to determine the aerosol surface area. 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; Wang et al., 2017a; Wang et al., 2017b). 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

25   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).

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 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. Bertram

5   et al. (2009) have suggested that a rate constant measured under such an assumption would be underestimated by up to 25%. 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).

10   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

15   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:

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

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

20   $$\Delta t = \int_0^\infty t E(t) dt.$$ (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.

25   ## 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 hr), 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 ambient pollutants

5   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 (R1–R6) in the ambient condition.

$O_3 + NO \rightarrow NO_2 + O_2$; k_3 (R3)

$NO_3 + NO \rightarrow 2NO_2$; $k_{NO3\text{-}NO}$ (R4)

10    $NO_3 + VOC \rightarrow products$; $k_{NO3\text{-}VOC}$ (R5)

$N_2O_5 + aerosols/wall \rightarrow products$, $k_{het} = k_{wall} + k_{aerosols}$ (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 $k_{NO3\text{-}VOC}$ from NO_3 reactions with VOCs (R5) was determined by ambient measured VOCs concentrations and rate coefficients from Atkinson and Arey (2003). The N_2O_5

15   heterogeneous loss rate coefficient k_{het} (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 N_2O_5 source. Given the constraint of measured parameters at the entrance of the flow tube

20   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

25   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:

$\gamma N_2O_5 = 4(k_{het}^{w/aerosols} - k_{het}^{wo/aerosols})/(c\ Sa)$ (5)

In circumstances without concurrent ambient measurement of NO_2 and O_3 and when accurate measurements are only available

30   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=Δt) 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 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 three minutes earlier data as input data considering the mean residence time of 150 s.

$$[NO_2]_0 = [NO_2]_{\Delta t} \times e^{\Delta t\, k1 [O_3]_{\Delta t}} - [NO]_0 \tag{6}$$

$$[O_3]_0 = [O_3]_{\Delta t} \times e^{\Delta t\, k1 [NO_2]_{\Delta t}} + [NO]_0 \tag{7}$$

$$[NO]_t = [NO]_0 \times e^{-t\, (k3[O_3]_0 + \frac{k4[N_2O_5]_0}{Keq[NO_2]_0})} \tag{8}$$

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 $k_{NO3-VOC}$ than k_{het} in the system or any other large uncertainty in the calculation (Wagner et al., 2013). This situation usually occurred under conditions of fresh NO emission; more discussion of the influence of NO is presented in section 6.

5. Laboratory test of N_2O_5 wall loss and overall uncertainty

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 time scale 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, especially 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

5   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% and a Sa of 1000 $\mu m^2/cm^3$. To minimize the magnitude of the variability in k_{wall}, the wall of the reactor was coated with PFA-Teflon, and the flow tube reactor was cleaned daily with distilled water. Ultrasonic baths were also utilized after a one-week period of ambient measurement to remove aerosol build-up from the wall of the flow tube reactor.

In addition to k_{wall} being affected by RH, uncertainty in $k_{aerosols}$ determination can occur due to N_2O_5 source variability, NO_3

10   reactivity with VOCs, and uncertainties associated with the measurement of all parameters. As described in Section 2.2, the stability of the N_2O_5 generation source was within $\pm 2\%$ over an hour. In the present study, online VOCs were measured with a time resolution of one hour. A $\pm\ 0.01\ s^{-1}$ variation of $k_{NO3-VOC}$ would lead to a single-point uncertainty in γN_2O_5 of $\pm\ 0.4 \times 10^{-3}$ for $Sa = 1000\ \mu m^2/cm^3$. 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

15   NO for a period of at least 5 minutes is required to ensure that the flow-tube reactor measurement and iterative model yield reasonable results.

The overall uncertainty in the γN_2O_5 determination associated with the different parameters was estimated with a Monte Carlo approach, as described in Groß et al. (2014), by assessing the uncertainty from individual key parameters 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. Fig. 5a shows the

20   uncertainty results of $\gamma N2O5$ 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 to $\pm\ 6.5 \times 10^{-3}$ and $\pm\ 5.1 \times 10^{-3}$ with RH increased to 70%, which would translate into uncertainty of 34% to 65% at γN_2O_5 around 0.01 and 9% to 17% at γN_2O_5 around 0.03 for RH ranging from 20% to 70% (Fig. 5b).

6. Demonstration of γN_2O_5 measurements under polluted conditions

25   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 Section 4, the process in the flow tube reactor was simulated with an assumed fixed Sa of 1000 $\mu m^2/cm^3$,

30   γN_2O_5 of 0.03, k_{wall} of 0.004 s^{-1}, and $k_{NO3-VOC}$ 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.

5   Fig. 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 varied 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 ere high. For example, at NO_2 = 40 ppbv and O_3 =100 ppbv, which may frequently be encountered in city cluster
10 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 two 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 into the flow-tube reactor. As the green line in Fig 7(a) indicates, the calculated γN_2O_5 will be greatly underestimated when NO concentration increases,
15 up to 43% at a NO level of 8 ppbv with an initial N_2O_5 level of 3.3 ppbv. Fig. 7(a) 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
20 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 7(b), 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. Fig. 7(b) also shows that the introduced box
25 model method could buffer against NO below 8 ppbv with an initial N_2O_5 level of 4.3 ppbv.

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 minutes to ensure 5 minutes' stable data at the exit for subsequent modeling analysis. The measured 5-min average

5   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 ℃, 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. The cases where γN_2O_5 measurement was

10   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 (c.f. Eq. 2) to calculate the γN_2O_5. Fig.8 exhibits the comparison of γN_2O_5 obtained using these two methods, and the uncertainty for the iterative model calculated by a Monte Carlo approach under the measurement conditions. 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<

15   0.8 ppbv/min, 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, the 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

20   mass changes. The fluctuations 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, 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).

Two example cases with large air mass changes are shown in Fig. 9. In Fig. 9(a), a case with high and fluctuating NO emission was observed on the night of March 21, 2017, with average ambient concentrations of NO of 6 ppbv, NO_2 of 27 ppbv, O_3 of 2

25   ppbv, and Sa 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 in aerosol mode. In Fig. 9(b), another case with fluctuating NO_2 and O_3 levels was observed on March 26, 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 Sa of 681 $\mu m^2/cm^3$, γN_2O_5 was determined to be 0.020 from the iterative model approach and a

30   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/O_3 and fresh NO emission.

8 Summary and conclusion

An in-situ experimental approach for direct measurement of N_2O_5 heterogeneous reactivity in a polluted environment was
5   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 with different conditions. For RH around 40%, the γN_2O_5 uncertainty estimated with a Monte Carlo approach is 38% for γN_2O_5 around 0.01, decreasing to 11% for γN_2O_5 around 0.03. k_{wall} variation due to RH fluctuation in high humidity
10   conditions could introduce higher uncertainty, which demonstrates the importance of maintaining a constant RH during a short measurement period. Field deployment of this system at a polluted suburban site in South 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
15   the heterogeneous reactivity of other trace gases on ambient aerosols in polluted environments.

Acknowledgment

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

References

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N2O5, J. Phys. Chem. A, 110, 10435-10443, 2006.
25   Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, Atmos. Environ., 37, 197-219, 2003.
Bertram, T. and Thornton, J.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmospheric Chem. Phys., 9, 8351-8363, 2009.

Bertram, T., Thornton, J., and Riedel, T.: An experimental technique for the direct measurement of N2O5 reactivity on ambient particles, Atmospheric Meas. Tech., 2, 231-242, 2009a.

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K., and Coffman, D. J.: Direct observations of N2O5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, 2009b.

Brown, S., Dubé, W., Osthoff, H., Wolfe, D., Angevine, W., and Ravishankara, A.: High resolution vertical distributions of NO 3 and N2O5 through the nocturnal boundary layer, Atmospheric Chem. Phys., 7, 139-149, 2007.

Brown, S. S., Stark, H., and Ravishankara, A.: Applicability of the steady state approximation to the interpretation of atmospheric observations of NO3 and N2O5, J. Geophys. Res.: Atmospheres, 108, 2003.

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N2O5: A Review, Aerosol Sci Technol., 45, 665-695, 2011.

Damian, V., Sandu, A., Damian, M., Potra, F., and Carmichael, G. R.: The kinetic preprocessor KPP-a software environment for solving chemical kinetics, Comput. Chem. Eng., 26, 1567-1579, 2002.

Danckwerts, P. V.: Continuous flow systems: distribution of residence times, Chemical engineering science, 2, 1-13, 1953.

Davis, J., Bhave, P., and Foley, K.: Parameterization of N2O5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, Atmospheric Chem. Phys., 8, 5295-5311, 2008.

Dentener, F. J. and Crutzen, P. J.: Reaction of N2O5 on tropospheric aerosols: Impact on the global distributions of NO x, O3, and OH, J. Geophys. Res.: Atmospheres, 98, 7149-7163, 1993.

Evans, M. and Jacob, D. J.: Impact of new laboratory studies of N2O5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophys. Res. Lett., 32, 2005.

Fuchs, N. and Sutugin, A. G.: High-dispersed aerosols. In: Topics in current aerosol research, Elsevier, 1971.

Groß, C., Dillon, T., Schuster, G., Lelieveld, J., and Crowley, J.: Direct kinetic study of OH and O3 formation in the reaction of CH3C (O) O2 with HO2, J. Phys. Chem. A, 118, 974-985, 2014.

Lambe, A., Ahern, A., Williams, L., Slowik, J., Wong, J., Abbatt, J., Brune, W., Ng, N., Wright, J., and Croasdale, D.: Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, Atmospheric Meas. Tech., 4, 445-461, 2011.

Li, Q., Zhang, L., Wang, T., Tham, Y. J., Ahmadov, R., Xue, L., Zhang, Q., and Zheng, J.: Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China, Atmospheric Chem. Phys., 16, 14875, 2016.

Lowe, D., Archer-Nicholls, S., Morgan, W., Allan, J., Utembe, S., Ouyang, B., Aruffo, E., Le, B. M., Zaveri, R. A., and Di, C. P.: WRF-Chem model predictions of the regional impacts of N2O5 heterogeneous processes on night-time chemistry over north-western Europe, 2015. 2015.

Morgan, W., Ouyang, B., Allan, J., Aruffo, E., Di Carlo, P., Kennedy, O., Lowe, D., Flynn, M., Rosenberg, P., and Williams, P.: Influence of aerosol chemical composition on N2O5 uptake: airborne regional measurements in northwestern Europe, Atmospheric Chem. Phys., 15, 973-990, 2015.

Phillips, G. J., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S., Bingemer, H., and Lelieveld, J.: Estimating N2O5 uptake coefficients using ambient measurements of NO 3, N2O5, ClNO2 and particle-phase nitrate, Atmospheric Chem. Phys., 16, 13231, 2016.

Riedel, T., Bertram, T., Ryder, O., Liu, S., Day, D., Russell, L., Gaston, C., Prather, K., and Thornton, J.: Direct N2O5

5 reactivity measurements at a polluted coastal site, Atmospheric Chem. Phys., 12, 2959-2968, 2012.

Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler‐Scharr, A., and Mentel, T.: Relative importance of organic coatings for the heterogeneous hydrolysis of N2O5 during summer in Europe, J. Geophys. Res.: Atmospheres, 114, 2009.

Sander, S. P., Friedl, R., Barker, J., Golden, D., Kurylo, M., Wine, P., Abbatt, J., Burkholder, J., Kolb, C., and Moortgat, G.: Chemical kinetics and photochemical data for use in Atmospheric Studies Evaluation Number 16: supplement to Evaluation

10 15: update of key reactions, Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space Administration, 2009, 2009.

Tang, M., Huang, X., Lu, K., Ge, M., Li, Y., Cheng, P., Zhu, T., Ding, A., Zhang, Y., Gligorovski, S., Song, W., Ding, X., Bi, X., and Wang, X.: Heterogeneous reactions of mineral dust aerosol: implications for tropospheric oxidation capacity, Atmos. Chem. Phys., 17, 11727-11777, 2017.

15 Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., and Bohn, B.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmospheric Chem. Phys., 16, 14959, 2016.

Thornton, J. A., Braban, C. F., and Abbatt, J. P.: N2O5 hydrolysis on sub-micron organic aerosols: The effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem. Phys., 5, 4593-4603, 2003.

20 Wagner, N., Riedel, T., Young, C., Bahreini, R., Brock, C., Dubé, W., Kim, S., Middlebrook, A., Öztürk, F., and Roberts, J.: N2O5 uptake coefficients and nocturnal NO2 removal rates determined from ambient wintertime measurements, J. Geophys. Res.: Atmospheres, 118, 9331-9350, 2013.

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S. C., Dubé, W. P., Blake, D. R., and Louie, P. K.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China,

25 J. Geophys. Res.: Atmospheres, 121, 2476-2489, 2016.

Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., Wang, W., Tham, Y. J., Wang, Z., and Yang, L.: Observations of N2O5 and ClNO2 at a polluted urban surface site in North China: High N2O5 uptake coefficients and low ClNO2 product yields, Atmos. Environ., 156, 125-134, 2017a.

Wang, Z., Wang, W., Tham, Y. J., Li, Q., Wang, H., Wen, L., Wang, X., and Wang, T.: Fast heterogeneous N2O5 uptake and

30 ClNO2 production in power plant and industrial plumes observed in the nocturnal residual layer over the North China Plain, Atmos. Chem. Phys. Discuss, 17, 12361, 2017b.

Yun, H., Wang, T., Wang, W., Tham, Y. J., Li, Q., Wang, Z., and Poon, S. C.: Nighttime NOx loss and ClNO2 formation in the residual layer of a polluted region: Insights from field measurements and an iterative box model, Sci. Total Environ., 622, 727-734, 2018.

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	$k_{NO3-VOC}$	0.01 s^{-1}	0.01 s^{-1}
Temperature	25 ℃	0.1℃	RH	20-70%	1%
Residence Time	150 s	2 s			

[a] 1σ standard deviation for the varied parameters.

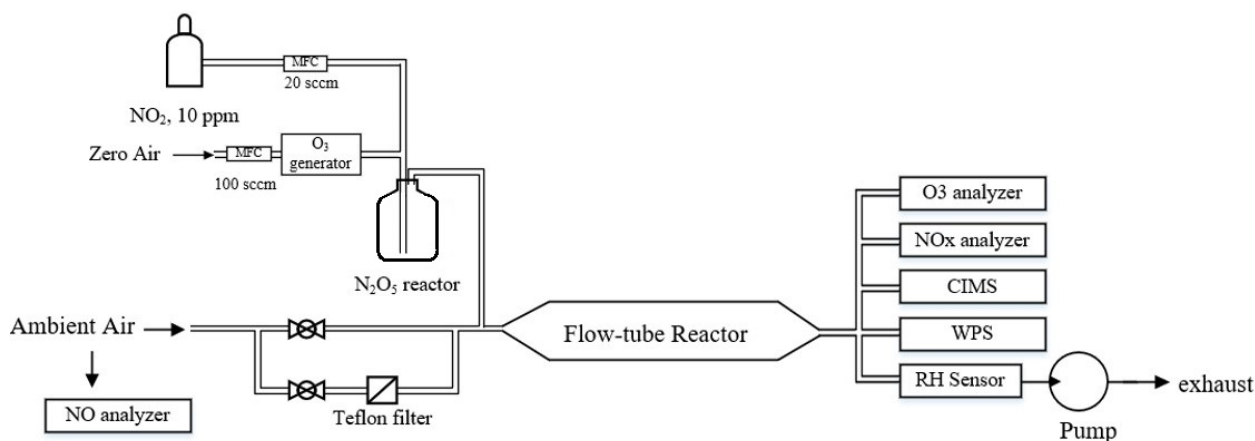



Figure 1: Schematic diagram of the aerosol flow tube system.

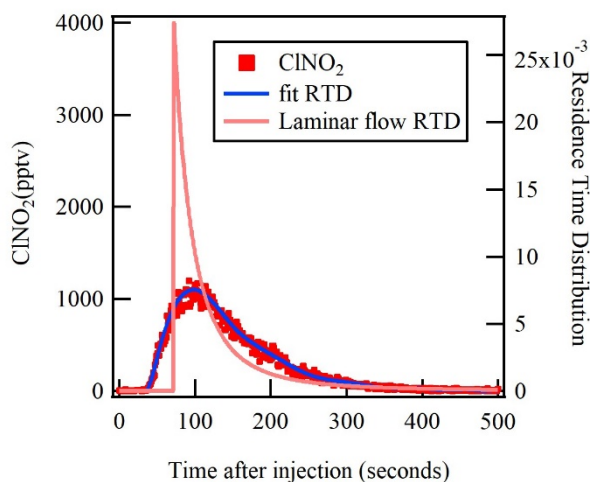



Figure 2: The measured residence time distribution of the injected ClNO₂ in the flow-tube reactor. The blue line represents the fitted residence time distribution of the ClNO₂ pulse injection experiment. The pink line represents the expected residence time distribution of an ideal laminar flow reactor without diffusion.

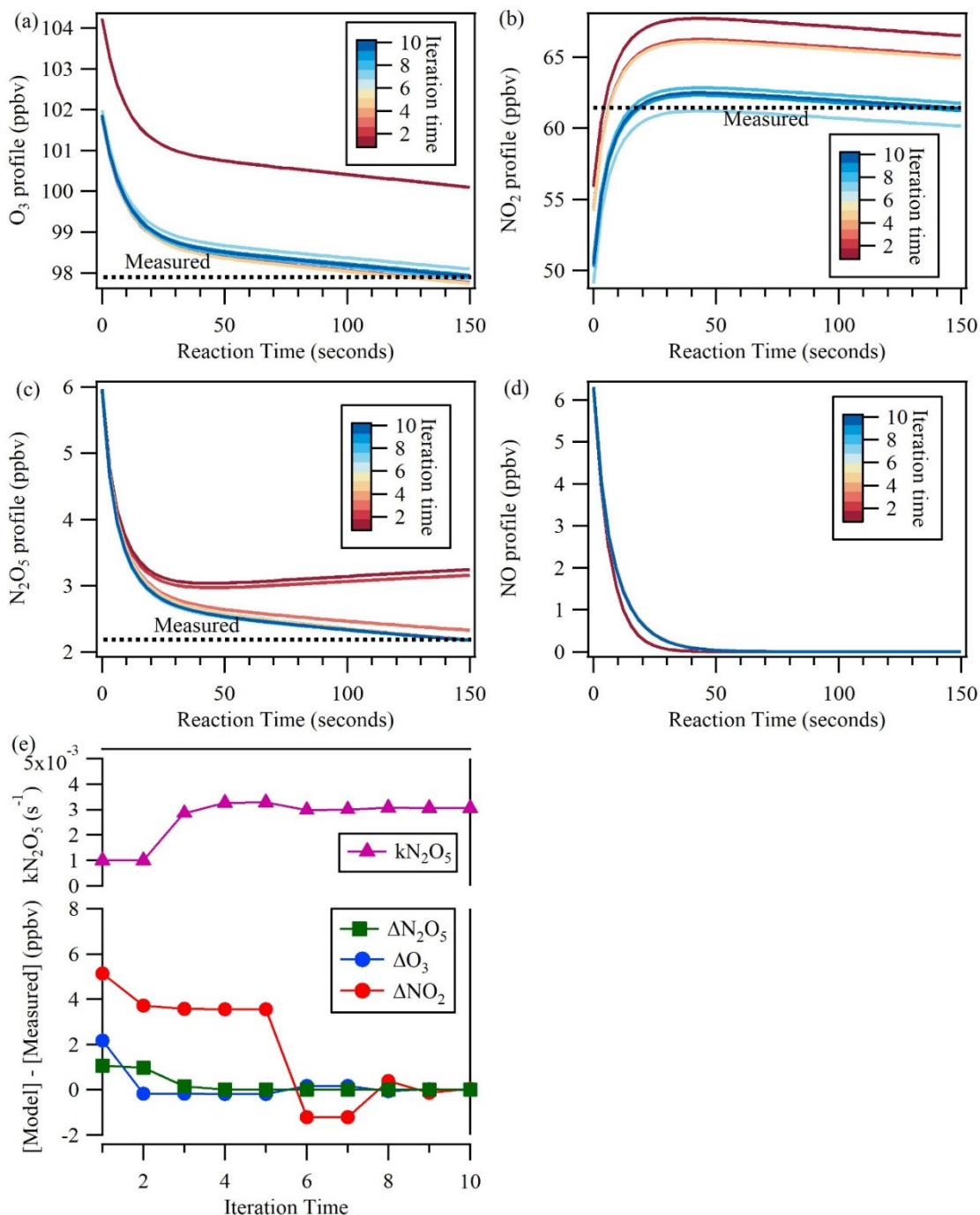



Figure 3: An example of the iterative box model simulation to derive k_{het} from the measured concentrations of NO_2, O_3 and N_2O_5 at the exit of the flow tube reactor. The concentration profiles obtained from the simulation in 10 iterations are shown for (a) O_3, (b) NO_2, (c) N_2O_5, and (d) NO.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

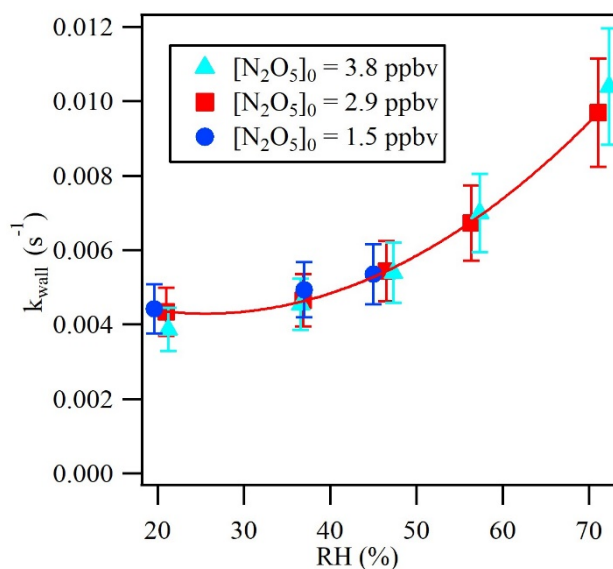



Figure 4: Relative humidity dependence of the wall loss rate coefficient (k_{wall}) of N_2O_5 in the flow reactor.

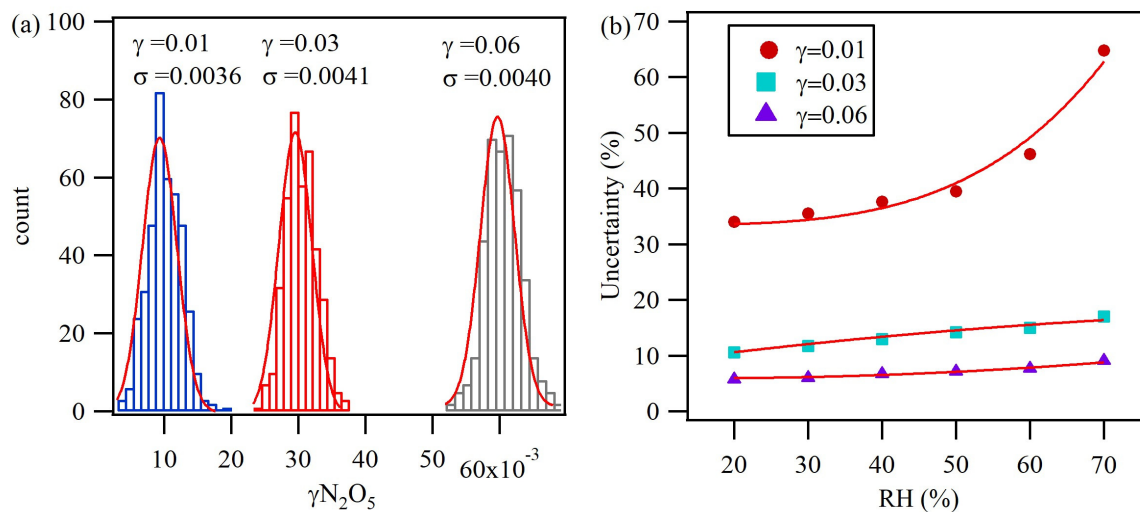



Figure 5: The uncertainty results for γN_2O_5 derived from Monte Carlo simulations for three individual sets with 400 simulations at (a) RH = 40% and (b) different RH values. In these three data sets, the condition was set as following: surface area=1000 μm²/cm³, reaction time = 150 s, initial O_3 = 80 ppbv, initial NO_2 = 50 ppbv, initial NO = 2 ppbv, initial N_2O_5 = 5 ppbv, temp = 25℃, $k_{NO3-VOC}$ = 0.01 s⁻¹.

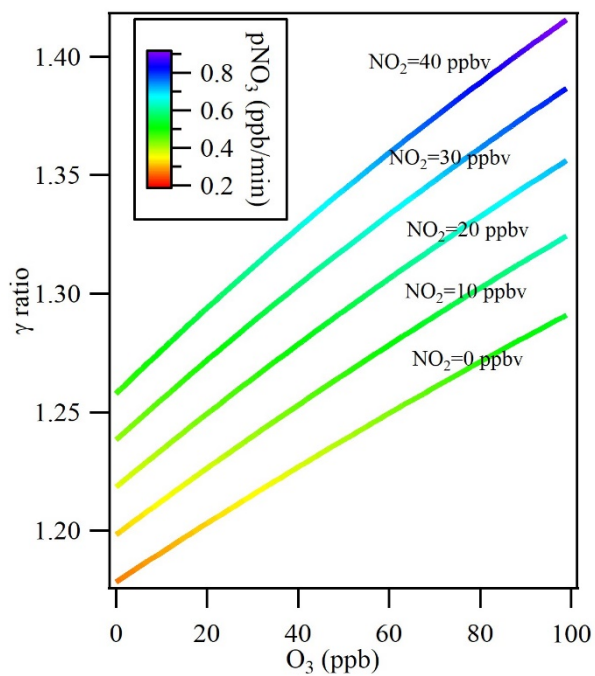



Figure 6: The influence of multiple reactions resulting from high ambient NO₂ and O₃ levels under different ambient NO₂ levels from 0-40 ppbv. The colors indicate the NO₃ production rate (pNO₃) at the entrance of the flow tube reactor after mixing with 106 ppbv of O₃ and 57 ppbv of NO₂ from the N₂O₅ source.

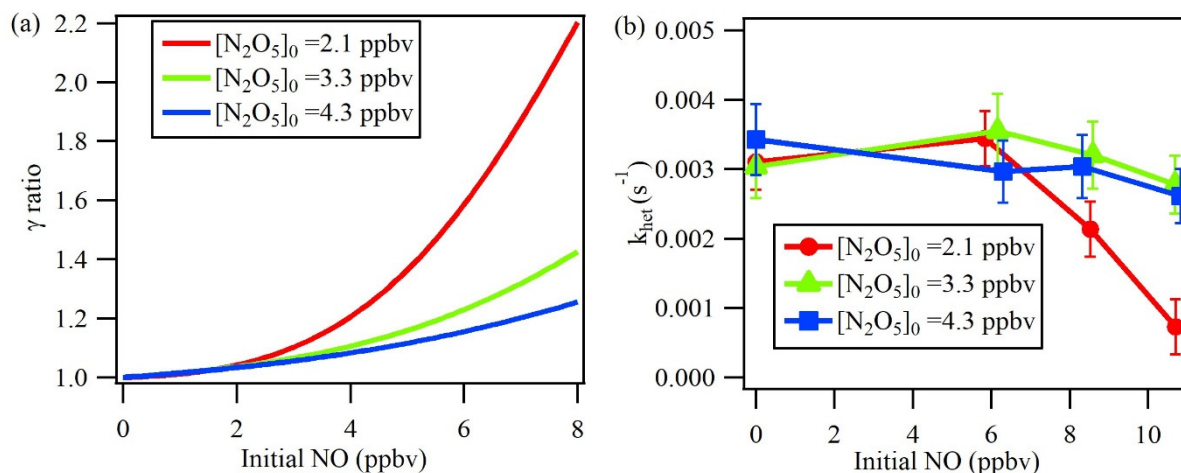



Figure 7: (a) Simulation results of NO titration effect on γN_2O_5. The γN_2O_5 ratio represents (γN_2O_5 from the iterative model) / (γN_2O_5 from ignoring reaction method). Initial NO and initial N_2O_5 represent the respective initial concentrations of NO and N_2O_5 in the flow tube reactor. (b) k_{het}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

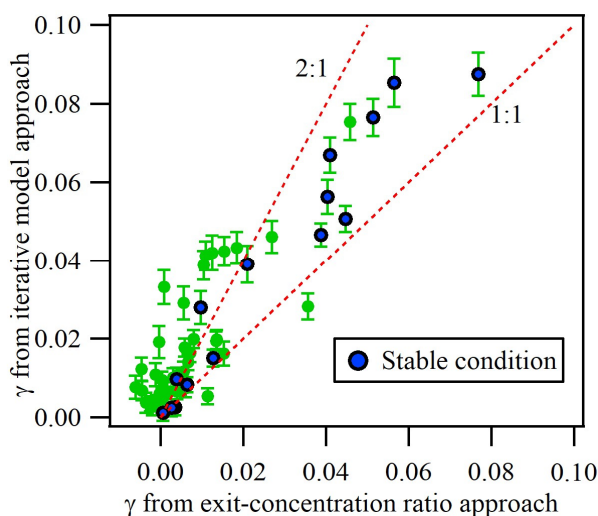



Figure 8: Comparison of γN_2O_5 determined from the exit-concentration ratio approach and the iterative model approach for all available data measured in the Heshan campaign. The blue points represent the data obtained under "clean and stable condition", while green points are data obtained from other 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, and the change of NO_2 and O_3 < 4 ppbv. The error bar represents the uncertainty calculated by Monte Carlo approach under the measurement condition.

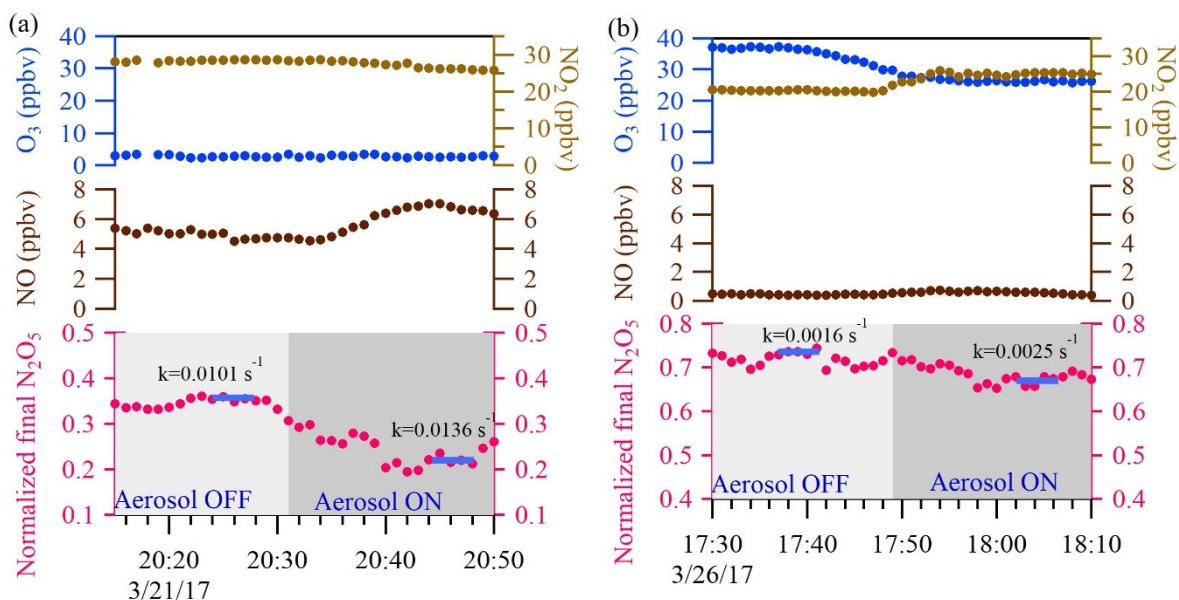



Figure 9: Two sample cases are shown. In the upper panel, the blue and light brown dots represent 1-min ambient O₃ and NO₂ data, respectively. In the middle panel, the brown dots represent 1-min ambient NO data. In the lower panel, the pink dots represent 1-min average of N₂O₅ concentration normalized to the initial N₂O₅ concentration in the flow-tube reactor. The calculated total N₂O₅ loss rate derived from the iterative model with 5-min average input data (the blue bar) is also shown for each cycle.