Response to Anonymous Referee #1

The authors present a flow tube measurement of the N2O5 uptake coefficient that is an extension of the work of Bertram, Riedel, and Thornton. The measurement system is described and it is similar to the earlier design. The main innovations presented here are a more detailed measurement of the residence time distribution in the flow tube and the application of an iterative box model to retrieve the uptake coefficient when ambient concentrations of NO, NO2 and O3 are high enough to make 2nd order reactions important in the flow tube. The authors also present ambient measurements of the uptake coefficient which are useful because these direct measurements are rare and limited geographically.

This is an important measurement and should be published in AMT with minor changes.

Suggestion: A method, complementary to the iterative box model analysis, would be to reduce the concentrations of the gas-phase interferers (NO, NO2, O3, VOCs) before the N2O5 addition using an actived-carbon scrubber that transmits aerosols, such as http://www.sunlab.com/denuders/ .

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

We also included the reviewer's suggestion of using active-carbon scrubber in the revised text, as follows,

"*For future development, an activated-carbon scrubber in the inlet to reduce the gas-phase interferers (NO, NO_2, O_3, VOCs) but transmit aerosols could be a complementary approach to apply the flow tube system coupled with iterative box model analysis to even higher polluted conditions.*"

Minor issues:

1) Typically laboratory measurements of the uptake coefficient on synthetic aerosol are less than 0.04. Although some ambient analyses (Wagner et al. 2013, McDuffie et al. 2018) report uptake coefficients above 0.04 (upto 0.1) for a small subset of the data. It is not clear if these are artifacts of the analysis or real measurements of the uptake coefficient. Here the authors also report a direct measurements of uptake coefficients between 0.04 and 0.1. I would encourage the authors to address the discrepancy between laboratory measurement and their ambient measurements.

If they are real what is aerosol composition? Can the measured uptake be reproduced in the lab with synthetic aerosol?

Response: The discrepancy of uptake coefficient between laboratory measurement and ambient measurements via the indirect method have been reported by many researchers. This is also one of the motivations to improve the direct uptake coefficient measurement technique with an aerosol flow tube on ambient aerosols. We also conducted laboratory tests with $(NH_4)_2SO_4$ aerosols by using the same system, and similar uptake coefficient around 0.02 was obtained under different

NO, NO_2, and O_3 conditions. The results are shown in the following table which has been added in the SI. The value is similar to previous laboratory results, which can serve as a validation of the applicability of the introduced system and also implies that the measured high uptake coefficient value is not due to the artificial of our aerosol flow tube system. The uptake coefficient on ambient aerosols in this study, however, was found to be more variable. During the campaign, the concentrations of water-soluble ions, organic/element carbon amount in the aerosol were also measured. However, it is hard to reproduce the complex aerosol composition as well as the mixing states in the laboratory. Thus, we will perform more studies and further analysis on the dependence of uptake coefficient on ambient aerosols compositions in the future works.

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) It is unclear what parameters were used in the uncertainty analysis. I suspect uncertainty due to the aerosol surface area measurement would be at least +/-25%. In figure 9, there are not smooth exponential decay transitions between filter ON and OFF periods, so I suspect the uncertainty in the N2O5 measurement is significant.

On page 8 line 18, please list the key parameters and the uncertainty associated with them.

Response: Thanks for pointing this out. 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 reason for not smooth exponential decay transitions between filter ON and OFF periods mainly due to air changes in ambient, flow turbulence when switching valves and diffusion/dispersion as a non-ideal reactor. As stated in our previous studies, the uncertainty of N_2O_5 measurement using the same instrument and same setup is 25% (Tham et al., 2016; Wang te al., 2017). We have revised this part to include these measurement uncertainties in the overall uncertainty estimation.

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 ± 0.01 s-1 variation of kNO3-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%. "*

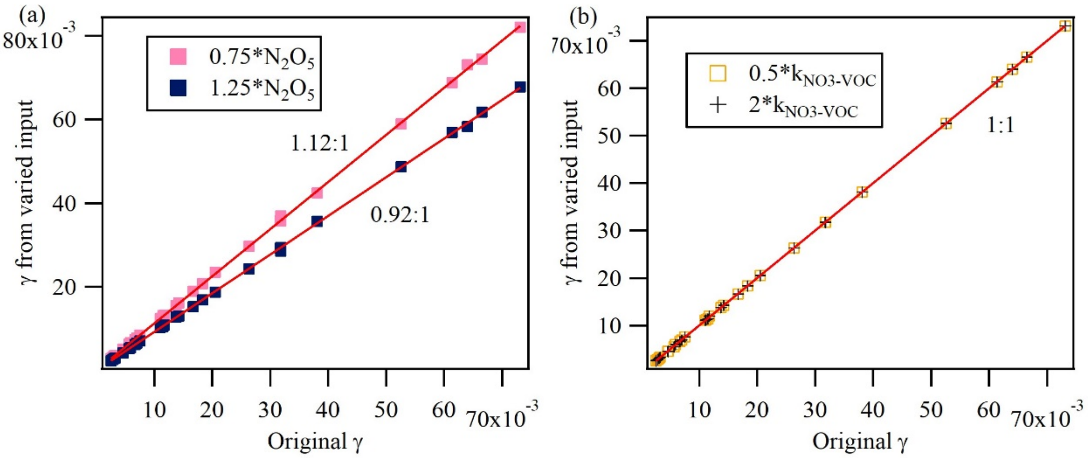

Figure S1. Sensitivity test of the iterative model via varying input N_2O_5 and $k_{NO3\text{-}VOC}$ in both modes.

3) Measurements of NO and VOCs are not described. Uncertainty due to reactions of NO3 with unmeasured VOCs should be bounded.

Response: The ambient NO was measured by another NOx analyzer while VOCs were measured by an online-GC. We have added this information in the manuscript:

"The ambient VOCs were determined using an online gas chromatograph (GC) coupled with a flame ionization detector (FID) and a mass spectrometer (MS). The VOCs concentrations were used to determine the $k_{NO3\text{-}VOC}$ *in the aerosol flow-tube system, which was treated as constant during the short-time period of flow tube measurement. The ambient NO level was measured by another chemiluminescence NOx analyzer (Thermo, Model 42i) equipped with a molybdenum converter."*

The uncertainty due to reactions of NO_3 with VOCs has been tested in a sensitivity test which used varied $k_{NO3\text{-}VOC}$ as input. It shows that the uncertainty of $k_{NO3\text{-}VOC}$ measurement could be negligible when comparing two modes. This information has been added in the text and SI, as details described in the above response.

4) The authors show that the residence time in the flow tube is a distribution (ranging over a factor of 2 in residence times), however in the iterative box model only the mean residence time is used. As the iterative box model likely depends in the residence time in a nonlinear way, the author should use a range of residence times in the iterative box model.

Response: Thanks for the valuable suggestion. Since 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. The comparison results showed that the use of mean residence time might underestimate the loss rate coefficient by 5% to 16% for different conditions. We have added this 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:*

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

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.*"

5) Have the authors measured particle losses in the flow tube? Diffusional and gravitational losses could be important. Could aerosol losses also be RH dependent? If so, please add a few sentences describing the results.

Response: Yes, we have measured the particle transmission in the introduced flow tube system using synthetic aerosols. This information has been added in the text, as follows,

"*The transmission of aerosols in the flow tube was evaluated using laboratory-generated* $(NH_4)_2SO_4$ *particles. The passing efficiency was around 50% for particles with a size of 20 nm, and more than 90% for particles larger than 100 nm. The total surface area loss in the flow tube was around 10-25%.*"

6) In figure 9, the periods chosen for analysis seems to be handpicked for stability. If different periods were chosen how would the results change?

Response: Since the mean residence time of the flow tube is more than 2 minutes, it is necessary to have at least 5 minutes of stable data for the calculation. We normally choose the 5 minutes data when all monitored parameters were relatively stable for each operation mode.

The fluctuation of the N2O5 signals in Fig.9a was mostly due to the variation of ambient air, such as change of NO levels. We have tried to use different time periods to perfume the calculation in the same case, as shown below, the different stable periods with different N2O5 and ambient NO level actually still gave similar results. We have included this information in the text and SI.

The revised text reads:

"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."*

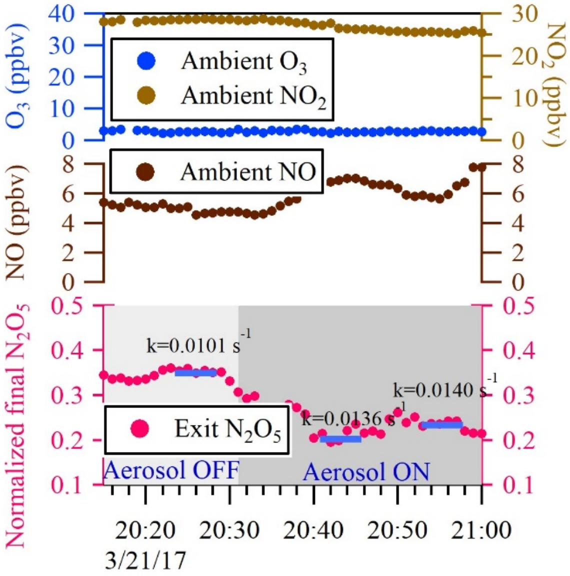

Figure S2. sample case on Mar 21st, two stable data point under different NO level are chosen to calculate the N_2O_5 loss rate constant.

Technical issues:
Pg 3, line 26: How does the flow tube pressure relate to ambient pressure?

Response: Since the measurement in the present study was conducted at a low altitude site (60 m a.s.l), the ambient pressure was mostly close to 1 atm. We measured the pressure in the flow tube with a pressure meter occasionally, and the pressure did not show obvious change.

Pg 4, line 14: how much NO2 is added with the N2O5 addition?

Response: After dilution in sample air in the flow tube, the injection of NO_2 concentration was 57 ppbv. This information has been added in the revised text, as follows,

"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*."*

Pg 7, line 4: This sentence is missing a subject

Response: Thanks for pointing out. The word “this” was added to the sentence. “this” here means consider NO_3 and N_2O_5 as one singular N_2O_5* in the box model.

“Doing this also makes backward reaction simulation possible by avoiding unstable equilibrium in the box model.”

Pg 7, line 20: Please give some more explanation about when non-physical results occur. When the uptake coefficient is small. When aerosol number is low? I expect that in a flow tube with high initial N2O5 the box model would work well in most cases.

Response: The low aerosol surface area and insignificant uptake could possibly result into negative uptake values when the heterogeneous loss on aerosols is small but the k_{NO3} or wall loss of N_2O_5 dominate the N_2O_5 loss in flow tube reactor and when the fluctuation of the wall loss due to temperature or RH is significant. Slightly higher initial N_2O_5 concentration could be useful to reduce the influence of these fluctuations but might also introduce other artifacts as suggested by Thornton (2003).

We have added more information in this part, as follows,

“This non-physical result might result from much larger fluctuations of k_{NO3} or k_{wall} in the system during each measurement cycle. When $k_{aerosol}$ is small due to the low S_a or insignificant uptake, the k_{NO3} or k_{wall} may dominate the N_2O_5 loss in flow tube reactor, and the fluctuations of k_{NO3} or k_{wall} due to the air mass or temperature/RH changes would bias the $k_{aerosol}$ determination and led to large uncertainty or negative values. This situation often occurred under conditions of fresh NO emission; more discussion of the influence of NO is presented in section 6.”

Pg 8, line 5: please add ‘respectively’

Response: The sentence has been revised as,

“This result would translate into an uncertainty of ($\pm 0.15\times10^{-3}$) to ($\pm 2.4\times10^{-3}$) in γN_2O_5 with RH of 20% to 70%, respectively, and a Sa of 1000 $\mu m^2/cm^3$.”

Pg 9 line 9: typo ‘ere’

Response: Corrected.

“The N_2O_5 regeneration effect on γN_2O_5 calculation was significant when O_3 and NO_x levels in the ambient air are high.”

Pg 9, line 16: Could you summarize the potential artifacts.

Response: Thornton (2003) reported a higher uptake coefficient obtained when using initial N_2O_5 of 6 ppbv than with 30 ppbv. They suggested that the artifacts could be the particulate NO_3^- formed via N_2O_5 hydrolysis inhibiting further ionization of N_2O_5 when initial N_2O_5 is too high.

Pg. 10 line 27: missing ‘the’, ‘in aerosol mode’

Response: Corrected.

“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.”*