An in-situ flow-tube system for direct measurement of N$_2$O$_5$ heterogeneous uptake coefficients in polluted environments

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Abstract. The heterogeneous reactivity of dinitrogen pentoxide (N$_2$O$_5$) 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 N$_2$O$_5$ on complex ambient aerosols, an in-situ experimental approach to direct measurement of N$_2$O$_5$ uptake coefficient ($\gamma$N$_2$O$_5$) 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 $\gamma$N$_2$O$_5$ from the depletion of synthetically generated N$_2$O$_5$ when mixed with ambient aerosols. Laboratory tests and model simulations were performed to characterize the system and the factors affecting $\gamma$N$_2$O$_5$, including mean residence time, wall loss variability with RH, and N$_2$O$_5$ formation and titration with high levels of NO/NO$_x$/O$_3$. The overall uncertainty was estimated to be 9%-17% at $\gamma$N$_2$O$_5$ 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$_2$/O$_3$ and fresh NO emission. The results demonstrate that the iterative model improved the accuracy of $\gamma$N$_2$O$_5$ calculations under polluted environments, and thus support the further field deployment of the system to study the impacts of heterogeneous N$_2$O$_5$ reactivity on photochemistry and aerosol formation.

1 Introduction

Dinitrogen pentoxide (N$_2$O$_5$) 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$_2$O$_5$ 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$_2$O$_5$) only accumulates under dark conditions (i.e., at night). The heterogeneous reactions of N$_2$O$_5$ 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$_2$O$_5$ loss rate on aerosols ($k_{aerosol}$)
depends on the uptake coefficient of \( \gamma_{N_2O_5} \) 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).

\[
  k_{aerosols} = \frac{1}{4} c_{N_2O_5} S_a \gamma_{N_2O_5}
\]  

where \( c_{N_2O_5} \) (m/s) is the mean molecular speed of \( N_2O_5 \) and \( S_a \) (\( \mu \)m\(^2\)/cm\(^3\)) is the aerosol surface area concentration. \( \gamma_{N_2O_5} \) is the reaction probability that a \( N_2O_5 \) molecule collides with the aerosol surface resulting in net removal via reactions on aerosols. Because \( \gamma_{N_2O_5} \) is a critical parameter to determine \( N_2O_5 \) uptake on aerosols, it is necessary to develop reliable methods to measure it.

\( \gamma_{N_2O_5} \) 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 references cited therein). The \( \gamma_{N_2O_5} \) 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 \( \gamma_{N_2O_5} \) 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 \( \gamma_{N_2O_5} \) 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 \( \gamma_{N_2O_5} \) 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 \( \gamma_{N_2O_5} \); Wagner et al. (2013) applied an iterative chemical box model to derive the appropriate \( \gamma_{N_2O_5} \) 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 \( \gamma_{N_2O_5} \) 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):

\[
  k_{aerosols} = \frac{1}{\Delta t} \ln \left( \frac{[N_2O_5]_{\text{w/aerosols}}}{[N_2O_5]_{\text{w/o aerosols}}} \right),
\]  

where \( \Delta t \) is the mean residence time in the flow tube reactor, and \( [N_2O_5]_M \) 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 \( \gamma_{N_2O_5} \) 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 $\gamma_{N_2O_5}$, 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 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$_2$O$_5$ 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 $\gamma_{N_2O_5}$ derived from ambient 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$_2$O$_5$ on complex ambient aerosols, a flow tube reactor approach was developed for direct N$_2$O$_5$ reactivity measurement under highly polluted conditions. In the following sections, we describe in detail the method used for determining the N$_2$O$_5$ 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$_2$/O$_3$ and fresh NO emission.

2 Methodology

2.1 Flow tube reactor

The flow tube system consists of an N$_2$O$_5$ 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 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 SLPM and includes 120 SCCM of N$_2$O$_5$ 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$_2$O$_5$, O$_3$, NO$_x$, and aerosol surface area.
2.2 Generation of N$_2$O$_5$

N$_2$O$_5$ 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).

\[ \text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R1)} \]
\[ \text{NO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R2)} \]

In this study, ozone was generated from O$_2$ photolysis with a mercury lamp in a commercial calibrator (Model 4010, Sabio Instrument Inc.). A 100 SCCM of produced O$_3$ flow was mixed with 20 SCCM of NO$_2$ (10 ppmv balanced in N$_2$; Arkonics, 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$_2$O$_5$. Concentrations of synthesized N$_2$O$_5$ were calculated from observed changes in NO$_2$ (before and after addition of O$_3$), and the N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ concentrations from 1 to 10 ppbv (after dilution in the flow tube). The stability of synthetic N$_2$O$_5$ source was tested continuously for eight hours, and the variation of the signal was within ±2% in each hour. More detailed description of the N$_2$O$_5$ 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 (WPS, model 1000XP, MSP Corporation, USA) to determine the aerosol surface area. The N$_2$O$_5$ 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$_3$I diluted in N$_2$ flow through a $^{210}$Po source. The N$_2$O$_5$ and ClNO$_2$ were detected as ion clusters of I(N$_2$O$_5$)$^-$ 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).
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 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).

Pulse injection of highly concentrated ClNO₂ was used in the present study to measure the RTD and hence determine the mean residence time. ClNO₂ is an inert gas within the dark Teflon-coated flow tube reactor and can be measured by CIMS with high time resolution (>1 Hz). ClNO₂ was synthesized in-situ via passing the N₂O₅ 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 N₂O₅ injection during the uptake measurement) of ClNO₂ was directly injected into the flow tube reactor; at t =2 s, the solenoid valve switched and the ClNO₂ 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:

\[
E(t) = \frac{C(t)}{\int_0^\infty C(t')dt'},
\]  

where the \(C(0)\) represents the ClNO₂ concentration measured at time t. Then the mean residence time can be calculated as follows:

\[
\Delta t = \int_0^\infty tE(t)dt.
\]  

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.

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

As described previously, the reactivity of N₂O₅ can be investigated using the aerosol modulation by comparing the loss rate of generated N₂O₅ 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\textsubscript{2}O\textsubscript{5} to obtain the N\textsubscript{2}O\textsubscript{5} loss rate on aerosols. However, air mass changes lead to different NO\textsubscript{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\textsubscript{2} and O\textsubscript{3} in the ambient air would affect the exit N\textsubscript{2}O\textsubscript{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 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\textsubscript{2}O\textsubscript{5} loss rate in both aerosol and non-aerosol mode, considering multiple reactions describing the production and loss of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} (R1–R6) in the ambient condition.

$$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2; \quad k_3 \quad (R3)$$

$$\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2; \quad k_{\text{NO}_3-\text{NO}} \quad (R4)$$

$$\text{NO}_3 + \text{VOC} \rightarrow \text{products}; \quad k_{\text{NO}_3-\text{VOC}} \quad (R5)$$

$$\text{N}_2\text{O}_5 + \text{aerosols/wall} \rightarrow \text{products}, \quad k_{\text{het}} = k_{\text{wall}} + k_{\text{aerosols}} \quad (R6)$$

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 $k_{\text{NO}_3-\text{VOC}}$ from NO\textsubscript{3} reactions with VOCs (R5) was determined by ambient measured VOCs concentrations and rate coefficients from Atkinson and Arey (2003). The N\textsubscript{2}O\textsubscript{5} heterogeneous loss rate coefficient $k_{\text{het}}$ (R6) including heterogeneous loss on both aerosol and reactor surfaces, was the only adjustable parameter while other parameters such as N\textsubscript{2}O\textsubscript{5}, NO, NO\textsubscript{2} and O\textsubscript{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\textsubscript{2}O\textsubscript{5} source. The initial concentrations of $[\text{NO}_2]_{t=0}$ and $[\text{O}_3]_{t=0}$ were calculated from the ambient measured levels of NO\textsubscript{2} and O\textsubscript{3} and those from N\textsubscript{2}O\textsubscript{5} source. Given the constraint of measured parameters at the entrance of the flow tube reactor, including $[\text{NO}]_{t=0}$, $[\text{NO}_2]_{t=0}$, $[\text{O}_3]_{t=0}$, $[\text{N}_2\text{O}_5]_{t=0}$, $[\text{VOCs}]_{t=0}$, 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\textsubscript{2}, O\textsubscript{3} and N\textsubscript{2}O\textsubscript{5}. The calculated concentrations were then compared with the measured concentrations at the exit of the flow tube reactor, and the N\textsubscript{2}O\textsubscript{5} loss rate coefficient was tuned until the N\textsubscript{2}O\textsubscript{5} concentration predicted by the box model agreed with the measured N\textsubscript{2}O\textsubscript{5} concentration, $[\text{N}_2\text{O}_5]_{\Delta t}$. Assuming that $k_{\text{wall}}$ 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, $k_{\text{aerosols}} = k_{\text{het}}^{\text{w/aerosols}} - k_{\text{het}}^{\text{wo/aerosols}}$. Then the uptake coefficient of N\textsubscript{2}O\textsubscript{5} on aerosol surfaces ($\gamma_{\text{N}_2\text{O}_5}$) can be calculated by the following equation:

$$\gamma_{\text{N}_2\text{O}_5} = 4(k_{\text{het}}^{\text{w/aerosols}} - k_{\text{het}}^{\text{wo/aerosols}})/(c_\text{Sa}) \quad (5)$$

In circumstances without concurrent ambient measurement of NO\textsubscript{2} and O\textsubscript{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 \((t=Δt)\) to obtain the initial concentrations. As the cycle between NO\(_3\) and N\(_2\)O\(_5\) is fast and quickly established in high NO\(_x\) conditions, the NO\(_3\) and N\(_2\)O\(_5\) are considered as one singular N\(_2\)O\(_5^*\) species by assuming NO\(_3\) and N\(_2\)O\(_5\) 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 \(\mathrm{O}_3\) 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 \([\text{NO}]\) profile can be estimated from a forward simulation with inputs of measured initial NO, N\(_2\)O\(_5\), guessed \(k_{\text{het}}\) and estimated initial NO\(_2\) and \(\mathrm{O}_3\) 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.

\[
[\text{NO}_2]_0 = [\text{NO}_2]_{\Delta t} \times e^{\Delta t k_{1}[\text{O}_3]_{\Delta t}} - [\text{NO}]_0 \quad (6)
\]

\[
[\text{O}_3]_0 = [\text{O}_3]_{\Delta t} \times e^{\Delta t k_{1}[\text{NO}_2]_{\Delta t}} + [\text{NO}]_0 \quad (7)
\]

\[
[\text{NO}]_t = [\text{NO}]_0 \times e^{-t(k_{3}[\text{O}_3]_0)\frac{k_{4}[\text{N}_2\text{O}_5]_0}{k_{\text{eq}}[\text{NO}_2]_0}} \quad (8)
\]

The estimated [NO] profile was then constrained in the backward model simulation, together with inputs of measured concentrations of N\(_2\)O\(_5\), NO\(_2\), and \(\mathrm{O}_3\) at the exit of the flow tube reactor and the initially guessed \(k_{\text{het}}\), to derive the initial mixing ratios. The box model was run forward and backward iteratively with updated values and adjusted \(k_{\text{het}}\) until simulated N\(_2\)O\(_5\) concentration matched the measurement at the exit of the flow tube reactor. The agreement of simulated NO\(_2\) and \(\mathrm{O}_3\) concentrations with measurements was also used as a check to validate the model calculation. Thus, the uptake coefficient of N\(_2\)O\(_5\) 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\(_2\)O\(_5\) loss rate coefficient. This non-physical result might result from much larger \(k_{\text{NO}_3-VOC}\) than \(k_{\text{het}}\) 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\(_2\)O\(_5\) wall loss and overall uncertainty

In the present work, the determination of \(k_{\text{aerosol}}\) is independent of the magnitude of \(k_{\text{wall}}\) but the stability of \(k_{\text{wall}}\) is critical for the accurate retrieval of \(k_{\text{aerosol}}\). \(k_{\text{wall}}\) 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 \(k_{\text{wall}}\) with RH in the current flow tube system. \(k_{\text{wall}}\) can be determined from the previously described iterative model with the measurement of N\(_2\)O\(_5\) loss through the flow tube in a zero air flow in the absence of aerosols. As shown in Fig. 4, \(k_{\text{wall}}\) has a strong positive relationship with RH, and increases with RH, especially when RH is higher than 50%. The
consistent \( k_{\text{wall}} \) at each RH condition with different initial \( \text{N}_2\text{O}_5 \) concentrations suggests that \( k_{\text{wall}} \) 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 \( \gamma_{\text{N}_2\text{O}_5} \) with RH of 20% to 70% and a \( S_a \) of 1000 \( \mu \text{m}^2/\text{cm}^3 \). To minimize the magnitude of the variability in \( k_{\text{wall}} \), 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 \( k_{\text{wall}} \) being affected by RH, uncertainty in \( k_{\text{aerosol}} \) determination can occur due to \( \text{N}_2\text{O}_5 \) source variability, \( \text{NO}_3 \) reactivity with VOCs, and uncertainties associated with the measurement of all parameters. As described in Section 2.2, the stability of the \( \text{N}_2\text{O}_5 \) 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 \( \pm 0.01 \text{ s}^{-1} \) variation of \( k_{\text{NO}_3-\text{VOC}} \) would lead to a single-point uncertainty in \( \gamma_{\text{N}_2\text{O}_5} \) of \( \pm 0.4 \times 10^{-3} \) for \( S_a = 1000 \mu \text{m}^2/\text{cm}^3 \). \( \text{NO} \) reacts at a faster rate with \( \text{NO}_3 \), having a larger impact on the \( \gamma_{\text{N}_2\text{O}_5} \) calculation compared to VOCs. With a constrained real-time NO concentration, the iterative model can buffer against small NO changes. Stability of 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 \( \gamma_{\text{N}_2\text{O}_5} \) 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. \( \gamma_{\text{N}_2\text{O}_5} \) was found to be most sensitive to RH, which was closely related to \( k_{\text{wall}} \) as discussed before. Fig. 5a shows the uncertainty results of \( \gamma_{\text{N}_2\text{O}_5} \) derived from Monte Carlo simulations with RH at 40%. The single-point uncertainty in \( \gamma_{\text{N}_2\text{O}_5} \) was estimated to be \( \pm 4.1 \times 10^{-3} \) for \( \gamma_{\text{N}_2\text{O}_5} \) around 0.03, and \( \pm 3.6 \times 10^{-3} \) for \( \gamma_{\text{N}_2\text{O}_5} \) 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 \( \gamma_{\text{N}_2\text{O}_5} \) around 0.01 and 9% to 17% at \( \gamma_{\text{N}_2\text{O}_5} \) around 0.03 for RH ranging from 20% to 70% (Fig. 5b).

6. Demonstration of \( \gamma_{\text{N}_2\text{O}_5} \) measurements under polluted conditions

In polluted environments, high concentrations of \( \text{NO}_2, \text{O}_3 \) or NO in ambient air would affect the determination of the \( \text{N}_2\text{O}_5 \) 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 \( \text{N}_2\text{O}_5 \) 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 \( S_a \) of 1000 \( \mu \text{m}^2/\text{cm}^3 \), \( \gamma_{\text{N}_2\text{O}_5} \) of 0.03, \( k_{\text{wall}} \) of 0.004 \text{ s}^{-1}, and \( k_{\text{NO}_3-\text{VOC}} \) of 0.01 \text{ s}^{-1}. Various conditions were simulated with different \( \text{O}_3, \text{NO}_2 \) and NO
levels introduced into the flow tube, and the resulting concentrations of \( \text{N}_2\text{O}_3 \), \( \text{NO}_2 \), and \( \text{O}_3 \) at the exit of the reactors with and without aerosols modes were obtained. The loss rate and uptake coefficients of \( \text{N}_2\text{O}_5 \) were then calculated using the simple exit-concentration ratio approach (Eq. 2) and time-dependent iterative box model, respectively. The difference in \( \gamma\text{N}_2\text{O}_5 \) obtained from these two methods reflects the effect of \( \text{N}_2\text{O}_5 \) regeneration and \( \text{NO} \) titration on uptake coefficient determination.

Fig. 6 shows the simulation results for the derived uptake coefficients regarding the effect of \( \text{N}_2\text{O}_5 \) formation in the flow-tube reactor, with \( \text{O}_3 \) varied in the range of 0-100 ppbv and \( \text{NO}_2 \) in the range of 0-40 ppbv without \( \text{NO} \) presence in the ambient air. The \( \text{N}_2\text{O}_5 \) source input was fixed at 4.3 ppbv, as measured in the laboratory, together with 106 ppbv of \( \text{O}_3 \) and 57 ppbv of \( \text{NO}_2 \) from the \( \text{N}_2\text{O}_5 \) source. The \( \text{N}_2\text{O}_5 \) regeneration effect on \( \gamma\text{N}_2\text{O}_5 \) calculation was significant when \( \text{O}_3 \) and \( \text{NO}_x \) levels in the ambient air were high. For example, at \( \text{NO}_2 = 40 \) ppbv and \( \text{O}_3 =100 \) ppbv, which may frequently be encountered in city cluster regions in China, neglecting \( \text{N}_2\text{O}_5 \) formation in the flow tube would result in underestimating \( \gamma\text{N}_2\text{O}_5 \) by 42%.

To demonstrate the influence of \( \text{NO} \) titration, simulation tests were performed with \( \text{NO} \) varying from 0 to 8 ppbv. Because the reaction rate of \( \text{NO} \) with \( \text{NO}_3 \) is two orders of magnitude faster than that of \( \text{NO} \) with \( \text{O}_3 \), the initial \( \text{N}_2\text{O}_5 \) level would affect the \( \text{NO} \) titration process. We performed the simulation with different initial \( \text{N}_2\text{O}_5 \) concentrations injected into the flow-tube reactor. As the green line in Fig 7(a) indicates, the calculated \( \gamma\text{N}_2\text{O}_5 \) will be greatly underestimated when \( \text{NO} \) concentration increases, up to 43% at a \( \text{NO} \) level of 8 ppbv with an initial \( \text{N}_2\text{O}_5 \) level of 3.3 ppbv. Fig. 7(a) also shows that a lower initial \( \text{N}_2\text{O}_5 \) leads to a larger underestimation of \( \gamma\text{N}_2\text{O}_5 \) in the presence of \( \text{NO} \). It is not desirable to use \( \text{N}_2\text{O}_5 \) concentrations above 5 ppbv to minimize the \( \text{NO} \) effect, because of other potential artifacts associated with working at high concentration (Thornton et al., 2003).

To explore which \( \text{NO} \) level would leave an extremely low \( \text{N}_2\text{O}_5 \) concentration in the exit of the reactor and make \( \text{N}_2\text{O}_5 \) loss rate measurement impossible, a series of experiments in clean air with additional \( \text{NO} \) was conducted in the laboratory to investigate \( \text{NO} \) titration effects and the performance of the iterative model in buffering against high \( \text{NO} \). As shown in Fig 7(b), the derived \( k_{\text{het}} \) showed consistent results for zero \( \text{NO} \) and \( \text{NO} < 6 \) ppbv conditions when RH and other parameters were unchanged. With higher \( \text{NO} \) addition and a lower initial \( \text{N}_2\text{O}_5 \) level, the calculated \( k_{\text{het}} \), however, could be underestimated due to greater uncertainty when \( \text{NO}_3 \) and \( \text{N}_2\text{O}_5 \) were insufficient to titrate with \( \text{NO} \). Fig. 7(b) also shows that the introduced box model method could buffer against \( \text{NO} \) below 8 ppbv with an initial \( \text{N}_2\text{O}_5 \) 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 \( \gamma\text{N}_2\text{O}_5 \). To reduce the \( \text{NO} \) titration effect, a relatively high level of \( \text{N}_2\text{O}_5 \) (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 \( \gamma\text{N}_2\text{O}_5 \) calculations.
7 Ambient measurement

During winter 2017, the flow tube system was deployed to measure the N$_2$O$_5$ 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 concentrations of initial NO and exit N$_2$O$_5$, NO$_2$ and O$_3$ were used as the inputs in the iterative box model to derive $k_{\text{het}}$ and $\gamma$N$_2$O$_5$. Most measurements were conducted during the daytime to avoid interruption of nighttime ambient N$_2$O$_5$, and daytime N$_2$O$_5$ levels could be neglected. The average ambient temperature, RH, NO, NO$_2$, and O$_3$ during the field campaign were 23 $^\circ$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$_{\text{wall}}$ and N$_2$O$_5$-NO$_3$ equilibrium, and thus upset $\gamma$N$_2$O$_5$ measurement. The cases where $\gamma$N$_2$O$_5$ 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 (c.f. Eq. 2) to calculate the $\gamma$N$_2$O$_5$. Fig.8 exhibits the comparison of $\gamma$N$_2$O$_5$ 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 < 0.8 ppbv/min, and fluctuation of NO$_2$ and O$_3$ < 4 ppbv), and the corresponding values of $\gamma$N$_2$O$_5$ 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 $\gamma$N$_2$O$_5$ mainly due to N$_2$O$_5$ regeneration reaction. For conditions with higher precursor concentrations and fluctuations, the larger discrepancy between $\gamma$N$_2$O$_5$ 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 fluctuations of NO, NO$_2$, and O$_3$ could greatly affect the exit N$_2$O$_5$ 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$_2$O$_5$ concentration ratio, which would lead to underestimation of $\gamma$N$_2$O$_5$ 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 ppbv, and Sa of 1880 $\mu$m$^2$/cm$^3$. $\gamma$N$_2$O$_5$ was determined to be 0.028 from the iterative model approach, and a higher $\gamma$N$_2$O$_5$ value of 0.036 was obtained from the exit-concentration ratio approach. The overestimated $\gamma$N$_2$O$_5$ 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$^3$, $\gamma$N$_2$O$_5$ 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\textsubscript{2}O\textsubscript{5} heterogeneous uptake coefficient under conditions of high NO\textsubscript{2}/O\textsubscript{3} and fresh NO emission.

8 Summary and conclusion

An in-situ experimental approach for direct measurement of N\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{5} on ambient aerosols with consideration of multiple reactions affecting N\textsubscript{2}O\textsubscript{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 γ\textsubscript{N\textsubscript{2}O\textsubscript{5}} uncertainty estimated with a Monte Carlo approach is 38\% for γ\textsubscript{N\textsubscript{2}O\textsubscript{5}} around 0.01, decreasing to 11\% for γ\textsubscript{N\textsubscript{2}O\textsubscript{5}} around 0.03. k\textsubscript{wall} variation due to RH fluctuation in high humidity 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\textsubscript{2}O\textsubscript{5} uptake coefficients in polluted environments with high ambient levels of O\textsubscript{3}, NO and NO\textsubscript{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 γ\textsubscript{N\textsubscript{2}O\textsubscript{5}} values. The introduced approach could also be used to investigate the heterogeneous reactivity of other trace gases on ambient aerosols in polluted environments.

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References


Table 1: Parameters varied in the Monte-Carlo simulations

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<th>Parameter</th>
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<th>Variation a</th>
<th>Parameter</th>
<th>Fixed value</th>
<th>Variation a</th>
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<td>0.3 ppbv</td>
<td>[N₂O₅]₀</td>
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<td>0.1 ppbv</td>
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<td>[NO]₀</td>
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<td>[N₂O₅]ₜ</td>
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<td>0.6 ppbv</td>
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<td>Residence Time</td>
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<td>2 s</td>
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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 $k_{\text{out}}$ from the measured concentrations of NO$_2$, O$_3$ and N$_2$O$_5$ 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$_2$O$_5$, and (d) NO. In the upper panel of (e), the adjusted N$_2$O$_5$ loss rate is shown for each iteration. The lower panel of (e) shows the concentration differences between the model simulation and measurements of N$_2$O$_5$, 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\textsubscript{2}O\textsubscript{5} in the flow reactor.

Figure 5: The uncertainty results for γN\textsubscript{2}O\textsubscript{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 μm\textsuperscript{2}/cm\textsuperscript{3}, reaction time = 150 s, initial O\textsubscript{3} = 80 ppbv, initial NO\textsubscript{2} = 50 ppbv, initial NO = 2 ppbv, initial N\textsubscript{2}O\textsubscript{5} = 5 ppbv, temp = 25°C, k_{NO\textsubscript{3}-VOC} = 0.01 s\textsuperscript{-1}.
Figure 6: The influence of multiple reactions resulting from high ambient NO$_2$ and O$_3$ levels under different ambient NO$_2$ levels from 0-40 ppbv. The colors indicate the NO$_3$ production rate (pNO$_3$) at the entrance of the flow tube reactor after mixing with 10$^6$ ppbv of O$_3$ and 57 ppbv of NO$_2$ from the N$_2$O$_5$ source.
Figure 7: (a) Simulation results of NO titration effect on $\gamma_{\text{N}_2\text{O}_5}$. The $\gamma_{\text{N}_2\text{O}_5}$ ratio represents ($\gamma_{\text{N}_2\text{O}_5}$ from the iterative model) / ($\gamma_{\text{N}_2\text{O}_5}$ from ignoring reaction method). Initial NO and initial N$_2$O$_5$ represent the respective initial concentrations of NO and N$_2$O$_5$ in the flow tube reactor. (b) $k_{\text{het}}$ calculated via the iterative model in laboratory experiments with constant RH of 21%, different initial N$_2$O$_5$, and varied NO additions.

Figure 8: Comparison of $\gamma_{\text{N}_2\text{O}_5}$ 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.