**Reply on RC2**

We appreciate the reviewer for the careful reading and their constructive comments on our manuscript. **As detailed below, the reviewer's comments are** normal font, **our response to the comments are shown as** *italicized font*. New or modified text is in blue.

All the line numbers refer to original version of Manuscript ID: **amt-2022-167**.

Wang et al describe an aerosol flow reactor for the measurement of the reactive uptake of $N_2O_5$ to ambient aerosol particles. This approach has already been reported in the literature and the approach taken by the authors is very similar to that previously reported. I suggest that the authors focus the paper on the specific aspects of the flow reactor system that are new and less on the aspects that are replication of prior work. In 2009, Bertram et al reported on the development of a flow reactor for measurement of the reactivity of ambient aerosol that is strikingly similar to this. In 2018, Wang et al reported on the use of an iterative box-model coupled to the flow reactor to improve the retrieval of the reactive uptake coefficients for $N_2O_5$ to ambient aerosol, which again is very similar to that used here. It is not clear what is new with this approach that would warrant a new publication. The authors need to make the case for what technological advancement has been made. It is also not clear that the uncertainty associated with the measurements have been reduced.

The authors do note that "simultaneous $N_2O_5$ measurement at both end of the flow tube" is a unique feature of this reactor. I find this statement to be misleading: 1) The measurement is NOT simultaneous. In this technique the top and the bottom of the flow tube are sampled sequentially within one duty cycle. 2) Sampling of the $N_2O_5$ concentration at the top and the bottom of the flow tube was also done in Bertram et al to retrieve daily wall loss terms (see section 3.2 of Bertram et al). The authors would need to argue that measuring the wall loss more frequently leads to a reduced uncertainty in the retrieved uptake coefficients if this is the primary technical advance of the paper.

*We thank this comment. The reviewer emphasized the similarity of our work to the two previous works and questioned the novelty of this study. While our work builds on the previous two studies and attempts to address some issues that were not well addressed in the above work.*

*First, accurate quantification of wall loss is essential for the quantification of $N_2O_5$ uptake coefficients as suggested in Bertram's paper, a better way to reduce the wall loss interference is to measure it frequently (Bertram et al., 2009, see section 4.3). This suggestion was subsequently adopted by Wang et al. but the concentration of the $N_2O_5$ source they used in determining the wall loss and the total $N_2O_5$ loss was an assumed stable value rather than an observed one. Here, we dynamically determine the $N_2O_5$ source concentration frequently, which is helpful to provide accurate data*

*on quantifying the wall loss as well as the total $N_2O_5$ loss in the flow tube in each measurement cycle. Figure R1 shows the example of difference of measured $N_2O_5$ wall loss at lab condition and ambient condition.*
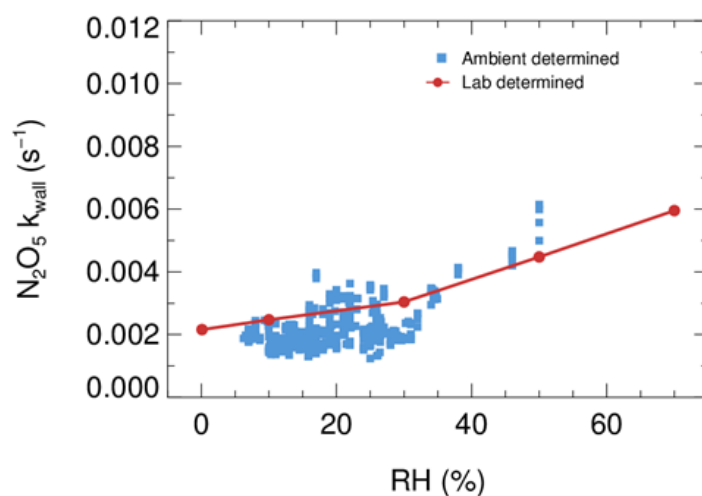


*Figure R1. The derived dependence of $N_2O_5$ wall loss on RH at laboratory condition (red dots) and field measurement (blue square)*

*Second, the use of an iterative box model approach to correct the potential bias, due to side reactions in the flow tube, is the highlight of the work of Wang et al. The iterative box model calculates backward to estimate the concentration of $NO_2$ and $O3$ before entering the flow tube,* **with estimated NO profile and measured $N_2O_5$ at the exit of flow tube.** *Here, the observed concentrations of $NO_2$, O3, and NO at "time zero" are obtained through programmed cyclic measurements, which can reduce the uncertainties by adding the model constrain (more details can be found in the reply for the following Question NO. 4). Figure R2(a) presents the box whisker of $N_2O_5$ and NO concentration before the entrance during a field campaign. The variation of initial $N_2O_5$ is much larger than that in lab condition with a very small standard deviation for $N_2O_5$ concentration (<1%, mentioned in line 180), highlights the influence of ambient air mass (e.g. varying NO and temperature) to injected $N_2O_5$. Figure 2R(b) shows the case of large underestimation by using a fixed initial $N_2O_5$ concentration rather than measured values as box model input. In addition, we simulate NO3-$N_2O_5$ relationship via specific reactions rather than approximating it in equilibrium and introducing the equilibrium coefficient (Keq) into calculation. Determining NO3 or $N_2O_5$ concentration by Keq could induce large bias (up to 90%) under the high aerosol loading and low temperature (Chen et al., 2021).*
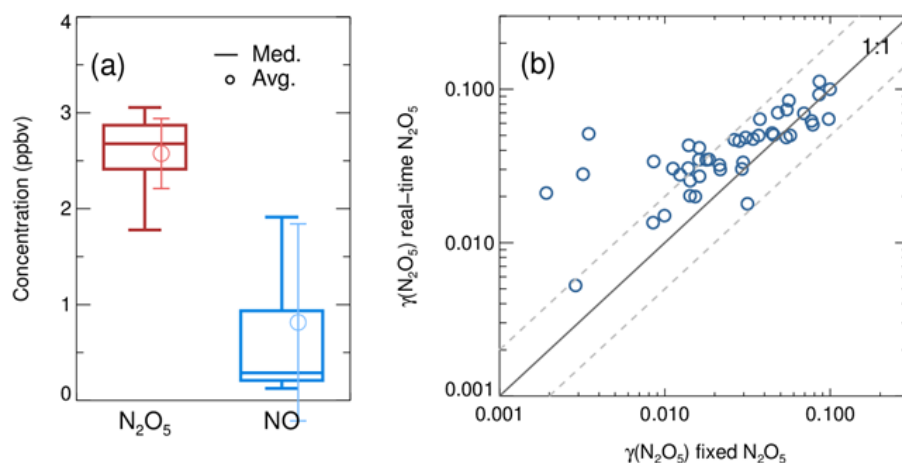
*Figure R2. (a) the box whisker of $N_2O_5$ source and NO measured before the entrance; (b) the inter-comparison of derived $N_2O_5$ uptake coefficient by using a fixed $N_2O_5$ and a dynamic measured $N_2O_5$ at the time zero in the iterative box model.*

*Third, to achieve the programmed cyclic measurement of key parameters such as $N_2O_5$, NOx and O3, we adopted a new design scheme of Y-tee and cyclic measurement setup, which were never used in the previous two studies.*

*In summary, we believe that the above innovation points of our study are advanced, while we may not address our innovation points well in the previous version. Thus, we have added an explanation of the novelty in the revised manuscript as follows.*

"The design of sampling module and aerosol flow tube in this work follows previous work for measuring $\gamma(N_2O_5)$ on ambient aerosols (e.g. Bertram et al., 2009). The major distinctions of this system from previous work are continuous monitor of NOx and $O_3$ concentration before the inlet of flow tube (after sampling air mixing with $N_2O_5$ source) and the sequential measurements of $N_2O_5$ concentration both at the inlet and the exit of flow tube within a duty cycle. Constraints of these variables during the subsequent data processing can improve the measuring accuracy."

"Overall, the introduction of box model method in this study is able to effectively avoid the underestimation caused by the lack of consideration of side reactions in the flow tube. Although an iterative box model, including backward and forward simulation, has been applied to the $\gamma(N_2O_5)$ measurements via an aerosol flow tube in polluted environments (Wang et al., 2018), the box model method combined with current flow tube system in this study can improve measuring accuracy on some aspects. First, we simulate $NO_3$-$N_2O_5$ relationship via specific reactions rather than approximating it in equilibrium and introducing the equilibrium coefficient ($K$eq) into calculation. Determining $NO_3$ or $N_2O_5$ concentration by $K$eq could induce large bias (up to 90%) under the high aerosol loading and low temperature (Chen et al., 2021). Second, it is more accurate to constrain the box model with directly measured NOx, $O_3$ and $N_2O_5$ at the entrance of the flow tube. Under a real atmosphere, the initial $N_2O_5$ concentration

after mixing with sampling air is not expected to be as stable as that in laboratory tests, due to the variations in temperature, NO concentration and other related parameters. Numerical simulations based on a constant initial $N_2O_5$ through backward simulation could then lead to significant uncertainty in $\gamma(N_2O_5)$ retrieval without careful data filtering."

*For the misleading statement pointed out by the reviewer, we replaced the word "simultaneous" with "sequential" thoroughly in the main text, and rephrased related statements.*

*The purpose of $N_2O_5$ measurement at both the top and bottom of the flow tube was not only for frequent wall loss determination, but reducing the uncertainty from $N_2O_5$ variation at the top of the flow tube due to air mass changing. During the field campaign, the ambient RH could vary from 21% to 40% within one day, which would produce around $5\times10^{-4}$ $s^{-1}$ difference on wall loss rate constant, leading to 50% bias for the scenario $\gamma(N_2O_5)$ of 0.02 and Sa of 800 $\mu m^2 \cdot cm^{-3}$. Similarly, we also found that the $N_2O_5$ at the inlet of the flow tube frequently varied over 0.5 ppbv due to strong NO emission, which could bias the $\gamma(N_2O_5)$ retrieval for an extra 20%. Therefore, the uncertainty of $\gamma(N_2O_5)$ measurement would be much higher without the $N_2O_5$ measurement at both the top and bottom of the flow tube than what we determined in this work (see also in section 5).*

There are a few aspects of the reported work and new directions that the authors could take this work that are (or would be) interesting:

- The residence time modeling in the flow tube was interesting, especially the conclusion that there are two flow paths. I think there is room for advancement in this technique if the distribution of reaction times was narrowed, while still preserving a long interaction time. Alternatively, it would also be interesting to try to use the RTD that is modeled within the framework of the $N_2O_5$ retrieval as it is not clear to me that an average residence time is appropriate with this type of RTD.

*Thanks for your suggestion. The RTD determined in this work is similar with that in previous flow tube system (Lambe et al., 2011;Wang et al., 2018), in which the average residence time was also used for calculating reaction rate parameters. We admit that such a simplification could lead to bias in the calculation. Therefore, we retrieved $\gamma(N_2O_5)$ by using RTD in the framework of this work and the result shows that the use of mean residence time produces 32% underestimation of $\gamma(N_2O_5)$ in the basic scenario (see table 3 in the main text). The uncertainty analysis on the use of mean residence time is presented in section 5 and as follows.*

"In addition, the mean residence time used in the box model method could bias the retrieved $\gamma(N_2O_5)$ due to the non-normal distribution of residence time with a

discernable tail. The reactants entrained by those slower streamlines close to the wall will take much longer time to reach the exit of the flow tube than that by the centerline. To evaluate the uncertainty caused by the distribution of residence time, we first performed simulations of $N_2O_5$ decay in the flow tube under the basic scenarios and calculate the exit $N_2O_5$ concentration according to the probability distribution function derived from RTD profile. Then the $\gamma(N_2O_5)$ can be retrieved from the box model method running for the duration of mean residence time, constrained by this calculated exit $N_2O_5$ concentration. The result shows that the use of mean residence time produces 32% underestimation of $\gamma(N_2O_5)$ in the basic scenario. The extent of underestimation is most sensitive to the level of $\gamma(N_2O_5)$ and RH."

- While there were some nice calculations of the uncertainty in the retrieved $N_2O_5$ uptake coefficient, actual measurements are most important. I would like to see systematic evaluation of the approach in the laboratory. Some example experiments that would be extremely informative might include: i) measurement of $g(N_2O_5)$ as a function of surface area for a model compound at constant RH and NO. ii) Modulation of NO (and RH above the deliquescent point) at the inlet while flowing a constant surface area concentration of a known aerosol composition. These experiments would confirm whether the modeled uncertainty holds for experimental conditions.

*We have conducted a series of lab experiments of $\gamma(N_2O_5)$ measurement on $(NH_4)_2SO_4$ aerosols with the modulation of Sa, NO and RH levels. In the base scenario, the RH, NO and Sa were set to 50%, 0 ppbv and 600 $\mu m^2$ $cm^{-3}$, respectively, at room temperature of 295 K with $N_2O_5$ concentration of 4.0 ppbv at the entrance of flow tube. The $\gamma(N_2O_5)$ was determined to be 0.01±0.002. In the sensitivity experiments, the RH was modulated from 10 to 55%, NO from 0 to 6 ppbv and Sa from 400 to 1000 $\mu m^2$ $cm^{-3}$. The results show that $\gamma(N_2O_5)$ holds within the range of Sa and NO variation, and increase with RH which is consistent with previous reported values (see the Figure R4).*
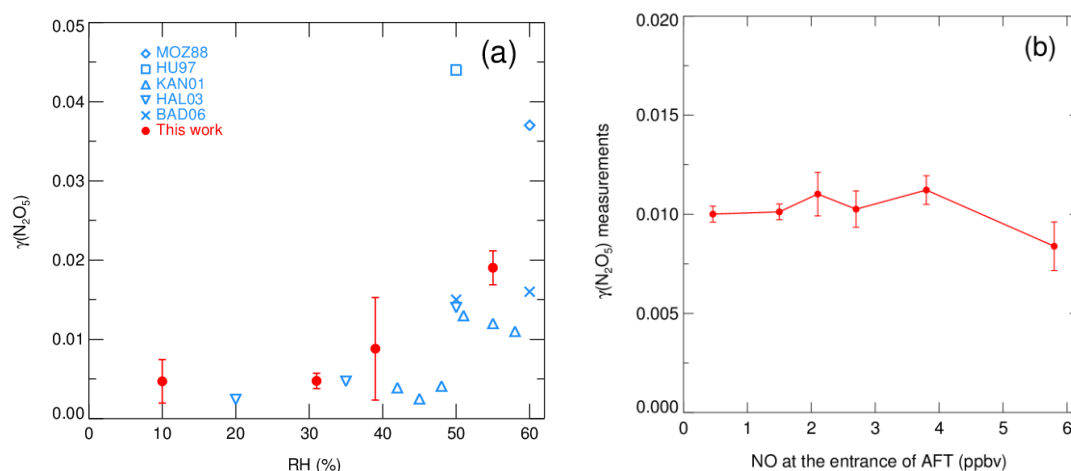


Figure R4. (a) The dependence of $\gamma(N_2O_5)$ on RH for laboratory-generated $(NH_4)_2SO_4$ aerosols; (b) $\gamma(N_2O_5)$ measurements on lab-generated $(NH_4)_2SO_4$ aerosols under different gradients of NO.

The Sa concentration varies from 400 to 1000 $\mu m^2$ $cm^{-3}$ at each level of NO. The red points with standard deviations represent the measured values. Previously reported values are indicated in blue marks.

**References**：

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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 Measurement Techniques, 4, 445-461, 2011.

Wang, W., Wang, Z., Yu, C., Xia, M., Peng, X., Zhou, Y., Yue, D., Ou, Y., and Wang, T.: An in situ flow tube system for direct measurement of N2O5 heterogeneous uptake coefficients in polluted environments, Atmospheric Measurement Techniques, 11, 5643-5655, 10.5194/amt-11-5643-2018, 2018.