Response to Anonymous Referee #2

General Comments

The authors propose a new variation of the N2O5 reactivity measurement introduced by Bertram et al in 2009. Specifically, the authors utilize an iterative box model coupled with measurements of NO, NO2, and O3 to compute the loss rate of N2O5 in the flow reactor when high and variable concentrations of NO, NO2, and O3 complicate the retrieval of N2O5 uptake coefficients. The paper is suitable for publication following the authors attention to the comments below:

Response: We thank the reviewer for his/her attention to this manuscript. We have made all the suggested changes and/or made clarifications. The reviewer's comment is in black and our response is in blue wording and the revised text is in italic.

1) I strongly encourage the authors to show results of laboratory tests on a model aerosol (e.g., NaCl or (NH4)2SO4) with varying inlet concentrations of NO, NO2, and O3 as this will cement the uncertainty analysis and the retrieval of N2O5 uptake coefficients that are reported here.

Response: Thanks for the valuable suggestions. The results of laboratory tests with $(NH_4)_2SO_4$ aerosols with the same system is now included in the revised text and SI.

The revised text reads,

"Laboratory tests of N_2O_5 *uptake on* $(NH_4)_2SO_4$ *aerosols were also performed with different NO,* NO_2*, and* O_3 *conditions, and the uptake coefficients were determined from the iterative box model analysis described above with input of measured concentrations. The determined uptake coefficient ranged from 0.018 to 0.026 (Table S1 in SI), which are similar to previous laboratory study results with* $(NH_4)_2SO_4$ *aerosols (Davis et al., 2008). The consistency also can serve as a validation of the applicability of the introduced system and method. In addition, we also compared the measured initial concentration of* NO_2 *and* O_3 *during the lab tests with that predicted from the iterative model (Fig 3f). The* NO_2 *concentration matched well between model prediction and measurement, while* O_3 *showed a little lower from the model simulation, which might be due to the wall loss or other loss ways of* O_3 *in the flow tube reactor."*

"*During the laboratory experiments, two initial* N_2O_5 *conditions with the input of additional 5 ppbv NO were also tested. The determined* γN_2O_5 *from iterative model simulation and exit-concentration method was compared and shown as cubes in Fig 7(a). The model results lie within the uncertainty range of the measurements, further cross-validating the NO influences and the model simulation.*"

The lab experiment conditions and derived uptake coefficients are also listed in Table S1 in SI.

Table S1. Lab experiments with $(NH_4)_2SO_4$ aerosols.

No.	Initial NO_2 (ppb)	Initial O_3 (ppb)	Initial NO (ppb)	Initial N_2O_5 (ppb)	RH (%)	Sa ($\mu m^2/cm^3$)	γ
1	62	57	0	2.1	25.1	848	0.0226
2	62	57	5.0	2.1	24.6	928	0.0208
3	57	106	0	4.3	22.9	965	0.0182
4	57	106	5.0	4.3	23.2	894	0.0212
5	57	106	0	4.3	48	1425	0.0259

2) Often, NO3 reactivity can be dominated by VOCs (e.g., isoprene)? If these VOCs are not measured, their effects on N2O5 uptake would not be captured by the model. Discussion of the potential effects should be included.

Response: Yes, the gas-phase reactions between NO_3 and VOCs can affect the N_2O_5 reactivity measurement. In the both flow tube methods introduced by Bertram et al. (2009) and that in the present study, the homogeneous reaction is expected to be independent of the aerosol and non-aerosol modes and is thus can be cancelled out in the calculation. Only strong atmospheric variation in VOC in short time period will influence the N_2O_5 uptake measurement. In the present study, VOCs including isoprene and monoterpenes were measured by an online-GC with time-resolution of 1 hour. Thus, the $k_{NO3\text{-}VOC}$ in the aerosol flow-tube system was treated as constant during each measurement cycle. The uncertainty from $k_{NO3\text{-}VOC}$ variation is addressed by Monte Carlo approach and is found that $\pm$ 0.01 s^{-1} variation of $k_{NO3\text{-}VOC}$ would lead to a single-point uncertainty in γN_2O_5 of $\pm 0.4\times10^{-3}$ for Sa = 1000 $\mu m^2/cm^3$. In addition, we have also run a sensitivity test with half or doubled $k_{NO3\text{-}VOC}$ as input value in the model, to address the effect of uncertainty in VOCs measurement, the results show that the effect of VOCs uncertainty was negligible. More information of the VOC measurements and more discussion on the potential influences are added in the revised text, as follows,

"Sensitivity tests with the iterative model calculation were performed to evaluate the uncertainty associated with measurement accuracy of N_2O_5 and VOCs, by varying the input N_2O_5 concentrations and $k_{NO3\text{-}VOC}$ in both modes. It is found that the N_2O_5 measurement uncertainty of 25% (Tham et al., 2016; Wang et al., 2017) would translate into an uncertainty of 12% in the γN_2O_5 (shown in SI). The VOCs measurement uncertainty, however, has negligible influence on γN_2O_5 calculation. In previous flow tube method introduced by Bertram et al., (2009), they also explained that the homogeneous reaction was expected to be independent of the aerosol and non-aerosol modes and was thus can be cancelled out in the calculation. Only strong atmospheric variation in VOC in short time period would influence the N_2O_5 uptake measurement."

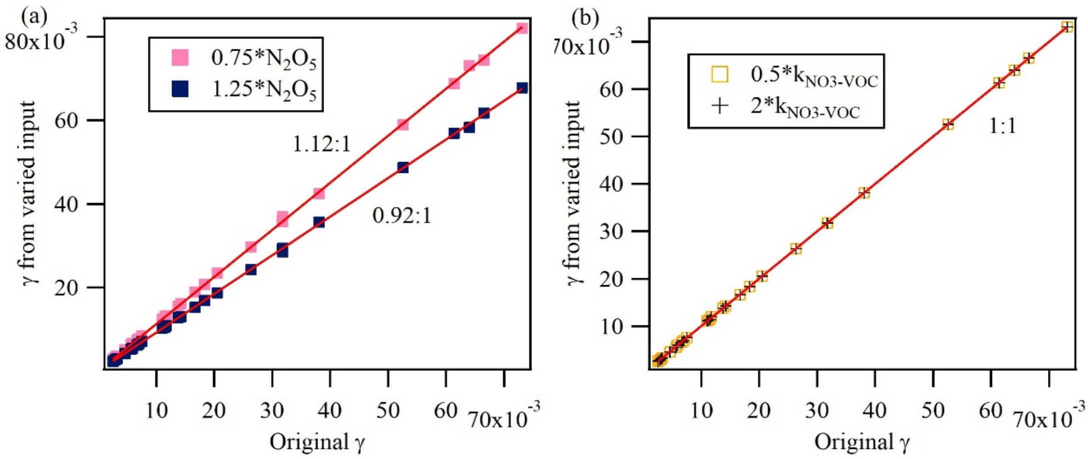

Figure S1. Sensitivity test of iterative model via varying input N_2O_5 and $k_{NO3\text{-}VOC}$ in both modes.

Specific Comments:

Page 2 Line 4: The units do not cancel when representing C in m/s and Sa in um2/cm3. Either remove the units or place all in common units m2/m3 for surface area.

Response: The unit of surface area is corrected as m^2/m^3.

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

Page 2 Line 9: What is a "pure" or "synthetic" aerosol? I would replace with model aerosol compounds based on the references cited.

Response: The sentence has been changed to:

"in the presence of pure inorganic and organic aerosols or mixed aerosols under different conditions"

Page 2 Line 27: The flow tube of Bertram et al was deployed to sites in Boulder, CO and Seattle, WA, and La Jolla, CA. I would not characterize any of these sites as rural, based on local NOx concentrations.

Response: Thanks for pointing this out. We have corrected the description to 'urban sites', as follows:

"This flow tube apparatus was deployed at two urban sites in Boulder and one coastal site in La Jolla to measure γN_2O_5 on ambient aerosols (Bertram et al., 2009b; Riedel et al., 2012)."

Page 4 Section 2.2: What is the concentration of NO2 and O3 in the flow tube?

Response: With the dilution of zero air, the concentration of NO_2 and O_3 was round 57 and 106 ppb at the top of the flow tube reactor. This information has been added in the revised text.

"In typical experiment used in the present study, the input of the N_2O_5 source to the top of flow tube contained 4.3 ppbv of N_2O_5, together with 106 ppbv of O_3 and 57 ppbv of NO_2."

Page 4 Section 2.3: Please confirm that surface area was measured at same RH of the flow tube. Also, was RH measured in the flow tube?

Response: Yes, the surface area was measured at same RH of the flow tube, because we didn't add any aerosol drier before the WPS when doing the flow tube measurement. The RH was continuously measured at the exit of the flow tube reactor, as shown in Fig. 1.

Section 3: The RTD by definition is a distribution of residence times. The shape of this distribution can bias the retrieved N2O5 uptake coefficients. If the distribution is normal, I would expect use of the mean residence time to be appropriate. If the distribution is not normally distributed, then the tails of the distribution can impact the retrieval of the N2O5 uptake coefficient. The authors site a mean of 149 +/-2, but that does not capture the distribution in residence time. Error induced by having a distribution of reaction times should be discussed in more detail here. I expect that this factor alone will carry uncertainty that is larger than the 9-17% cited in the abstract.

Response: Thanks for the valuable suggestion. We agree with the reviewer that using the mean residence time could bring large errors into the uptake coefficient determination. Because it is very difficult to include the RTD function in the iterative model calculation, we have performed a simplified test to estimate the uncertainty that may arise from the use of mean residence time. As also stated in the response to reviewer #1, we have added more information and more discussion in the revised text, as follows,

"*The RTD function in Fig. 2 is clearly different from the ideal laminar flow reactor. Bertram et al. (2009) have suggested that the determined rate constant would be underestimated by up to 25% due to non-ideal plug flow condition. More discussion of the uncertainty in γN_2O_5 calculation associated with residence time distribution is presented in section 5."*

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

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

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

Section 5: The propagation of errors and calculation of the overall uncertainty from the Monte Carlo method is interesting. It should be clearly stated that the uncertainty is a strong function of Sa. The number cited are for 1000 um2/cm3, for delta RH (aerosol on vs off) of less than 1% and for a specific delta in NO3 reactivity (0.01 s-1, between aerosol on and off). This should be cast in terms of an equivalent [NO].

Response: According to our and other previous studies, the uncertainty of the aerosol surface area measurement from the WPS system could be around 20-30% (Wang et al., 2017; Tham et al., 2018). The Monte Carlo simulation was only used to consider the k_{wall} changes, VOCs variation, and the variation of the different parameters during two modes in the measurement cycle. In addition, sensitivity tests were also included and the overall uncertainty by incorporating all of the factors are now updated. The revised text is as follows,

"The uncertainty of the aerosol surface area measurement was 20-30% (Wang et al., 2017; Tham et al., 2018)."

"In addition to k_{wall} being affected by RH, uncertainty in $k_{aerosols}$ determination can also result from N_2O_5 source variability, NO_3 reactivity with VOCs, precision as well as accuracy associated with the measurement of all parameters. The long period of measurement cycle may also bring uncertainty due to concentrations variation in two operation modes. As described in Section 2.2, the stability of the N_2O_5 generation source was within ±2% over an hour. In the present study, online VOCs were measured with a time resolution of one hour. A $\pm 0.01\ s^{-1}$ variation of $k_{NO3\text{-}VOC}$ would lead to a single-point uncertainty in γN_2O_5 of $\pm 0.4\times10^{-3}$ 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 NO, NO_2, O_3, and N_2O_5 for a period of at least 5 minutes for each mode is required to ensure that the flow-tube reactor measurement and iterative model yield reasonable results. The measurement precision and variation of these species during each cycle might also introduce uncertainty in the iterative model calculation.

The uncertainty in the γN_2O_5 determination associated with k_{wall} changes, VOCs variation, and the variation of the different parameters during the measurement cycle was estimated with a Monte Carlo approach, as described in Groß et al. (2014), by assessing the uncertainty from individual key parameters (shown in Table 1) in the calculation model. γN_2O_5 was found to be most sensitive to RH, which was closely related to k_{wall} as discussed before. Fig. 5a shows the partial uncertainty of γN_2O_5 derived from Monte Carlo simulations with RH at 40%. The single-point uncertainty in γN_2O_5 was estimated to be $\pm 4.1\times10^{-3}$ for γN_2O_5 around 0.03, and $\pm 3.6\times10^{-}$

^{3} for γN_2O_5 around 0.01, with RH of 40%. The uncertainty increased with RH and would be 9% to 17% at γN_2O_5 around 0.03 for RH ranging from 20% to 70% (Fig. 5b).

Sensitivity tests with the iterative model calculation were performed to evaluate the uncertainty associated with measurement accuracy of N_2O_5 and VOCs, by varying the input N_2O_5 concentrations and $k_{NO3\text{-}VOC}$ in both modes. It is found that the N_2O_5 measurement uncertainty of 25% (Tham et al., 2016; Wang et al., 2017) would translate into an uncertainty of 12% in the γN_2O_5 (shown in SI). The VOCs measurement uncertainty, however, has negligible influence on γN_2O_5 calculation. In previous flow tube method introduced by Bertram et al., (2009), they also explained that the homogeneous reaction was expected to be independent of the aerosol and non-aerosol modes and was thus can be canceled out in the calculation. Only strong atmospheric variation in VOC in short time period would influence the N_2O_5 uptake measurement. The uncertainty introduced by the aerosol surface area measurement including aerosol loss influence would be propagated to an uncertainty in the γN_2O_5 calculation of 30%.

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

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

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

By incorporating all of these factors, the estimated total uncertainty is propagated to be 37% to 40% at γN_2O_5 around 0.03 with 1000 $\mu m^2/cm^3$ Sa for RH ranging from 20% to 70%. "

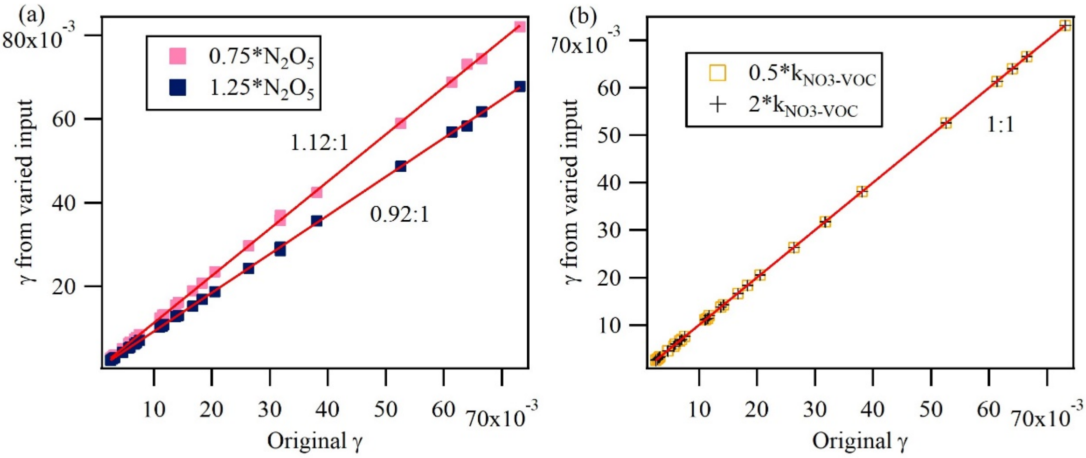

Figure S1. Sensitivity test of the iterative model via varying input N_2O_5 and $k_{NO3\text{-}VOC}$ in both modes.

Page 9 Line 11: The retrieval of the N2O5 uptake coefficient is sensitive to a difference in NO3 reactivity between the aerosol on and off states. It would be helpful if the authors also stated how the difference in NO concentration between the on and off states impacted the retrieval.

Response: The NO titration effect would underestimate the uptake coefficient even when NO concentration is the same level between two modes, as shown in Fig. 7a. When NO concentration is higher, for example in aerosol ON mode, the measured N_2O_5 concentration would be lower due to NO titration, thus overestimate the uptake coefficient if only compare exit concentration ratio of N_2O_5 in two modes. In the ambient measurement case in Fig. 9a in section 7, we have compared the uptake coefficients derived from the iterative model method and exit-concentration ratio method when NO was fluctuated between aerosol on and off states. The determined γN_2O_5 was overestimated by 28% for the NO increase of about 1.5 ppbv. For comparison, we also chose different periods in aerosol existing state corresponding to different NO conditions in this case, and the iterative model derived similar loss rate constants and uptake coefficients, demonstrating the applicability of the iterative model in buffering against fluctuated NO.

The revised text is as follows,

"The overestimated γN_2O_5 from the exit-concentration ratio approach could be explained by the increased NO level (~ 1.5 ppbv) in the aerosol mode. For comparison, another two periods of data points in the March 21 case (Fig. 9a) with different NO levels were also selected to derive the k_{het}, and the results showed good consistency (0.0136-0.0140 s^{-1}) (Fig S2 in SI), also demonstrating the applicability of the iterative model in buffering against fluctuated NO."

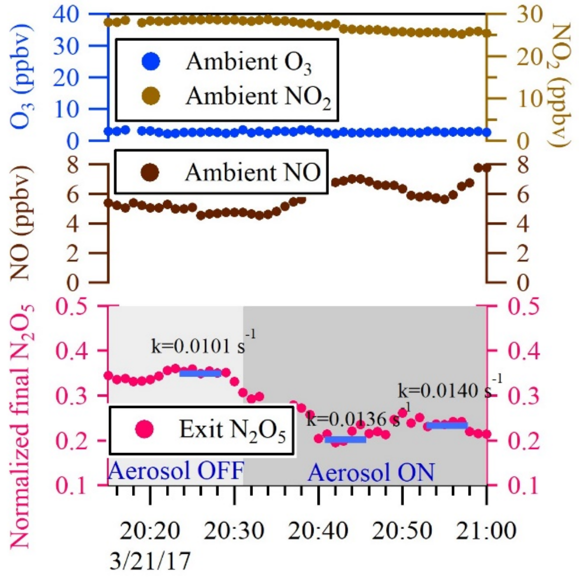

Figure S2. sample case on Mar 21st, two stable data point under different NO level are chosen to calculate the N_2O_5 loss rate.