Response to Referee #1

Tham et al report N2O5 uptake coefficients and ClNO2 yields based on measurements of N2O5, ClNO2, and PM2.5 aerosol size distribution and composition at Wangdu in the summer 2014. The N2O5 uptake coefficients and ClNO2 yields were estimated based on observed production of ClNO2, (bulk) particulate nitrate, and in situ N2O5 concentration and aerosol surface area. These observed values are compared with predictions from several literature parameterizations. The authors show that γ(N2O5) increases with relative humidity (and aerosol liquid water content) and decreases with increasing particulate nitrate content. ClNO2 yields were variable and appeared to show a decreasing trend in the presence of BB aerosol.

The paper is written well and will be a useful addition to the literature once the authors have satisfactorily addressed the comments below.

Response: We thank the reviewer for his/her attention to this 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 *italic*.

Major comments:

1) Bulk aerosol properties are used in the analysis to calculate, for example, aerosol liquid water content at equilibrium, N2O5 uptake, and ClNO2 yield.
In reality, however, the aerosol will consist of particles that have varying degrees of external (and internal) mixing. This may be particularly important for N2O5 to ClNO2 conversion, which takes place very efficiently on (supermicron) sea salt derived aerosol or in certain power plant plumes, but hardly at all on secondary aerosol that contains little chloride. Furthermore, the conversion of N2O5 to ClNO2 occurs mainly on the aerosol surface and not in the bulk. The authors should add more discussion on the limitations arising from the use of bulk aerosol properties in their analysis.

Response: We agree with the reviewer, and we are aware of the possible bias resulted from the assumption on bulk reaction and the lack of aerosol mixing information. Current parameterizations (e.g., Bertram and Thornton, 2009) were based on the laboratory experiments with pure or internally mixed aerosols, and derived the uptake dependence on the bulk composition of wet aerosols. The E-AIM model used to calculate the aerosol liquid water content at equilibrium is also based on bulk aerosol composition. Thus, most of the recent studies and parameterizations did not specifically consider the mixing states of the aerosols, which may largely affect the N_2O_5 uptake and $ClNO_2$ yield on complex ambient aerosols. To clarify, we have added more information on the method and more discussion of the limitations in different parts of the revised text, as follows,

In introduction:

"*Several reasons have been proposed for the discrepancies between the parameterization and*

observation values, including the failure of parameterization to account for 1) the complex mixture of organic composition (Bertram et al., 2009; Mielke et al., 2013); 2) the "real" nitrate suppression effect (Riedel et al., 2012; Morgan et al., 2015); and 3) the varying mixing states of the particles (Ryder et al., 2014; Wang X. et al., 2017); and 4) bulk or surface reactions on different particles (e.g., Gaston and Thornton, 2016)."

In section 3.3:

"The parameterization of N_2O_5 uptake coefficients derived from Bertram and Thornton (2009) ($\gamma_{B\&T}$) assumed a volume-limited reaction of N_2O_5 on mixed aerosols and considered the bulk amount of nitrate, chloride, and water in the aerosol as the controlling factors, which can be expressed by equation (6):"

"The concentration of aerosol liquid water ($[H_2O]$) used in this study was estimated from the E-AIM model IV with inputs of measured bulk aerosol composition of NH_4^+, Na^+, SO_4^{2-}, NO_3^- and Cl^- (http://www.aim.env.uea.ac.uk /aim/model4/model4a.php) (Wexler and Clegg, 2002), and the V/S_a was taken from the field measurement at Wangdu. It should be noted that the parameterization and calculation here assume an internal mixing of the aerosol chemical species, and the size distribution of $[H_2O]$, $[NO_3^-]$, and $[Cl^-]$ in aerosols was not considered due to lack of measurement information. The uptake process would vary with size and mixing state of the particles, thus the predicted γ values here may be biased as a result but represent an average over bulk aerosols."

"The different results from these parameterizations may suggest more complex aerosol composition, mixing states and other physical-chemical properties in the real ambient atmosphere than in the aerosol sample used in the laboratory study."

In section 3.4:

"The aqueous concentration of Cl^- in the present study is relatively higher than previous laboratory studies (e.g., Bertram and Thornton, 2009; Roberts et al., 2009), and might not be fully involved in the reaction R4, for example, the possible effect of nonuniform distribution of chloride within the aerosols. It might contribute to the overestimation and less variability of ϕ predicted from the parameterization (Riedel et al., 2013), and the positive relationship of field-derived ϕ with $[H_2O]$ (see Figure 7b) might also imply that the increase of water content could increase the availability of the aerosol Cl^-, thus prompting the reaction R4 to increase the $ClNO_2$ production yield."

Reference:

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 10.5194/acp-9-8351-2009, 2009.

Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K.,

and Coffman, D. J.: Direct observations of N_2O_5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, L19803, 10.1029/2009gl040248, 2009.

Mielke, L. H., Stutz, J., Tsai, C., Hurlock, S. C., Roberts, J. M., Veres, P. R., Froyd, K. D., Hayes, P. L., Cubison, M. J., Jimenez, J. L., Washenfelder, R. A., Young, C. J., Gilman, J. B., de Gouw, J. A., Flynn, J. H., Grossberg, N., Lefer, B. L., Liu, J., Weber, R. J., and Osthoff, H. D.: Heterogeneous formation of nitryl chloride and its role as a nocturnal NOx reservoir species during CalNex-LA 2010, J. Geophys. Res.-Atmos., 118, 10638-10652, 10.1002/jgrd.50783, 2013.

Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N_2O_5 uptake: airborne regional measurements in northwestern Europe, Atmos. Chem. Phys., 15, 973-990, 10.5194/acp-15-973-2015, 2015.

Riedel, T. P., Bertram, T. H., Ryder, O. S., Liu, S., Day, D. A., Russell, L. M., Gaston, C. J., Prather, K. A., and Thornton, J. A.: Direct N_2O_5 reactivity measurements at a polluted coastal site, Atmos. Chem. Phys., 12, 2959-2968, 10.5194/acp-12-2959-2012, 2012.

Wang, X., Wang, H., Xue, L., Wang, T., Wang, L., Gu, R., Wang, W., Tham, Y. J., Wang, Z., Yang, L., Chen, J., and Wang, W.: Observations of N_2O_5 and $ClNO_2$ at a polluted urban surface site in North China: High N_2O_5 uptake coefficients and low $ClNO_2$ product yields, Atmos. Environ., 156, 125-134, https://doi.org/10.1016/j.atmosenv.2017.02.035, 2017.

Gaston, C. J., and Thornton, J. A.: Reacto-Diffusive Length of N2O5 in Aqueous Sulfate- and Chloride-Containing Aerosol Particles, The Journal of Physical Chemistry A, 120, 1039-1045, 10.1021/acs.jpca.5b11914, 2016.

Wexler, A. S., and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-,Cl^-, Br^-, and H_2O, J. Geophys. Res.-Atmos., 107, 10.1029/2001jd000451, 2002.

2) A major limitation, which unfortunately has become quite common in the literature, is to perform analysis with in situ variables (i.e., ClNO2 and N2O5 concentrations) and with variables that will integrate over the air mass's history, such as aerosol nitrate, and then to assume that upwind conditions were similar. This is a major assumption, of course, and many preceding papers spent a lot of time justifying it. It may be useful to add more discussion on what the upwind air masses typically would experience prior to observation (e.g., absence/presence of local sources etc.) at Wangdu.

Response: It is true that assuming that upwind conditions were similar is a major assumption. We agree with the reviewer to add a statement on what the upwind air masses typically would experience prior to observation at Wangdu in the selected nights. According to the wind direction and our air masses analysis (Tham et al., 2016), the air mass before arriving at the site was typically influenced by the emission from the nearby villages/cities, coal-fired power plants and biomass burning activities in the region. In our analysis, we carefully select the plumes during the nighttime with certain criteria to make sure a relatively stable period for at least 1.5 hours to perform the analysis as mentioned in the text. For example, we restricted our analysis to data with NO/NO_x ratio lower than 0.1 to remove period with possible

influence from nearby strong NO_x emissions, and the rate of changes for NO_x/NO_y ratio within the period should be smaller than 0.1 min^{-1} to avoid significant changes in the air mass age. To make it clearer, we have added more information and revised the text as follows,

"*The plume age, represented by the ratios of NO_x to NO_y, was relatively stable (change <0.1 min^{-1}), and no drastic changes were seen in other variables such as the wind conditions, particle surface area, RH, or temperature. Typically, the air masses in the selected cases can be influenced by the emissions from nearby village/urban area, coal-fired power plants and biomass burning activities in the region prior to the arrival at the site (see Tham et al., 2016). Hence, the concentration of NO in the plume must be relatively constant (change of NO/NO_2 ratio <0.1 min^{-1}) as the presence of a transient NO plume may affect the concentration of N_2O_5, which can bias the estimation of $\gamma(N_2O_5)$.*"

Reference:

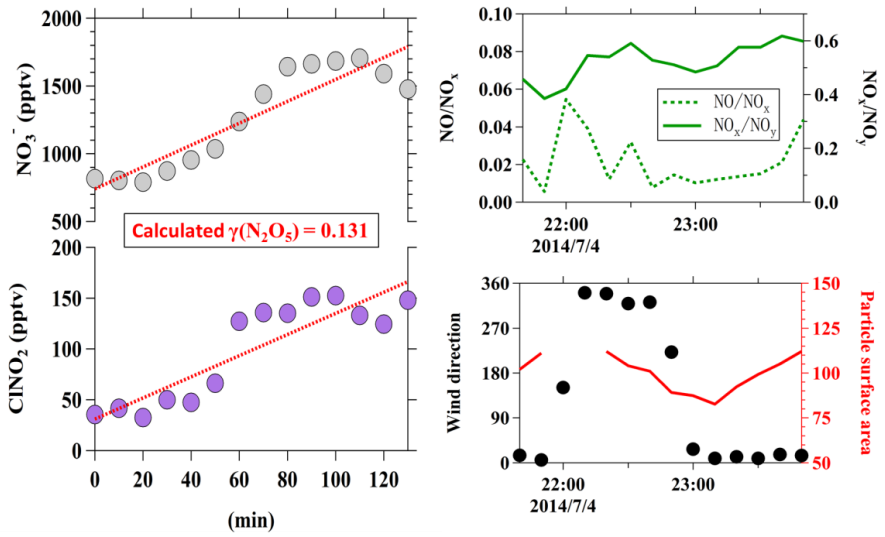
Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 10.5194/acp-16-14959-2016, 2016.

3) In part because of (2), data were selected in the analysis. While the selection criteria are stated, it is in principle worrisome and may lead to selection bias. Can anything be said about the data that were excluded from analysis? For example, what fraction of the data were excluded, and can you give an indication as to what happens in terms of N2O5 to ClNO2 conversion during those periods - were the mixing ratios of ClNO2 high or low, and was the uptake of N2O5 fast or slow? Could these data be analyzed and added with a lighter shade to some of the Figures?

Response: As discussed in major comment (2), we primarily restricted our analysis to data with NO/NO_x ratio lower than 0.1 to remove period with possible influence from nearby strong NO_x emissions, and the rate of changes for NO_x/NO_y ratio within the period should be smaller than 0.1 min^{-1} to avoid significant changes in the air plume age. Sometimes, even if the data comply with the NO_x criteria, we still need to exclude the data based on the mentioned criteria in the text. There are typically two characteristics of the excluded data set if we tried to analyze them. For example, when the data are:

1) 'unstable' conditions within a short period

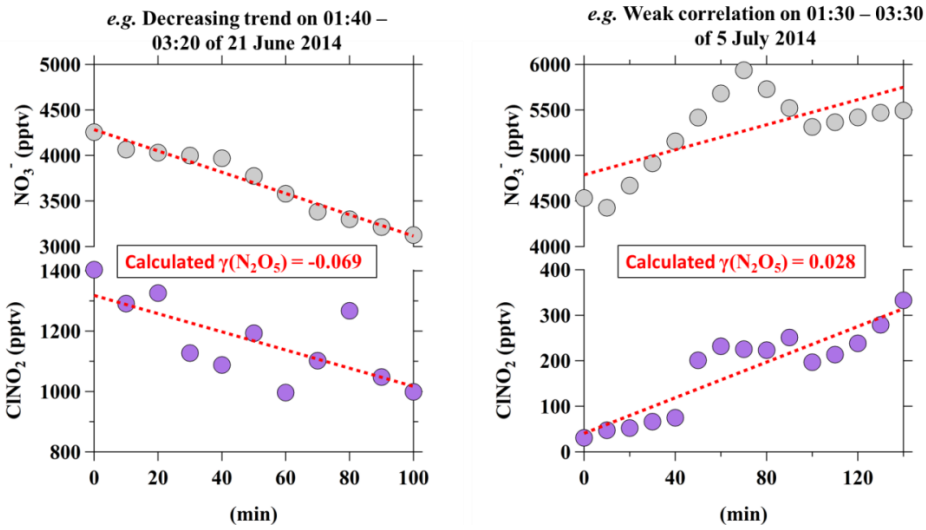
   In the period when the environment condition changes (*e.g.* wind direction and surface area, even though NO/NO_x ratio and the rate of changes for NO_x/NO_y ratio is low (see figure below), the calculated $\gamma(N_2O_5)$ is 0.131, an extremely large value, which we think is not reasonable and we will exclude them from the analysis.



2) 'Non-concurrent' increase or 'bad' correlation for $ClNO_2$ and NO_3^-

As has been stated in the manuscript, the analysis only considered the concurrent increase of both $ClNO_2$ and NO_3^-, while the period with decreasing trend in either/both $ClNO_2$ and/or NO_3^- were excluded from the analysis because they will result in negative N_2O_5 uptake and $ClNO_2$ yield in the calculations.

There are also a few cases that the $ClNO_2$ and NO_3^- increased together but the correlation of the $ClNO_2$ and NO_3^- was weak (R^2<0.5). Even they may give reasonable values (*e.g.* below $\gamma(N_2O_5)$ = 0.028), we will still exclude them due to the high uncertainty from the correlation and may be affected by the changing of the air masses.



Therefore, we think these excluded cases and periods cannot be used to derive the valid uptake coefficient and yield, and thus were not included in the further analysis and the figures. We also revised the text to make it clearer on the fraction of the data was selected, as follows,

"With these methods and selection criteria, we can derive $\gamma(N_2O_5)$ and ϕ for 10 different nighttime plumes in 8 out of 13 nights with full CIMS measurement."

4) The conversion of N2O5 to ClNO2 is often stratified vertically, with usually rapid N2O5 losses at the surface, and higher ClNO2 production rates aloft. How does stratification / vertical mixing affect the analysis?

Response: We agree with the reviewer that the production of $ClNO_2$ is closely related to the vertical mixing and the ground-based measurement is always subjected to this phenomenon.

In our previous publication (refer to Tham et al. 2016), we measured a typical nighttime concentration of $ClNO_2$ of about 300 pptv, and the $ClNO_2$ concentration increased up to 2 ppbv after the sunrise. Our model analysis showed that the increase after sunrise is caused by the strong production of $ClNO_2$ in the residual layer during the nighttime and is mixed downward after the break-up of the boundary layer when the sun rises. However, during the nighttime, our previous results suggested that the $ClNO_2$ at Wangdu was mostly produced from the near-surface layer and the mixing between the nocturnal boundary layer and the residual layer is limited. Therefore, we believe that the stratification/vertical-mixing had little or no impact on our analysis of nocturnal N_2O_5 and $ClNO_2$ at ground level prior to sunrise.

As this issue is still an assumption, we have added the "*limited vertical mixing*" into assumption 1 and a sentence has been added to clarify that this effect is likely not affecting the analysis in the manuscript.

"*Our previous analysis showed that the nighttime vertical mixing is limited at the ground-site of Wangdu (Tham et al., 2016), and likely will not affect the analysis of $ClNO_2$ and NO_3^-.*"

Reference:

Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 10.5194/acp-16-14959-2016, 2016.

Minor comments:

page 1 / line 19 - replace "10" with "ten"; state on what basis cases were selected and how the N2O5 uptake coefficients and ClNO2 yields were estimated

Response: Revised.

"*The N_2O_5 uptake coefficient and $ClNO_2$ yield were estimated by using the simultaneously measured $ClNO_2$ and total nitrate in ten selected cases, which have concurrent increases in the $ClNO_2$ and nitrate concentrations and relatively stable environmental conditions.*"

line 21 - grammar: "an average", but then two values (one for N2O5 and one for ClNO2) are given; formatting for the ranges given in brackets is not consistent; The authors should state

their estimated errors of the "observed" N2O5 and ClNO2 uptake parameters here.

Response: Thanks for pointing out the issue. The word "an" was removed from the sentence. The ranges have been replaced by the standard deviation values of the observed N_2O_5 uptake and $ClNO_2$ yield. The modified sentence in the text is as follows:

"*The determined $\gamma(N_2O_5)$ and ϕ values varied greatly, with an average of 0.022 for $\gamma(N_2O_5)$ ($\pm$0.012, standard deviation)) and 0.34 for ϕ ($\pm$0.28, standard deviation).*"

line 25 - "by the amount of water in the aerosol, a phenomenon that differs from other field observations". Most models and the Bertram/Thornton parameterization (Eq 3) that contains a water term and would have been included in other field studies. Is the author's statement then really true?

Response: Yes, most models and Bertram and Thornton parameterization did include the water and other chemical terms, and yet they cannot reproduce most of the variability of the N_2O_5 uptake determined in the field, thus were subjected to a debate on their applicability in 'real' and different environments. Although some laboratory studies (e.g., Thornton et al., 2003; Bertram and Thornton, 2009 and references therein) had found the dependence of N_2O_5 uptake on RH and aerosol water content under low water content condition, the field studies previously conducted in Europe and US (e.g., UK, Germany, Boulder, and Texas) did not show a clear dependence of N_2O_5 uptake on water content. Previous field studies have linked it with some chemical substances in the aerosol like the nitrate, chloride and organic coatings, as the important factors. Our observation here, however, showed a direct good correlation of $\gamma(N_2O_5)$ with the aerosol water instead of strong dependence on the chemical substances, which was different from other reported field results. We revised the text to make it clearer,

"*…This result suggests that the heterogeneous uptake of N_2O_5 in Wangdu is mostly governed by the amount of water in the aerosol, and is strongly water limited, which is different from most of the field observations in the United States and Europe.*"

line 26 - "Laboratory-derived parameterization also overestimated the ClNO2 yield."
Please correct the grammar here.

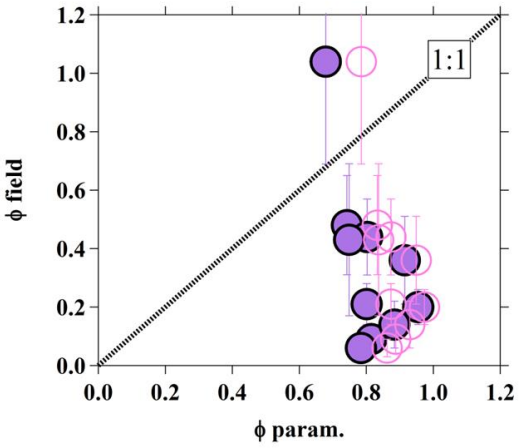
Response: Corrected.

"*The $ClNO_2$ yield estimated from the parameterization was also overestimated comparing to that derived from observation.*"

pg 3/ line 11 - "450" Roberts et al. Geophys. Res. Lett., 36, L20808, 10.1029/2009GL040448, 2009 give a much larger value here; consider adding a second set of Ï¸Tparm calculations with the Roberts et al. value and add to Figure 7a.

Response: Roberts et al. (2009) and Behnke et al., (1997) recommended the k_{R4}/k_{R3} values in

the parameterization to be 450 and 836, respectively. We used the value of 483 from Bertram and Thornton (2009), which is in the range of the values from the previous two studies. As Robert's value of 450 is very close to 483 that we used, we then added the results with a value of 836 into our calculation for comparison of parameterized $ClNO_2$ yields, which are also depicted in Figure 7a (figure below) and explained in the figure caption.



"***Figure 7**: Scatter plots for (a) yield derived from the field versus yield calculated from the parameterization, using k_{R4}/k_{R3} of 483 (recommended by Bertram and Thornton, 2009; solid circle) and 836 (recommended by Behnke et al., 1997; pink open circle). Error bars represent the uncertainty of field-derived ϕ, the black dotted line represents the 1:1 ratio and the red dotted line shows the quadratic fitting line of the data); (b) field-derived yield versus aerosol water content; (c) field-derived yield versus chloride; and (d) field-derived yield versus CH_3CN/CO.*"

Reference:

Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, Journal of Geophysical Research: Atmospheres, 102, 3795-3804, 10.1029/96jd03057, 1997.

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmospheric Chemistry and Physics, 9, 8351-8363, 2009.

page 4 / line 11 "We first derive values for γ(N2O5) and Ï¸T with the measurement data". Please state briefly here how this is done.

Response: A brief statement has been added to the text.

"*We first derive values for $\gamma(N_2O_5)$ and ϕ from the regression analysis of $ClNO_2$ and total nitrate (HNO_3 and particulate NO_3^-) data set and then compare the values obtained in the field with various parameterizations derived from the laboratory studies.*"

page 5. Please add a table summarizing the various measurements made. Without one, statements such as "Volatile organic compounds including methane, C2-C10 hydrocarbons, formaldehyde, and oxygenated hydrocarbons and acetonitrile (CH3CN) were measured with a cavity ring–down spectroscopy technique instrument, an on-line gas chromatograph equipped with a mass spectrometer and a ï˘n ´Came ionization detector, a Hantzsch ï˘n ´Cuorimetric monitor, and a proton-transfer-reaction mass spectrometer, respectively" are unnecessarily confusing.

Response: Thanks for the suggestion. Actually, a table for instrument list and the measurement techniques, detection limits, time resolution in this campaign has been detailed reported in our previous paper and other publications on this Wangdu campaign. The readers are referred to those publications for more information. We have revised the text to make this clearer,

"The present study was supported by other auxiliary measurements of aerosol, trace gases, and meteorological parameters, and the detailed instrumentation for the measurement has been listed in a previous paper (Tham et al., 2016)."

"Detailed description of these instrumentation and measurement techniques at Wangdu can be found in previous publications (e.g., Wang Y. et al., 2016; Min et al., 2016; and Tham et al., 2016)."

Reference:

Min, K. E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor, Atmos. Meas. Tech., 9, 423-440, 10.5194/amt-9-423-2016, 2016.

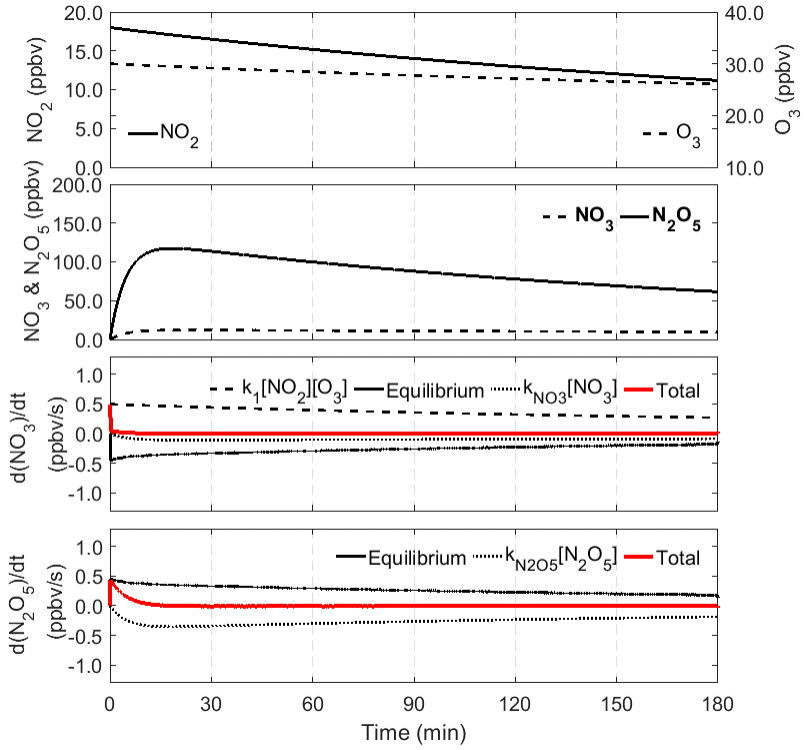
Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 10.5194/acp-16-14959-2016, 2016.

Wang, Y., Chen, Z., Wu, Q., Liang, H., Huang, L., Li, H., Lu, K., Wu, Y., Dong, H., Zeng, L., and Zhang, Y.: Observation of atmospheric peroxides during Wangdu Campaign 2014 at a rural site in the North China Plain, Atmos. Chem. Phys., 16, 10985-11000, 10.5194/acp-16-10985-2016, 2016.

line 28 - "steady-state" Brown et al. (J. Geophys. Res., 108, 4539, 10.1029/2003JD003407, 2003) showed that the time to achieve a steady state can be substantial, especially in polluted conditions. Have the authors verified (e.g., through box model simulations) that the steady-state approximation is valid?

Response: We did verify the steady-state conditions for the campaign by a simple box model calculation similar to that in Brown et al. (2003). For instance, in average condition during

the campaign, the level of NO_2 was 18ppb, O_3 was 30 ppb, loss rate of N_2O_5 (k_{N2O5}) was 3 x 10^{-3} s^{-1} and loss rate of NO_3 (k_{NO3}) is 9 x 10^{-3} s^{-1}. Under these conditions, the NO_3 and N_2O_5 achieved steady-state in less than 30 min after sunset (as shown in below figure). However, we should also note that interception of fresh emissions could lead to the failure of the N_2O_5 steady-state approximation in the air mass (e.g., Brown et al. 2003, 2011, 2016).



Reference:

Brown, S. S., Dubé, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J. A., te Lintel Hekkert, S., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Feshenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, Journal of Geophysical Research: Atmospheres, 116, 10.1029/2011JD016544, 2011.

Brown, S. S., Dubé, W. P., Tham, Y. J., Zha, Q., Xue, L., Poon, S., Wang, Z., Blake, D. R., Tsui, W., Parrish, D. D., and Wang, T.: Nighttime Chemistry at a High Altitude Site Above Hong Kong, Journal of Geophysical Research: Atmospheres, 10.1002/2015jd024566, n/a-n/a, 10.1002/2015jd024566, 2016.

Brown, S. S., Stark, H., and Ravishankara, A. R.: Applicability of the steady state approximation to the interpretation of atmospheric observations of NO3 and N2O5, Journal of Geophysical Research: Atmospheres, 108, 4539, 10.1029/2003jd003407, 2003.

page 7 / line 23 "what drive" Grammar (either "what drives" or "what factors drive")

Response: The phrase has been revised to "*what drives*" as suggested.

page 8 / the "observed" γ(N2O5) is really an aggregate value for N2O5 uptake on the entire aerosol distribution

line 2 - [H2O], [NO3-], and [Cl-] will likely be functions of aerosol size; please add a

disclaimer that this calculation assumes that they are not, and that the predicted gamma values may be biased as a result.
Out of curiosity - is it possible that ClNO2 is produced mainly on sea salt aerosol at Wangdu?

Response: Yes, the observed $\gamma(N_2O_5)$ is an aggregate value for uptake on entire aerosol distribution, and the size distribution of different chemical species was not considered in the present study. As stated in the response to major comment (1), a disclaimer has been added in the text as below:

"*It should be noted that the parameterization and calculation here assume an internal mixing of the aerosol chemical species, and the size distribution of* $[H_2O]$, $[NO_3^-]$, *and* $[Cl^-]$ *in aerosols was not considered due to lack of measurement information. The uptake process would vary with size and mixing state of the particles, thus the predicted* γ *values here may be biased as a result but represent an average over bulk aerosols.*"

For the question on whether the $ClNO_2$ can be produced mainly on sea-salt aerosol at Wangdu, we think that this possibility is low at Wangdu because the site is located about 200 km away from the nearest coast area (Bohai Sea) and the 24 hours air-mass back trajectories showed that there's no indication of marine influence originated air mass. The $PM_{2.5}$ chemical analysis also showed that the chloride to sodium ratio is much higher than the ratio in sea-salt, suggesting that the anthropogenic chloride sources are more important in this location (see Tham et al., 2016 for more information on the chloride source).

line 4 - the E-AIM allows for inclusion of organics, which would alter the liquid water content (maybe). Has this been considered.

Response: The effects of the organics on the liquid water content are not considered in this analysis. It is because we have only very limited days/amount of organic data (as stated in the text), which made the analysis harder to consider this organic effect. A quick test-run in the E-AIM Model (IV) was performed by adding the preset organics into the model (*i.e.* malonic acid and succinic acid) with a mixing ratio of 3×10^{-7} molar (highest organics level observed in this study period) and 0. The comparison showed that there is only a small difference (<9%) in the liquid water content when considering the organics. We revised the text to be specific on what was used in the model, as follows,

"*The concentration of aerosol liquid water (*$[H_2O]$*) used in this study was estimated from the E-AIM model IV with inputs of measured bulk aerosol composition of* NH_4^+, Na^+, SO_4^{2-}, NO_3^- *and* Cl^- *(http://www.aim.env.uea.ac.uk /aim/model4/model4a.php) (Wexler and Clegg, 2002), and the* V/S_a *was taken from the field measurement at Wangdu.*"

line 12 what values of Rc and Rp were used in the B&T+org calculation, and are these values realistic for this comparison? (see also major comment 2).

Response: The R_p was obtained from the measured median radius of the particle surface area

distribution, with average values about 150 nm. The organic coating thickness L was calculated from the volume ratio of the inorganics to total particles volume following the method in Reimer et al. (2009) by assuming a complete internal mixture. And the R_c was calculated by subtracting the *L* from R_p. We think these values are relatively realistic for this environment as the calculations are based on the measurement of organics in PM_1 (from AMS measurement). The assigned density was 1.77 g/cm^3 for inorganic density and 1.23 g/cm^3 for organics, which are close to the values reported in the measurements of aerosol densities in China (*e.g.* Hu et al., 2012; Li et al., 2016). We have revised the text to make this clearer, as follows,

"*The particle radius R_p was determined from the measured median radius of the particle surface area distribution. The L was calculated from the volume ratio of the inorganics to total particles volume following the method in Reimer et al. (2009) with the assumption of hydrophobic organic coating (density, 1.27 g cm^{-3}) on the aqueous inorganic core (with a density of 1.77 g cm^{-3}). The aqueous core radius R_c was calculated by subtracting the L from R_p.*"

Reference:

Hu, M., Peng, J., Sun, K., Yue, D., Guo, S., Wiedensohler, A., and Wu, Z.: Estimation of Size-Resolved Ambient Particle Density Based on the Measurement of Aerosol Number, Mass, and Chemical Size Distributions in the Winter in Beijing, Environ. Sci. Technol., 46, 9941−9947, 2012.

Li, C., Hu, Y., Chen, J., Ma, Z., Ye, X. Yang, X., Wang, L., Wang, X., Mellouki, A.: Physiochemical properties of carbonaceous aerosol from agricultural residue burning: Density, volatility, and hygroscopicity, Atmos. Environ.,140, 94-105, 2016.

Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N2O5 during summer in Europe, Journal of Geophysical Research: Atmospheres, 114, 10.1029/2008JD011369, 2009.

pg 9 / line 16 - sulfate should be doubly charged

Response: Thanks for pointing out the typo. The sulfate has been changed to double charge.

pg 10 / factors that affect ClNO2 yield - this is an interesting paragraph, but I am a bit skeptical about what appear to be low field yields.
Have the authors considered that the lack of agreement may be due to breakdown of the assumptions going into the calculation (uneven distribution of chloride throughout the aerosol, for example)?

Response: Yes, we did think of this effect, but we have no information on the size distribution of chloride in the field measurement, and therefore, our conclusion is that the biomass burning activities could partly explain the $ClNO_2$ yield at Wangdu. To clarify, we have revised the statement at the end of the paragraph to acknowledge this possibility and suggest for more future studies of the chloride distribution in the region.

"*The aqueous concentration of Cl^- in the present study is relatively higher than previous laboratory studies (e.g., Bertram and Thornton, 2009; Roberts et al., 2009), and might not be fully involved in the reaction R4, for example, the possible effect of nonuniform distribution of chloride within the aerosol. It might contribute to the overestimation and less variability of ϕ predicted from the parameterization (Riedel et al., 2013) and the positive relationship of field-derived ϕ with $[H_2O]$ (see Figure 7b) might also imply that the increase of water content could increase the availability of the aerosol Cl^-, thus prompting the reaction R4 to increase the $ClNO_2$ production yield.*"

Reference:

Riedel, T. P., Wagner, N. L., Dubé, W. P., Middlebrook, A. M., Young, C. J., Öztürk, F., Bahreini, R., VandenBoer, T. C., Wolfe, D. E., Williams, E. J., Roberts, J. M., Brown, S. S., and Thornton, J. A.: Chlorine activation within urban or power plant plumes: Vertically resolved ClNO2 and Cl2 measurements from a tall tower in a polluted continental setting, Journal of Geophysical Research: Atmospheres, 118, 8702-8715, 10.1002/jgrd.50637, 2013.

page 22 - Please increase the font size on figures 2a and 2c (they are too small).

Response: The figures have been revised.

In Figures 2b and 2d, do the axis intercepts allow an assessment of how much aerosol nitrate is derived from daytime vs nighttime chemistry?

Response: In principle yes when the NO_3^- in y-axis and $ClNO_2$ in the x-axis, if we assume that the $ClNO_2$ concentration is zero at sun-set and the air mass does not change in that period.