Response to Referee #1

The authors present new measurements of the N2O5 uptake coefficient from field measurements in China. The additional measurements are of great value to the ongoing interpretation of N2O5 heterogeneous chemistry. The manuscript is well written and should be published following the authors attention to the following details:

Response: We appreciate the reviewer for the encouraging and helpful comments on our manuscript. We have made all of the suggested changes and clarifications. The reviewer's comments are in black, and our responses are in blue, and the changes in the manuscript are in red.

Line 78: It would be helpful to clarify what "rural" refers to. If this is meant to denote a chemical regime, it would be helpful to classify by chemical composition (e.g., PM2.5, NOx, O3, CO, etc).

Response: Heshan site was considered as a semi-rural site because the site is located outside towns and far from the urban area. The site was mostly affected by natural emission and some agriculture activities, with limited influences from the transport of anthropogenic emissions (e.g., industry and vehicles). The average concentrations of $PM_{2.5}$ and trace gases during the campaign were shown in Fig. 1b. We have revised the text to make it clearer, as follows,

"Field measurements of γ_{N2O5} and related parameters were conducted at a semi-rural site (Heshan) in southern China from 22 February to 28 March 2017 and at a mountain site (Mt. Tai) in northern China from 11 March to 8 April 2018. Heshan site was located on a small hill (22.73°N, 112.92°E, 60 m a.s.l), surrounded by subtropical trees and some farmlands. A small city, Heshan, is 10 km to the northeast of the site, and three large cities, Guangzhou (the capital of Guangdong Province), Foshan and Jiangmen, are 80 km to the northeast, 50 km to the northeast and 30 km to the southwest of the site, respectively. The site is affected by vehicle emissions from three highways and two provincial roads within 10 km and some residential/agriculture activities in the area, and thus was considered as a semi-rural site."

"All the sites are regionally representative sites, as they are situated in an area with limited anthropogenic influences (Tham et al., 2016; Wang et al., 2017a; Yun et al., 2018; Wang et al., 2016). The detailed information of the sampling sites, instrumentation, and γ_{N2O5} determination approach have been described in the previous publications (Wang et al., 2016; Tham et al., 2016; Wang et al., 2017a), and site descriptions are briefly summarized in the SI. The locations of all the measurement sites are shown on the map in Fig. 1a. The statistics of the trace gases and $PM_{2.5}$ measured during the campaigns were summarized in Fig. 1b, representing general pollution conditions at these sites. The mean concentration of O_3, NOx and $PM_{2.5}$ at these sites ranged from 43 to 80 ppbv, 2.4 to 14.5 ppbv and 9.9 to 80.2 µg m^{-3}, respectively."

Lines 92 – 121: A reference to the original work of Bertram et al should be included here as the design and sampling approach appear to very closely replicate the technique described in

Bertram et al., AMT 2009. Also, the uncertainty is a function of the surface area and RH, I find it nearly impossible that the uncertainty ranges only between 37-40% for the range of atmospheric conditions sampled. If this is correct, more discussion should be included.

Response: Thanks for the suggestions. The reference to Bertram et al. has been added to the manuscript. The uncertainty was described in detail in our previous paper (Wang et al., 2018) and γ_{N2O5} was found to be most sensitive to RH, and more discussion was added in the revised manuscript.

The revised text reads,

"The uptake coefficient of N_2O_5, γ_{N2O5}, was derived from the direct measurement of the loss rate coefficient of N_2O_5 on ambient aerosols using an aerosol flow tube based on the design of Bertram et al. (2009), with some improvements and coupling with an iterative box model for polluted environments (Wang et al., 2018)."

"The uncertainty introduced by S_a measurement would be propagated to an uncertainty of 30% in the calculated γ_{N2O5}. The improvement with the use of the box model in the system could minimize the influences from the variability of ambient conditions as well as fresh NO emission, and a Monte Carlo approach was employed to evaluate the uncertainty from different parameters (Wang et al., 2018). The estimated uncertainty ranged from 37% to 40% at γ_{N2O5} around 0.03 and from 34% to 65% at γ_{N2O5} around 0.01 with $S_a = 1000$ μm^2 cm^{-3} when RH varied from 20% to 70 %, and could be higher at RH>70%."

References
Bertram, T., Thornton, J., and Riedel, T.: An experimental technique for the direct measurement of N_2O_5 reactivity on ambient particles, Atmospheric Measurement Techniques, 2, 231-242, 2009a.
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 N_2O_5 heterogeneous uptake coefficients in polluted environments, Atmospheric Measurement Techniques, 11, 5643-5655, 10.5194/amt-11-5643-2018, 2018.

Line 156: It is not clear how the uptake coefficient at 50M H2O which is essentially pure water is significantly larger than 0.03 (that measured for pure water in the laboratory). The authors should provide some discussion for how the 'measured' uptake coefficients are exceeding the rate for N2O5 with pure water? The limit observed in Hallquist, Thornton, ad Bertram and Thornton (all laboratory studies) correspond to reaching the upper limit of N2O5 uptake to pure water.

Response: Thanks for the suggestions. We were aware that many previous laboratory studies (Hallquist et al., 2000; Hallquist et al., 2003; Thornton et al., 2003; Thornton et al., 2005) had observed the N_2O_5 uptake on different particles (e.g., sulfuric acid, ammonium sulfate/bisulfate, malonic acid and sea salt) showing strong dependence on RH below 50% but reaching an upper

limit around 0.036 at RH around 50%-80%. However, there were also higher γ_{N2O5} values measured by different laboratory studies. For example, Mozurkewich and Calvert (1988) reported an upper limit of γ_{N2O5} on NH_4HSO_4 particles of 0.056 at RH = 55% at 293K, which increased to around 0.1 at 274K. Kane et al. (2001) observed a strong RH dependent γ_{N2O5} on NH_4HSO_4 particles, increasing from 0.018 to 0.069 with RH from 56% to 99%. Moreover, several field measurements also reported the γ_{N2O5} exceeding 0.04 at high RH or water molarity (e.g. Philips et al., 2016; McDuffie et. al, 2018; Wang H et al., 2017; Tham et. al, 2018), and some of them found the similar positive relationship between γ_{N2O5} and water molarity (McDuffie et. al, 2018). Although uncertainties may exist in the calculation of aerosol surface and uptake coefficient at high ambient RH conditions, our results here indicate that the aerosol water content strongly affects the activity of N_2O_5 uptake, and the N_2O_5 hydrolysis is always limited by aerosol water content. It is unclear what exact mechanism or process (e.g., phase change different from laboratory-made particles, or acidity involved) promote more effective uptake on ambient aerosols at higher RH and water content condition due to the limited measurement data in laboratory and field. More detailed investigation of N_2O_5 uptake on nano-size water/aerosol droplets in the real (or close to real) ambient conditions are clearly warranted.

More discussion is added in the revised text, as follows:

"Although the positive correlation of γ_{N2O5} with the humidity or aerosol water has been observed in the low range in previous laboratory studies, the γ_{N2O5} reached plateaus at a value around 0.036 at RH> 50% or $[H_2O]$ > 15 M (Hallquist et al., 2003; Thornton et al., 2003; Bertram & Thornton, 2009). In contrast, other laboratory studies also measured higher γ_{N2O5} values on NH_4HSO_4 particles. For example, Mozurkewich and Calvert (1988) reported an upper limit of γ_{N2O5} of 0.056 at RH = 55% at 293 K, which increased to around 0.1 at 274 K. Kane et al. (2001) observed a strong RH dependent γ_{N2O5}, increasing from 0.018 to 0.069 with RH from 56% to 99%, which is largely consistent with the field results in the present study. Moreover, several field measurements also observed γ_{N2O5} value exceeding 0.04 at high RH or water molarity (e.g. Philips et al., 2016; McDuffie et. al, 2018a; Wang et al., 2017c; Tham et. al, 2018), and some of them also found the similar positive relationship between γ_{N2O5} and water molarity (McDuffie et. al, 2018a). Although uncertainties may exist in the calculation of aerosol surface and uptake coefficient at high ambient RH conditions, our results with a consistently increasing trend of γ_{N2O5} with $[H_2O]$ from below 10 M up to 50 M suggest that the aerosol water content strongly affects the activity of N_2O_5 uptake, and that N_2O_5 hydrolysis is always limited by aerosol water content under all the encountered ambient conditions. Since limited measurement data of γ_{N2O5} from laboratory and fields are available at RH > 80% condition, it is unclear what exact mechanism or process (e.g., phase change different from laboratory-made particles or acidity involved) promote more effective uptake on ambient aerosols at higher aerosol water content condition. Therefore, more detailed investigations of N_2O_5 uptake on nano-size water/aerosol droplets in the real (or close to real) ambient conditions are clearly warranted."

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Wang, H., Lu, K., Chen, X., Zhu, Q., Chen, Q., Guo, S., Jiang, M., Li, X., Shang, D., and Tan, Z.: High N_2O_5 concentrations observed in urban Beijing: Implications of a large nitrate formation pathway, Environmental Science & Technology Letters, 4, 416-420, 2017c.

Line 158: Linear not liner.

Response: Corrected.

Line 180: Correct use of the Bertram and Thornton parameterization involves calculating the aerosol water content for both the organic and inorganic components. Also, something doesn't seem to add up in the parameterization of the uptake coefficient. What value for V/S and KH were used and what temperature was this run at? It was my understanding that the parameterization could not exceed 0.03 based on the hydrolysis rate and henry's law coefficient used in the parameterization.

A note on empirical parameterizations: I think there is an opportunity to use field measurements to tune mechanistic parametrizations. Although, it seems unlikely that field measurements will do a better job than laboratory measurements at constraining rate coefficients or ratios of rate coefficients for the inorganic reactions. Laboratory experiments are designed to do this, using targeted simple 1-2 component systems and 1000x the aerosol surface area. I would expect the

real power is looking at the variability in the hydrolysis rate or henry's law terms that are required to match the measurements with the models. This is where the complexity of the atmospheric aerosol will cause issues in laboratory parameterizations.

Response: Thanks for the helpful comments. First, we want to clarify that the V_a/S_a values varied from 3.30×10^{-8} m to 9.29×10^{-8} m in different cases, and were measured from the particle number and size distribution by WPS or SMPS in different campaigns. The Henry's law dimensionless constant of K_H was taken as 51, following the Bertram and Thornton parameterization. The temperature ranged from 3℃ to 28℃ in different cases in the five campaigns.

Secondly, as shown in the Bertram and Thornton parameterization, γ_{N2O5} was linearly dependent on the V_a/S_a value by assuming a volume-limited reaction. Because the average V_a/S_a of 3.75×10^{-8} m was used in their study, the upper limit of γ_{N2O5} at high [H_2O] from the parameterization was around 0.036. And the upper limit of γ_{N2O5} would increase proportionally to the increase of V/S value.

In addition, since Bertram and Thornton observed that the γ_{N2O5} was insensitive to RH above 50%, they treated the reaction rate coefficient of [N_2O_5] with [H_2O] as an inverse exponential function of [H_2O]. In the present study, we use the original second-order rate definition of water reaction term as k_{2f}[H_2O], which leads to a linear dependence of γ_{N2O5} on [H_2O] and is consistent with our field observation results. The secondary order rate constant k_{2f} was fitted to be $(3.0\pm0.4)\times10^4$ M^{-1} s^{-1}, which is in reasonable agreement with the values of $(2.7-3.8)\times10^4$, $\sim3.9\times10^4$ and 2.6×10^4 M^{-1} s^{-1} determined from ammonium bisulfate, ammonium sulfate (Gaston et al., 2016) and aqueous organic acid particles (Thornton et al. 2003), respectively.

We agree with the reviewer that it would be an opportunity to use the field data to tune mechanistic parameters such as Henry's law term. Different K_H values have been used in previous studies, e.g., ~50 (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009) or ~120 (corresponding to a Henry's law of 5M/atm at 298K) (e.g., Gaston et al., 2014; 2016; Griffiths et al., 2009). The γ_{N2O5} in the parameterization is also linearly dependent on the K_H, and thus an increase of K_H value would proportionally increase the γ_{N2O5} value but cannot account for the large variability of measured γ_{N2O5} comparing to the parameterized values. In addition, there is lack of an explicit function of effective Henry's law constant for N_2O_5 to include the 'salting-in' effect and other processes, therefore in the present study, we use the value of 51 suggested by Bertram and Thornton and enclosed the influences from the aerosol composition in the last 'chemical' term. The derived empirical ratios in the last 'chemical' term not only represent the competing ratio of these reactions but also include other unspecified effects or influences (e.g., organic coating, mixing state, other nucleophiles reactions, etc.).

We have clarified this and added more discussion in the revised text, as follows,

"where V_a/S_a is the measured aerosol volume to surface area ratio, ranging from 3.30×10^{-8} to 9.29×10^{-8} m in the five campaigns; K_H is Henry's law coefficient, taken as 51 (Bertram &

Thornton, 2009; Fried et al., 1994);"

"In view of the linear dependence of γ_{N2O5} on the aerosol water content in this study and reaction mechanism (Bertram & Thornton, 2009), the second-order reaction rate coefficient with water (refer to k'$_{2f}$ in Eq. (2) and Eq. (3)) was fitted as a linear function of [H$_2$O], as $(3.0\pm0.4) \times 10^4 \times$ [H$_2$O]. This value is in reasonable agreement with the values of $(2.7-3.8) \times 10^4$, $\sim3.9 \times 10^4$, and 2.6×10^4 M^{-1} s^{-1} determined from ammonium bisulfate, ammonium sulfate (Gaston et al., 2016) and aqueous organic acid particles (Thornton et al. 2003), respectively. Compared to original BT09 (Eq. (3)), the newly fitted k'$_{2f}$ is smaller for [H$_2$O] < 38 M, but become higher with the increasing of aerosol water content (Fig. S2). Different dimensionless K$_H$ values have been used in previous studies, e.g., ~50 (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009) or ~120 (e.g., Gaston et al., 2014; 2016; Griffiths et al., 2009), which correspond to a Henry's law constant of 2 or 5 M atm^{-1} at 298K. As γ_{N2O5} in the parameterization is linearly dependent on the K$_H$, an increase of K$_H$ value would proportionally increase the γ_{N2O5} value but cannot account for the large variability of measured γ_{N2O5} values. Given the lack of an explicit function of effective Henry's law constant for N$_2$O$_5$ to include the different process (e.g., 'salting-in' effect and surface processes), we use the value of 51 suggested by Bertram and Thornton (2009) and enclose those effects from the aerosol composition in the last 'chemical' term. The derived empirical ratios in the last 'chemical' term not only represent the competing ratio of these reactions but also include other unspecified effects or processes (e.g., organic coating, mixing state, other nucleophiles reactions, etc.)."

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