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:

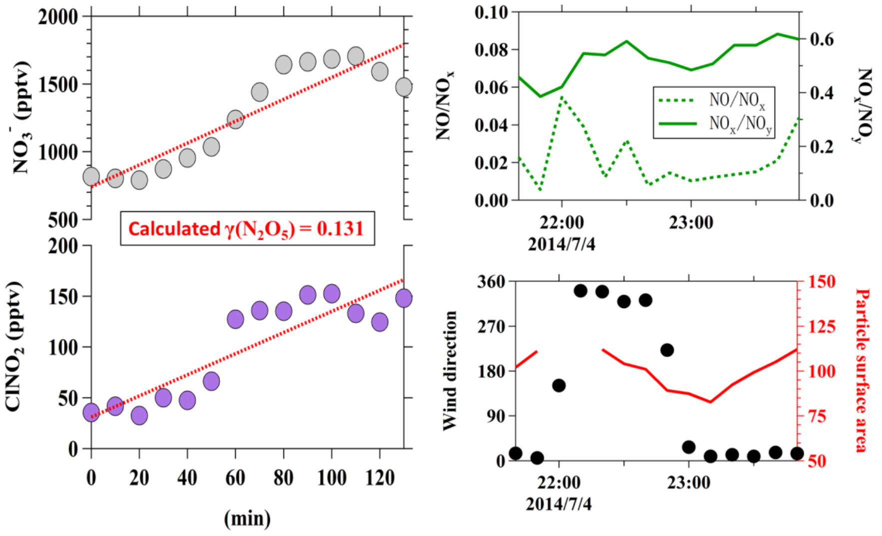
Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone 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.

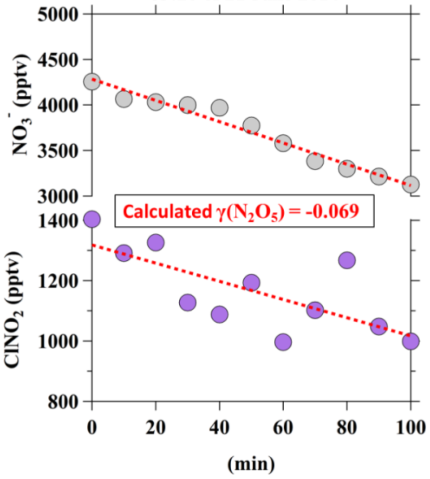


2) ‘Non-concurrent’ increase or ‘bad’ correlation for $ClNO_2$ and NO_3^-

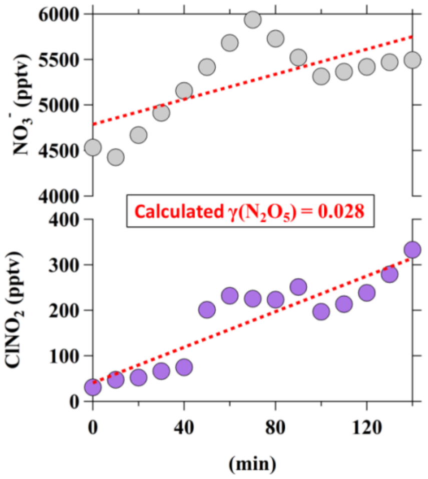
   As has been stated in the manuscript, the analysis only considered the concurrent increase of both $ClNO_2$ and NO_3^-, while the period with decreasing trend in either/both $ClNO_2$ and/or NO_3^- were excluded from the analysis because they will result in negative N_2O_5 uptake and $ClNO_2$ yield in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

e.g. **Decreasing trend on 01:40 – 03:20 of 21 June 2014**



e.g. **Weak correlation on 01:30 – 03:30 of 5 July 2014**



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.*”

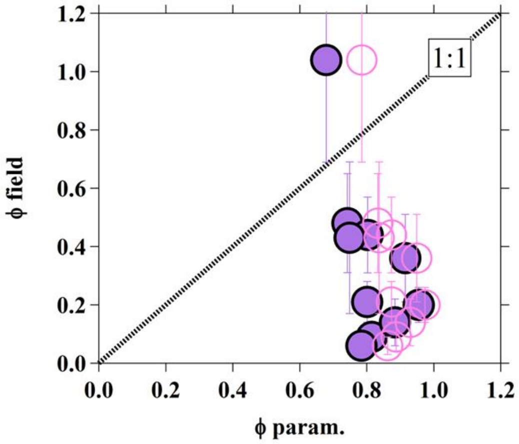
line 26 - "Laboratory-derived parameterization also overestimated the ClNO2 yield."
Please correct the grammar here.

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 flame ionization detector, a Hantzsch fluorimetric 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:

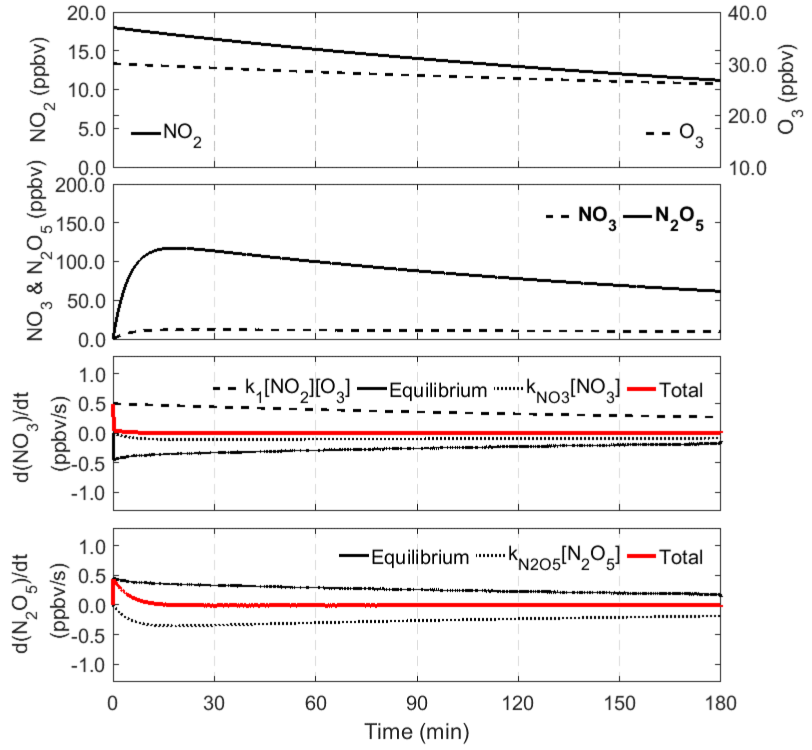
Min, K. E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water 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.

Response to Referee #2

General Comments:

This paper reports an analysis of N2O5 uptake coefficients and ClNO2 yields from a polluted site in the North China Plain during a summer 2014 field intensive. The analysis finds variation of N2O5 uptake coefficients that is characteristic of data sets in other parts of the world. Comparisons between field determinations and laboratory based parameterizations, and between the determined uptake coefficients and other variables, shows that aerosol liquid water / relative humidity is a determining factor. This finding is in contrast to field studies in the U.S. and Europe. ClNO2 yields are shown to be lower than current parameterizations based on the competition between chloride and liquid water, consistent with findings from other regions.

The authors suggest ClNO2 suppression on biomass burning derived particles despite higher chloride content in these aerosol.

Overall, the paper adds to the growing database of these analysis and will be a valuable contribution to the literature. Publication is recommended after the authors address the following comments.

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

Specific comments:

Page 2, line 4: "yielding N2O5" rather than "yielding a N2O5".

Response: Corrected.

Page 3, line 20: Also add Morgan et al., 2015 and McDuffie et al., 2018, to this list.

Response: The references have been added to the text (highlighted in yellow).

Page 3, line 22: sentence not clear. Does "laboratory parameterizations can be overestimated" mean that the observations are higher than or lower then the parameterizations?

Response: We have revised the sentence to clarify this, as follows:

"*Large discrepancies were observed between the $\gamma(N_2O_5)$ and ϕ values determined in the fields and the laboratory parameterizations derived with pure or mixed aerosol samples, and the differences can be up to an order of magnitude.*"

Page 3, line 32: "NO3- aerosol downwind of" rather than "NO3- aerosol in downwind of"

Response: The phrase has been revised to *"NO_3^- aerosol downwind of"*.

Page 4, line 8: Is the quoted N2O5 a maximum or an average? Please specify.

Response: The N_2O_5 level mentioned here is the maximum concentration. It has been revised to *"(1 min-average maximum of 430 pptv)"* in the text.

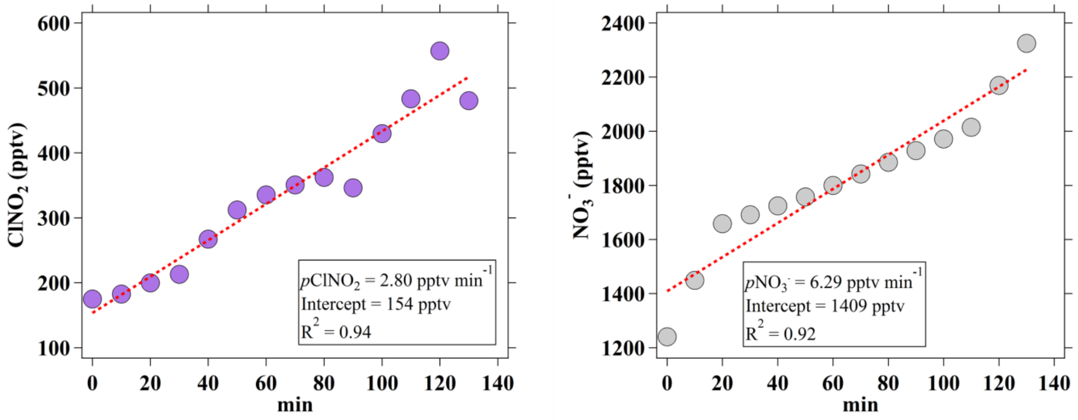
Page 5, lines 25-26: Are the quoted average production rates of NO3 for nighttime only for nighttime and daytime?

Response: It is the average for the night-time only. The word *"night-time"* has been added to the sentence to clarify it.

Page 5, equation 4: The method of Phillips et al. (2016) is referenced, but the method for calculating the production rates in the numerator in the right hand side of the equation is not specified for the data here. How are these quantities (pClNO2 and pNO3-) determined?

Response: The $pClNO_2$ and pNO_3^- in the equation 4 were obtained from the slope of linear plot of $ClNO_2$ versus time and NO_3^- versus time, respectively (see the plots below for one example of the selected cases). An additional sentence on determining the pClNO2 and pNO3- have been included in the text, as follows,

"*The $pClNO_2$ and pNO_3^- were determined from the linear fit of the increase of $ClNO_2$ and total NO_3^- (sum of HNO_3 and particulate NO_3^-) with time, while $[N_2O_5]$ is mean concentration of N_2O_5 for the specific duration.*"



Example plots for determining the $pClNO_2$ and pNO_3^- used in the case on the night of 29 June.

Page 5, line 33: Define "most nights" – how many nights had r2 > 0.6 for the stated correlation?

Response: The sentence has been redefined in the text as the following:

".... with a coefficient of determination (r^2) of greater than 0.6 on 10 out of 13 nights (with

full CIMS measurement),"

Page 6, line 14-15: Assumption 3 is not reasonable. HNO3 is in equilibrium with aerosols regardless of how it is produced. That is, HNO3 equilibration and N2O5 uptake are not separate processes, but tightly coupled ones. The assumption is more likely intended to state that N2O5 heterogeneous uptake during the night of observations is a larger source of total soluble nitrate (HNO3 plus NO3-) than soluble nitrate production from the preceding day, or that the correlation with ClNO2 is determined by the nighttime produced nitrate rather than the background that was present at sunset.

Response: Thanks to the reviewer for the suggestion and clarification. We have revised the sentences to make the assumption more reasonable and clearer in the text.

"...that N_2O_5 *heterogeneous uptake is a dominant source of total soluble nitrate during the night rather than the gas homogenous production or nitrate production from the preceding daytime."*

Page 6, line 19: remove the word "have"

Response: Removed.

Page 6, line 22: Is there a quantitative definition of "drastic changes" here? In other words, is the data filtering arbitrary, or done in a well-defined manner using characteristics of time rates of change.

Response: It is difficult to quantify the changes in a well-defined manner for variables like wind direction, RH, temperature and particle surface area for a longer period. These variables will never remain at a constant value in the real environment (*e.g.* the RH is increasing, while the temperature is decreasing with time). These rates of change varied between nights and it is hard to give a 'fix acceptance' values for these changes (*e.g.* it's hard to justify if it has a significant effect for a shift of 20^{o} in the wind direction).

However, for the parameters such as the NO to NO_x ratio and rates of change of NO_x to NO_y ratio, we can filter them in a more defined-manner. For example, we restrict to data with NO/NO_x ratio lower than 0.1 to remove periods 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 masses.

In other words, we primarily filter the data with the NO_x parameters and then judge and select the period with least changes in other parameters (can be seen in the data in Figure 2a and 2c in the main text) and exclude the data if there's an 'unreasonable' change within the measurement period. We have revised the sentences as below:

"The plume age, represented by the ratios of NO_x *to* NO_y*, were 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 γ(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.

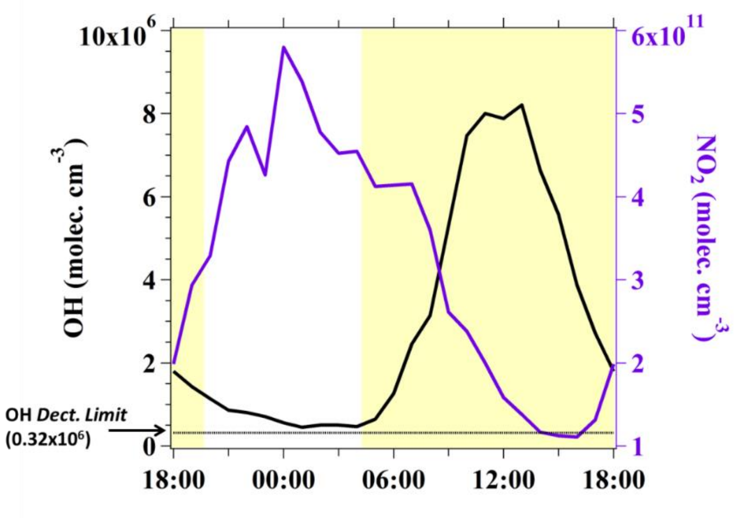
Page 6, lines 26-28: See comment above. The partitioning of total nitrate between gas and particle phase is an important limitation, and it would be useful to define any quantitative information, such as an aerosol thermodynamic model, that would indicate where this partitioning is. The photochemical soluble nitrate production should be in the background of the correlation (i.e., the intercept) and so might not affect the results.

Response: Yes, we agree with the reviewer that the photochemical soluble nitrate production may not affect the results. As for the partitioning, the gas-phase HNO_3 measurement showed that it is only 7% (on average) of the total NO_3^- during the nighttime (see Figure 3b in the main text), suggesting that the partitioning from particle to the gas phase is not significant. This information has been included in the text.

"*It is clear that particulate NO_3^- was the dominant species during the night-time at Wangdu, while the nighttime gas-phase HNO_3 is only 7% (on average) of the total NO_3^- (Figure 3b).*"

Text on pages 6-7 and Figure 3: Explain why there is significant OH + NO2 during the night. Explain how particulate NO3- production from NO3 + VOC is calculated. Many NO3 + VOC reactions produce organic nitrates rather than HNO3, so it is not clear how this source of HNO3 has been calculated based on the information given. The total production rate of NO3- is also referenced in the text but not shown in the figure. The differentiation between day and night in Figure 3 is not clear. Presumably the time axis is local time, not UTC? Please specify for clarity. The times of day and night should be shown, preferably with a shaded region to indicate night. Data for gas phase HNO3 are presented here for the first time. Why in the preceding analysis was ClNO2 only correlated against particulate phase NO3- if gas phase HNO3 is also available? The analysis should be done from the correlation between ClNO2 and total nitrate (HNO3+ NO3-) since the two are in rapid equilibrium on the time scale of ClNO2 production through N2O5 uptake.

Response: Regarding the significant contribution of OH+NO_2 after sunset, it is mostly due to the non-zero OH concentration, though decreasing towards the night, but is still above the instrument detection limits (3.2 × 10^5 for 30s average, 1σ), together with the significant increase of NO_2 level during the night time. Significant levels of OH concentration and reactivity are frequently observed in polluted China environments (*e.g.* Lu et al., 2013; Fuch et al., et al., 2017). The figure below shows the diurnal average of the OH and NO_2 for Wangdu during the measurement period.



For the NO_3+VOC calculation, we need to clarify that there's a mistake in the figure where the rate of NO_3+VOC was already multiplied by 100 times (for it to be 'visible' in the figure), but somehow was not indicated in the legend. As the reviewer suggests, many NO_3+VOC reactions, especially the biogenic VOC (e.g. isoprene, alpha-pinene, etc.), produce organic nitrates rather than HNO_3. However, there are some NO_3+VOC reactions which can produce HNO_3 via H abstraction (according to the IUPAC and NIST reaction kinetic datasheet). Some major VOCs, of which measurements are available, have significant concentrations and significant reaction rate, were chosen for the calculation. The table below summarizes the reactions of NO_3+VOC used in the analysis. We also need to emphasize that the purpose of this NO_3+VOC calculation is just for showing that the NO_3+VOC are not a significant source for HNO_3 at this site, especially during the nighttime where the NO_3 is significant. Therefore, correction on the figure has been made in the text and the information of VOCs used for this calculation has been added in the text too.

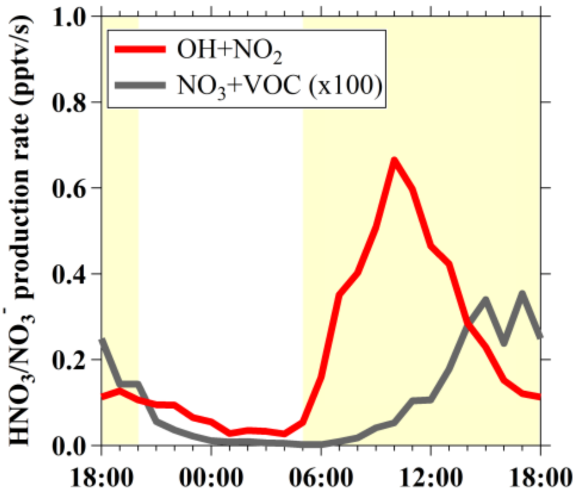
Reaction	**Products**	***k* (cm^3 molecule^{-1} s^{-1} at 25° C)**
$NO_3 + C_2H_6$	$\cdot C_2H_5 + HNO_3$	1.0 x 10^{-17} [a]
NO3 + C_3H_6	$\cdot CH_2CH{=}CH_2 + HNO_3$	4.8 x 10^{-16} [b]
NO3 + C_3H_8	$\cdot CH_3CH_2CH + HNO_3$ $\cdot CH_3CHCH_3 + HNO_3$	7.0 x 10^{-17} [a]
NO_3 + HCHO	·HCO + HNO_3	5.5 x 10^{-16} [a]
$NO_3 + CH_3OH$	$\cdot CH_2OH + HNO_3$	2.3 x 10^{-16} [b]
$NO_3 + C_2H_4O$	$\cdot CH_3CO + HNO_3$	2.7 x 10^{-15} [a]
$NO_3 + CH_3C(O)CH_3$	$\cdot CH_3C(O)CH_2 + HNO_3$	3.0 x 10^{-17} [a]

[a]from IUPAC Atmospheric Chemical Kinetic Data [b]from NIST Chemical Kinetics Database

The revised text reads,

"To check the validity of assumptions (2) above, we also calculated the production rate of NO_3^-/HNO_3 *via reaction of* $OH+NO_2$ *(=*$k_{OH+NO2}[OH][NO_2]$*) and* NO_3+VOC *(=*$\Sigma_i k_i[VOC_i][NO_3]$*, where* VOC_i *=* C_2H_6*,* C_3H_6*,* C_3H_8*, HCHO,* CH_3OH*,* C_2H_4O*,* $CH_3C(O)CH_3$*), as shown in the average diurnal profiles of related species in Figure 3."*

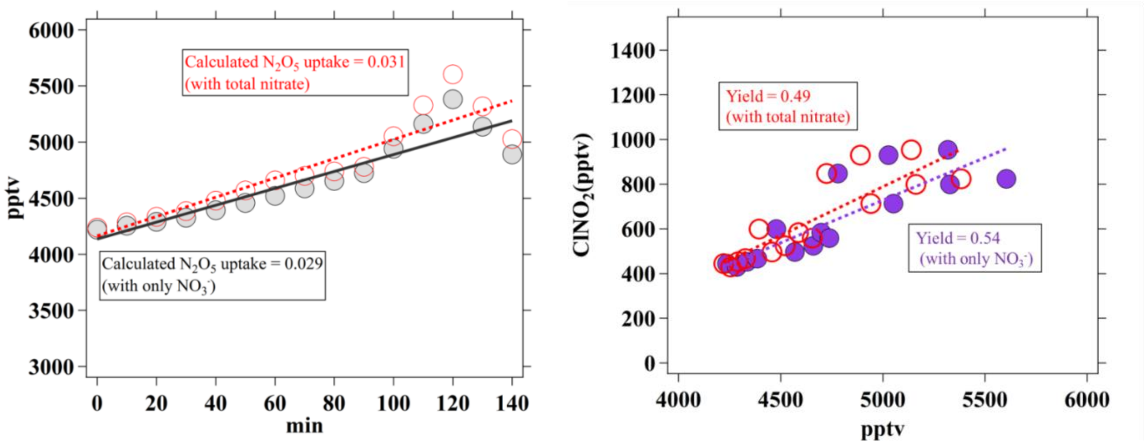
The revised Figure 3c as below:



The average pNO_3^- referenced in the text here was determined from the slope of nighttime diurnal particulate NO_3^- in Figure 3b. This information has been added in the text.

The time axis in Figure 3 is local time. This information has been added in the figure caption. Also, an indication of day and night time (shading) has been added in the figure.

The reason that we only correlated the $ClNO_2$ against the particulate phase NO_3^- was that the gas-phase HNO_3 concentration during the nighttime was very low (on average about 7% of total NO_3^-) and was often below the detection limit (300 pptv) of the measurement by gas and aerosol collector (GAC) (Dong et al., 2012). The inclusion of gas-phase HNO_3 in the analysis does not significantly affect the outcome of the $\gamma(N_2O_5)$ and ϕ, and the changes are still falling within the calculated uncertainty. An example of the difference by adding HNO_3 into the analysis can be seen in the figure below. Despite the small changes, we decided to revise all the calculation to include the HNO_3 (gas-phase) as suggested by the reviewer to make the analysis more accurate. All the relevant changes have been made in the text.



Example of the difference in the analysis for 20 June case

Reference:

Fuchs, H., et al.: OH reactivity at a rural site (Wangdu) in the North China Plain: contributions from OH reactants and experimental OH budget, Atmos. Chem. Phys., 17, 645-661, 10.5194/acp-17-645-2017, 2017.

Lu, K. D., et al.: Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO2 concentrations in summer 2006, Atmos. Chem. Phys., 13, 1057–1080, doi:10.5194/acp-13-1057-2013, 2013.

Dong, H. B., Zeng, L. M., Hu, M., Wu, Y. S., Zhang, Y. H., Slanina, J., Zheng, M., Wang, Z. F., and Jansen, R.: Technical Note: The application of an improved gas and aerosol collector for ambient air pollutants in China, Atmos. Chem. Phys., 12, 10519-10533, 10.5194/acp-12-10519-2012, 2012.

Page 7, line 22: “The question that arises” rather than “The question arises”

Response: The word *“that”* has been added to the sentence.

Page 7, line 33: “coefficients” rather than “coefficient”

Response: Corrected.

Page 8, line 21: Figure 5 would be clearer if the field data were on the y-axis and the parameterization on the x-axis.

Response: Figure 5 has been revised accordingly.

Page 9, line 22: “to changes in RH” rather than “on the changes in RH”

Response: Revised.

Page 9, lines 25-30: Is [H2O]V/Sa really independent of aerosol water itself? It seems that the effects discussed here and on the rest of page 9 can be determined from laboratory experiments under controlled conditions but not easily determined from field data. The authors should be careful to phrase this argument as consistent with laboratory data rather than a determination of these effects from field measurements.

Response: First, we need to clarify that the purpose of correlating the N_2O_5 uptake with $[H_2O]V/Sa$ is to show the $\gamma(N_2O_5)$ is increasing with the volume growth (aerosol water and volume of the aerosol).

Second, the major aim of this paragraph on page 9 is to explain the possible reason of good correlation of $\gamma(N_2O_5)$ with aerosol water content, which is consistent with the laboratory experiments, but such an effect has not been seen in other field measurements from the US and Europe and could be an important factor for N_2O_5 uptake in China. Therefore, we have rephrased the sentence as below:

"These results are consistent with several laboratory studies which have demonstrated that an increase in RH enhanced the particle aqueous volume and increased the bulk reactive N_2O_5 uptake on aqueous sulfate and organic acids (e.g., malonic, succinic, and glutaric acid) containing aerosols (Thornton et al., 2003; Hallquist et al., 2003)."

Reference:

Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N2O5 on sub-micron sulfate aerosols, Phys. Chem. Chem. Phys., 5, 3453-3463, 2003.

Thornton, J. A., Braban, C. F., and Abbatt, J. P.: N2O5 hydrolysis on sub-micron organic aerosols: The effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem. Phys., 5, 4593-4603, 2003.

Page 9, first paragraph: The major conclusion is that RH, and by extension the calculation of aerosol liquid water, was the determining factor for N2O5 uptake. In this context, it will be helpful to say more about the measurement of the wet aerosol surface area and its associated uncertainties, since wet aerosol surface area is often a difficult quantity to measure, and the measurement or calculation can itself introduce an RH dependence to the aerosol surface area measurement. The description in the methods section (Page 5, lines 7-9) is brief. A more comprehensive description of this measurement and statement of its potential dependence on RH, along with the uncertainty in the aerosol surface area, is needed.

Response: Thanks for the valuable suggestion. The sentences have been revised and the following information has been added into the text to make it clearer.

"The particle surface area concentrations (S_a) were calculated based on the wet ambient particle number size distribution by assuming spherical particles. In brief, dry-state particle number size distribution was measured with a mobility particle size spectrometer (covering mobility particle diameter of 4 to 800 nm) and an aerodynamic particle size spectrometer (for aerodynamic particle diameter 0.8 to 10 µm). The wet particle number size distributions as a function of the relative humidity were calculated from a size-resolved kappa-Köhler function

determined from real-time measurement of a High Humidity Tandem Differential Mobility Analyzer (Hennig et al., 2005; Liu et al., 2014). It should be noted that the major uncertainty of S_a calculation was the assumption and application of κ at different size-range, leading to an overall uncertainty of ±19%."

Reference:

Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90% and 98% relative humidity, J. Aerosol Sci., 36, 1210-1223, 10.1016/j.jaerosci.2005.01.005, 2005.

Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Muller, K., and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain, Atmos. Chem. Phys., 14, 2525-2539, 10.5194/acp-14-2525-2014, 2014.

Page 10, line 22, Figure 7a: As for figure 5, this would be clearer with the field data on the y-axis. All other plots in figure 7 have field data on the y-axis, and the same should be done for figure 7.

Response: The figures have been edited accordingly.

Page 10, line 24: remove the word "in". Also "Such a discrepancy" rather than "Such discrepancy".

Response: The word "in" was removed from the text and the phrase was revised to *"Such a discrepancy"*.

Page 10, line 29: What is meant by "from quadratic fitting"? Is there a polynomial fit that should appear in Figure 7?

Response: The sentence has been revised to *"correlation from a quadratic fitting"* The Figure7 was edited by adding the quadratic fit line into the plots.

Page 10, line 33: Remove the word "good" or else replace by something more specific, such as "statistically significant", if appropriate. Also, the term "quadratic data fitting" appears again here without explanation or a displayed fit.

Response: Thanks for pointing it out. The "good" was removed from the sentence. The display of the quadratic fitting has been added in Figure7.

Heterogeneous N_2O_5 uptake coefficient and production yield of $ClNO_2$ in polluted northern China: Roles of aerosol water content and chemical composition

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Abstract. Heterogeneous uptake of dinitrogen pentoxide (N_2O_5) and production of nitryl chloride ($ClNO_2$) are important nocturnal atmospheric processes that have significant implications for the production of secondary pollutants. However, the understanding of N_2O_5 uptake processes and $ClNO_2$ production remains limited, especially in China. This study presents a field investigation of the N_2O_5 heterogeneous uptake coefficient ($\gamma(N_2O_5)$) and $ClNO_2$ production yield (ϕ) in a polluted area of northern China during the summer of 2014. The N_2O_5 uptake coefficient and $ClNO_2$ yield were estimated by using the simultaneously measured $ClNO_2$ and total nitrate in ten ~~10~~ selected cases, which have concurrent increases in the $ClNO_2$ and nitrate concentrations and relatively stable environmental conditions. ~~using simultaneously measured concentrations of $ClNO_2$ and particulate nitrate.~~ The determined $\gamma(N_2O_5)$ and ϕ values varied greatly, with an average of 0.022 for $\gamma(N_2O_5)$ (± 0.012, standard deviation~~in range of 0.006-0.034~~) and 0.34 for ϕ (±0.28, standard deviation~~range, 0.07-1.04~~). The variations in $\gamma(N_2O_5)$ could not be fully explained by the previously derived parameterizations of N_2O_5 uptake that consider nitrate, chloride, and the organic coating. Heterogeneous uptake of N_2O_5 was found to have a strong positive dependence on the relative humidity and aerosol water content. This result suggests that the heterogeneous uptake of N_2O_5 in Wangdu is governed mainly 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. ~~a phenomenon that differs from other field observations in the United States and Europe.~~ The $ClNO_2$ yield estimated from the parameterization was also overestimated comparing to that derived from the observation.~~Laboratory-derived parameterization also overestimated the $ClNO_2$ yield.~~ The observation-derived ϕ showed a decreasing trend with an increasing ratio of acetonitrile to carbon monoxide, an indicator of biomass burning emissions, which suggests a possible suppressive effect on the production yield of $ClNO_2$ in the plumes influenced by

biomass burning in this region. The findings of this study illustrate the need to improve our understanding and to parameterize the key factors for $\gamma(N_2O_5)$ and ϕ to accurately assess the photochemical and haze pollution.

1 Introduction

The nocturnal heterogeneous reaction of dinitrogen pentoxide (N_2O_5) with aerosols is a loss pathway of NO_x and a source of aerosol nitrate and gas-phase nitryl chloride ($ClNO_2$) (Brown et al., 2006; Osthoff et al., 2008; Thornton et al., 2010; Sarwar et al., 2014) and thereby has important implications on air quality (e.g., Li et al., 2016; Tang et al., 2017). The process begins with the accumulation of gas-phase nitrate radical (NO_3) after sunset via the oxidation of nitrogen dioxide (NO_2) by O_3 and further reaction of NO_3 with another NO_2, yielding ~~a~~ N_2O_5. The accommodation of N_2O_5 on the aqueous surface of the aerosol (R1) and reaction with liquid water (H_2O) leads to the formation of a protonated nitric acid intermediate ($H_2ONO_2^+$) and a nitrate (NO_3^-) (R2; Thornton and Abbatt, 2005; Bertram and Thornton, 2009).

$$N_2O_5\ (g) \leftrightharpoons N_2O_5\ (aq) \qquad \text{(R1)}$$

$$N_2O_5\ (aq) + H_2O\ (l) \leftrightharpoons NO_3^-(aq) + H_2ONO_2^+(aq) \qquad \text{(R2)}$$

The $H_2ONO_2^+$ will proceed by reacting with another H_2O to form an aqueous nitric acid (HNO_3; R3). If chloride (Cl^-) is present in the aerosols, the $H_2ONO_2^+$ will undergo another pathway to produce a nitryl chloride ($ClNO_2$) through R4, which is a dominant source of highly reactive chlorine radicals in the troposphere (e.g., Riedel et al., 2012a; 2014).

$$H_2ONO_2^+(aq) + H_2O\ (l) \rightarrow H_3O^+(aq) + HNO_3(aq) \qquad \text{(R3)}$$

$$H_2ONO_2^-(aq) + Cl^-(aq) \rightarrow ClNO_2 + H_2O(l) \qquad \text{(R4)}$$

The heterogeneous loss rate of N_2O_5 ($k(N_2O_5)_{het}$) and the $ClNO_2$ production rate ($p(ClNO_2)$) are fundamentally governed by the probability of N_2O_5 lost upon collision with particle surface area in a volume of air (i.e., uptake coefficient, $\gamma(N_2O_5)$) and the $ClNO_2$ yield (ϕ), which is defined as the branching ratio between the formation of HNO_3 via R3 and $ClNO_2$ via R4. Assuming that the gas-phase diffusion to the aerosol surfaces is negligible, their relationship can be described by equations (1) and (2), in which c_{N2O5} is the average molecular speed of N_2O_5 and S_a is the aerosol surface area.

$$k(N_2O_5)_{het} = \frac{1}{4} c_{N2O5} \gamma(N_2O_5) S_a \qquad \text{(Eq 1)}$$

$$p(ClNO_2) = k(N_2O_5)_{het}[N_2O_5]\phi \qquad \text{(Eq 2)}$$

N_2O_5 uptake has been shown in the laboratory to be susceptible to changes in the water content, chloride, nitrate, and organic particle coatings in aerosols (e.g., Mentel et al., 1999; Bertram and Thornton, 2009; Tang et al., 2014). The presence of liquid water on the aerosols allows the accommodation of N_2O_5 (R1) and acts as a medium for the solvation process of N_2O_5 (R2). It has been found that N_2O_5 uptake is significantly enhanced in humid conditions than in dry conditions (e.g., Hallquist et al., 2003; Bertram and Thornton, 2009; Gržinic et al., 2015). Higher loading of NO_3^- in the aerosol can dramatically decrease N_2O_5 uptake by reversing the solvation/ionization process of N_2O_5, shifting the equilibrium in R2 to the left to reproduce N_2O_5, which can be diffused out of the aerosol (known as the “nitrate suppression” effect). The rate of reversible reaction of R2 (i.e., $H_2ONO_2^+$ with NO_3^-) was documented to be 30 to 40 times faster than the reaction of

$H_2ONO_2^+$ with liquid water in R3 (Bertram and Thornton, 2009; Griffiths et al., 2009). The presence of Cl^- in the aerosol, in contrast, can enhance the reactive uptake because Cl^- reacts effectively with $H_2ONO_2^+$ (in R4), thus negating the "nitrate suppression" effect by shifting the equilibrium in R2 to the right (Finlayson-Pitts et al., 1989; Bertram and Thornton, 2009). The uptake of N_2O_5 can also be hindered by the presence of organics, because the organic coating layer on the aerosol could lower the liquid water content and/or limit the surface activity, thus suppressing the accommodation of N_2O_5 (e.g., Cosman et al., 2008; Gaston et al., 2014).

As for the $ClNO_2$ yield from N_2O_5 heterogeneous reactions, it was found to be dependent on the fate of $H_2ONO_2^+$ and thus on the relative amount of Cl^- and water content (Benhke et al., 1997; Roberts et al., 2009; Bertram and Thornton, 2009). Therefore, ϕ can be expressed by the following equation (Eq.3).

$$\phi_{\text{param.}} = \frac{1}{\frac{k_{R3}[H_2O]}{k_{R4}[Cl^-]} + 1} \qquad \text{(Eq 3)}$$

Roberts et al. (2009) and reference therein reported that the coefficient rate of k_{R4} is about 450 - 836 times faster than that of k_{R3}, indicating that $H_2ONO_2^+$ proceeds more favorably via R4, even with a small amount of Cl^-. However, some laboratory experiments have suggested that the presence of halides (i.e., bromide), phenols, and humic acid may significantly reduce the ϕ (e.g., Schweitzer et al., 1998; Ryder et al., 2015).

The parameterization of $\gamma(N_2O_5)$ and ϕ as a function of the aerosol water content and aerosol chemical composition, derived based on the findings of the laboratory studies mentioned above (e.g., Antilla et al., 2006; Bertram and Thornton, 2009; Davis et al., 2008), has recently been compared with the ambient observations in different environments (Morgan et al., 2015; Phillips et al., 2016; Chang et al., 2016; Wang Z. et al., 2017; McDuffie et al., 2018). Large discrepancies were observed between the $\gamma(N_2O_5)$ and ϕ values determined in the fields and the laboratory parameterizations derived with pure or mixed aerosol samples, and the differences can be up to an order of magnitude.~~where the laboratory parameterization values can be overestimated by up to an order of magnitude.~~ 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., 2012b; 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). These results suggest the lack of comprehensive understanding of the N_2O_5 uptake and $ClNO_2$ production yield in various atmospheric environments around the world.

Most of the previous field studies of N_2O_5 uptake and $ClNO_2$ production have been conducted in the United States (US) and Europe regions (Brown et al., 2009; Chang et al., 2016). Direct field investigation of the N_2O_5 heterogeneous processes in China is very limited. Pathak et al. (2009, 2011) analyzed the aerosol composition and suggested that the accumulation of fine NO_3^- aerosol ~~in~~ downwind of Beijing and Shanghai was due to significant N_2O_5 heterogeneous reactions. Wang et al. (2013) linked the observed NO_3^- with the precursors of N_2O_5 (i.e., NO_2 and O_3) in urban Shanghai and suggested that the N_2O_5 heterogeneous uptake dominated NO_3^- formation on polluted days. However, field measurements of N_2O_5 and $ClNO_2$ were not available until recently at several sites in southern and northern China (Tham et al., 2014; Wang Z. et al., 2017).

In the summer of 2014, a field campaign was carried out to investigate $ClNO_2$ and N_2O_5 at a semirural ground site at Wangdu in polluted northern China (Tham et al., 2016). Elevated levels of $ClNO_2$ up to 2070 pptv (1 min-average), but relatively low values of N_2O_5 (1 min-average maximum of 430 pptv), were observed on most nights at this site, and heterogeneous processes have been shown to have a significant effect on the following day's radical and ozone production at the site (Tham et al., 2016). Yet, the factors that drive the N_2O_5 heterogeneous uptake and $ClNO_2$ production yield remain unclear. In this study, we further analyze the dataset to investigate this topic. 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^-) ~~with the measurement~~ dataset and then compare the values obtained in the field with various parameterizations derived from the laboratory studies. With the aid of the aerosol composition and meteorological measurements, we illustrate the factors that drive or influence the variations in $\gamma(N_2O_5)$ and ϕ at Wangdu. The values for $\gamma(N_2O_5)$ and ϕ obtained here are also compared with field results from the literature to provide an overview of the N_2O_5-$ClNO_2$ heterogeneous process observed in various environments around the world.

2 Methods

The measurement site (38.66°N, 115.204°E) is located at a semirural area in Wangdu county of Hebei province, in the northern part of China. The Wangdu site is situated within the agricultural land but is bounded by villages and towns. Beijing (the national capital) is about 170 km to the northeast, Tianjin is about 180 km to the east, Shijiazhuang is about 90 km to the southwest, and Baoding is ~33 km to the northeast. Dozens of major coal-fired power stations are also located in the region. During the study period, frequent biomass burning activity was observed in the surrounding regions. Analysis of the air masses' back trajectories showed that the sampling site was frequently affected by these surrounding anthropogenic sources. Details on the sampling site and the meteorological conditions during the campaign can be found in Tham et al. (2016).

In this study, N_2O_5 and $ClNO_2$ were measured with an iodide chemical mass ionization mass spectrometer (CIMS), with which the N_2O_5 and $ClNO_2$ were detected as the iodide-cluster ions of $I(ClNO_2)^-$ and $I(N_2O_5)^-$, similar to those outlined by Kercher et al. (2009). The detection principles, calibration, and inlet maintenance were described in detail in our previous studies (Wang T. et al., 2016; Tham et al., 2016). The CIMS measurement at the Wangdu site was performed from 20 June to 9 July 2014. A corona discharge ion source setup (for generation of iodide primary ions) was used in the CIMS measurement from 20 to 26 June 2014 with a detection limit of 16 pptv for N_2O_5 and 14 pptv for $ClNO_2$ (3σ; 1 min-averaged data) but was replaced by a radioactive ion source from 27 June 2014 until the end of the study with a detection limit of 7 pptv for N_2O_5 and 6 pptv for $ClNO_2$ (3σ; 1 min-averaged data). The overall uncertainty of the CIMS measurement was estimated to be ±25%, with a precision of 3%.

The present study was supported by other auxiliary measurements of aerosol, ~~and~~ trace gases and meteorological parameters, and the detailed instrumentation for these measurements has been listed in a previous paper (Tham et al., 2016). Trace gases including NO, NO_2, O_3, SO_2, CO, and total odd nitrogen (NO_y) were measured with online gas analyzers (Tan et al., 2017). A gas aerosol collector–ion chromatography system was used to measure the ionic compositions of $PM_{2.5}$, including NO_3^-, Cl^-, SO_4^-, NH_4^+, and gas-phase HNO_3 (Dong et al., 2012). The particle surface area concentrations (S_a) were calculated based on the wet ambient particle number size distribution by assuming spherical particles. In brief, dry-state particle number size distribution was measured with a mobility particle size spectrometer (covering mobility particle diameter of 4 to 800 nm) and an aerodynamic particle size spectrometer (for aerodynamic particle diameter 0.8 to 10 μm). The wet particle number size distribution as a function of the relative humidity were calculated from a size-resolved kappa-Köhler function determined from real- time measurement of a High Humidity Tandem Differential Mobility Analyzer (Hennig et al., 2005; Liu et al., 2014). It should be noted that the major uncertainty of S_a calculation was the assumption and application of κ at different size-range, leading to an overall uncertainty of ±19%.~~The particle surface area concentrations (S_a) were calculated based on the wet ambient particle number size distribution predicted from the size-resolved kappa-Köhler function determined from real-time measurement with a high humidity tandem differential mobility analyzer (Hennig et al., 2005; Liu et al., 2014).~~

Hydroxyl radical (OH) was measured with the laser-induced fluorescence technique (Tan et al., 2017). Volatile organic compounds including methane, C_2-C_{10} hydrocarbons, formaldehyde, and oxygenated hydrocarbons and acetonitrile (CH_3CN) were measured with a cavity ring–down spectroscopy technique instrument, an online gas chromatograph equipped with a mass spectrometer and a flame ionization detector, a Hantzsch fluorimetric monitor, and a proton-transfer-reaction mass spectrometer, respectively (Yuan et al., 2010; Wang et al., 2014). Meteorological data including the wind profile, relative humidity (RH), and temperature were measured with an ultrasonic anemometer and a weather station on a 20m tower. Detailed descriptions of these instrumentation and measurement techniques ~~observations of the aerosols, trace gases, and meteorological parameters~~ at Wangdu can be found in previous ~~other~~ publications (e.g., Wang Y. et al., 2016; Min et al., 2016; ~~and~~ Tham et al., 2016; and Tan et al., 2017).

3 Results and Discussion

3.1 Nocturnal heterogeneous N_2O_5 reaction at Wangdu

Figure 1 illustrates the time series of NO_x, O_3, N_2O_5, $ClNO_2$, particulate NO_3^-, S_a, the calculated production rate of NO_3, and the lifetime of N_2O_5 observed at Wangdu between 20 June and 9 July 2014. Abundance of NO_x and O_3 was observed at night-time (20:00 to 05:00 local time); with average night-time mixing ratios of 21 and 30 ppbv, respectively. The elevated night-time NO_x and O_3 levels led to the active production of NO_3, with an average nighttime production rate of NO_3 (=$k_{O3+NO2}[NO_2][O_3]$) of 1.7 ppb h^{-1} and a maximum level of 8.3 ppb h^{-1} for the entire campaign. Even with the rapid production of NO_3 and the high NO_2 level at night, the observed N_2O_5 concentrations were typically low (i.e., average nighttime concentration of 34 ± 14 pptv). The low N_2O_5 value is consistent with the short steady-state lifetime of N_2O_5 ($\tau(N_2O_5)$) for the study period, ranged from 0.1 to 10 min, suggesting that the direct loss of N_2O_5 via heterogeneous reaction and/or indirect loss of N_2O_5 via decomposition to NO_3 (i.e., reactions of NO_3 with NO and volatile organic compounds [VOCs]) were rapid in this region. The good correlation between the night-time levels of $ClNO_2$ and fine particulate NO_3^- (the products of heterogeneous reactions of N_2O_5 via R3 and R4, respectively), with a coefficient of determination (r^2) of greater than 0.6 on 10 out of 13 ~~most~~ nights (with full CIMS measurement), provides field evidence of active N_2O_5 heterogeneous uptake processes in this region.

3.2 Estimation of N_2O_5 uptake coefficient and $ClNO_2$ production yield

The consistent trends and clear correlation between $ClNO_2$ and ~~fine particulate~~ the NO_3^- could be used to quantify N_2O_5 heterogeneous uptake following the method described by Phillips et al. (2016). The uptake coefficient of N_2O_5, $\gamma(N_2O_5)$, was estimated based on the production rate of $ClNO_2$ ($pClNO_2$) and the nitrate formation rate (pNO_3^-) from the following equation (4). The $pClNO_2$ and pNO_3^- were determined from the linear fit of the increase of $ClNO_2$ and total NO_3^- (sum of HNO_3 and particulate NO_3^-) with time, while $[N_2O_5]$ is mean concentration of N_2O_5 for the specific duration.

$$\gamma(N_2O_5)=\frac{2(pClNO_2+pNO_3^-)}{C_{N2O5}S_a[N_2O_5]} \qquad \text{(Eq 4)}$$

The yield of $ClNO_2$ was determined from the regression analysis of $ClNO_2$ versus total ~~particulate~~ NO_3^- (Wagner et al., 2012; Riedel et al., 2013). The slope (m) from the regression plot was fitted into equation (5) to obtain the ϕ.

$$\phi = \frac{2m}{1+m} \qquad \text{(Eq 5)}$$

The concentrations of $ClNO_2$, N_2O_5, total ~~particulate~~ NO_3^-, and other related data used for this analysis were averaged or interpolated into 10 min. This analysis assumes 1) that the air mass is stable, vertical mixing is limited and losses of $ClNO_2$ and total NO_3^- are insignificant within the duration of analysis; ~~2) that the NO_3^- produced via N_2O_5 heterogeneous uptake remains in the particle phase and does not significantly degas as HNO_3;~~ and ~~3~~2) that N_2O_5 heterogeneous uptake is a dominant source of total soluble nitrate during the night rather than the gas homogeneous production or nitrate production from the preceding daytime. ~~the night-time production of NO_3^- through the net HNO_3 uptake to aerosols is not important compared to that formed via N_2O_5 heterogeneous uptake.~~

The limitation of this method is that it cannot predict the $\gamma(N_2O_5)$ with negative changes in the concentrations of $ClNO_2$ or ~~particulate~~ total NO_3^-, which may be a result of differences in the origin or age of the air mass. In accordance with this limitation and with assumption (1) above, we carefully select plumes during the night-time that ~~have~~ meet the following criteria for the analysis: shorter periods of data, usually between 1.5 and 4 hours, with concurrent increases in $ClNO_2$ and total NO_3^-. The ~~wind conditions and air mass age in the~~ plume age, represented by the ratios of NO_x to NO_y, ~~were~~ was relatively stable (change <0.1 min^{-1}), and no drastic changes were seen in other variables such as wind conditions, the particle surface area, RH, or temperature. ~~In addition,~~ 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 $\gamma(N_2O_5)$. Figure 2 shows two examples of relatively constant conditions of relevant chemical composition and environmental variables, together with a plot of $ClNO_2$ versus ~~particle~~ total NO_3^- for the night. 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 total NO_3^-. It should also be noted that ~~partitioning of NO_3^- to gas-phase HNO_3 and the~~ contribution of total ~~particulate~~ NO_3^- from other sources, like the reaction of OH with NO_2 and the oxidation of VOCs by NO_3, can bias the values predicted for $\gamma(N_2O_5)$ and ϕ.

To check the validity of assumptions (2) ~~and (3)~~ above, we also calculated the production rate of NO_3^-/HNO_3 via reaction of $OH+NO_2$ ($=k_{OH+NO2}[OH][NO_2]$) and NO_3+VOC ($=\Sigma_i k_i[VOC_i][NO_3]$, where $VOC_i = C_2H_6, C_3H_6, C_3H_8$, HCHO, CH_3OH, C_2H_4O, $CH_3C(O)CH_3$), as shown in the average diurnal profiles of related species in Figure 3. It is clear that particulate NO_3^- was the dominant species during the night-time at Wangdu, while the nighttime gas-phase HNO_3 is only 7% (on average) of the total NO_3^- (Figure 3b). The strong correlation between $ClNO_2$ and ~~particulate~~ nitrate during the night indicates that the heterogeneous process of N_2O_5 was the dominant source of particulate nitrate. Moreover, the production rate of HNO_3, as calculated from the gas-phase reactions of $OH+NO_2$ and NO_3+VOC, shows a decreasing trend towards the night (Figure 3c), and the combination of these rates on average is ~~only about~~ less than one-third of the average pNO_3^-~~.~~, which was determined from the slope of nighttime particulate NO_3^- in Figure 3b. ~~during the night.~~ The increase in night-time NO_3^- was also accompanied by an increase in ammonium (NH_4^+), which suggests that the repartition process to form ammonium nitrate was efficient, thus limiting the release of HNO_3 (Figure 3d). These results support the validity of the above assumptions and the determination of uptake and yield in this analysis.

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. ~~With these methods and selection criteria, we can derive $\gamma(N_2O_5)$ and ϕ for 10 night-time plumes.~~ Table 1 shows the estimated N_2O_5 uptake coefficients and $ClNO_2$ yields at Wangdu together with the errors that account for the scattering of data in the analysis and uncertainty from the measurement of N_2O_5, $ClNO_2$, aerosol surface area, and ~~particulate~~ total NO_3^-. The estimated $\gamma(N_2O_5)$ values ranged from 0.005 to 0.039~~0.006 to 0.034~~, with a ~~median~~ mean value of ~~0.023~~0.022. A large variability was found in ϕ (range, 0.06~~0.07~~ to 1.04). The relatively larger $\gamma(N_2O_5)$ and ϕ values observed on the night of 20–21 June are consistent with the observation of the highest $ClNO_2$ concentration, whereas the lower $\gamma(N_2O_5)$ and ϕ values on the night of 28–29 June explain the observation of the elevated N_2O_5 and small $ClNO_2$ mixing ratios (c.f. Figure 1). The observed $\gamma(N_2O_5)$ and ϕ values at Wangdu were compared with literature values derived from previous field observations in various locations in North America, Europe, and China, as summarized in Figure 4 and Table 2. The variable values of $\gamma(N_2O_5)$ in this study fall in the range of $\gamma(N_2O_5)$ (<0.001 to 0.11) and ϕ (0.01–1.38) reported around the world. The values are also within the range of N_2O_5 uptake coefficients and $ClNO_2$ yields determined in regions of China regions ($\gamma(N_2O_5)$ = 0.004–0.103; ϕ = 0.01–0.98), which are in the middle to upper end of the values reported around the world. The observed significant $ClNO_2$ concentrations and high yields of ϕ here, consistent with other studies at inland sites (c.f. Table 2), also point to the fact that $ClNO_2$ production can be efficient in regions far from the oceanic source of chloride and further highlight the important role of anthropogenic chloride emissions in the chlorine activation process and the next-day's photochemistry. The question that arises here is what drives the large variability in the $\gamma(N_2O_5)$ and ϕ at Wangdu.

3.3 Factors that control the N_2O_5 uptake coefficient

Heterogeneous uptake of N_2O_5 is governed by various factors, including the amount of water and the physical and chemical characteristics of the aerosols (Chang et al., 2011; Brown and Stutz, 2012). To gain better insight into the factors that drive the N_2O_5 heterogeneous uptake, the determined $\gamma(N_2O_5)$ values were compared with those predicted from complex laboratory-derived parameterizations, and their relationships with the aerosol water content and aerosol compositions observed at Wangdu were examined.

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

$$\gamma_{B\&T} = Ak\left(1 - \frac{1}{\left(\frac{k_{R3}[\mathrm{H_2O}](\mathrm{l})}{k_{R2b}[\mathrm{NO_3^-}]}\right) + 1 + \left(\frac{k_{R4}[\mathrm{Cl^-}]}{k_{R2b}[\mathrm{NO_3^-}]}\right)}\right) \qquad \text{(Eq 6)}$$

where A is an empirical pre-factor calculated from the volume of aerosol (V), S_a, c_{N2O5}, and Henry's law coefficient of N_2O_5 ($A = 4/c_{N2O5} \times V/S_a \times H_{aq}$); $k = 1.15 \times 10^6 - (1.15 \times 10^6)^{\exp(-0.13[H2O])}$; $k_{R3}/k_{R2b} = 0.06$; and $k_{R4}/k_{R2b} = 29$. 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 assumes 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 represents an average over bulk aerosols. ~~This~~ The $\gamma_{B\&T}$~~, however,~~ also does not account for the suppression of $\gamma(N_2O_5)$ from the organics, but it is frequently used with the parameterization formulated by Anttila et al. (2006), who treated the organic fraction in the aerosols as a coating, as given in equation (7) (e.g., Morgan et al., 2015; Phillips et al., 2016; Chang et al., 2016). The net uptake of N_2O_5 onto an aqueous core and organic coating ($\gamma_{B\&T+Org}$) can be determined by equation (8).

$$\gamma_{Org} = \frac{4\,RTH_{org}D_{org}R_c}{C_{N2O5}LR_p} \qquad \text{(Eq 7)}$$

$$\frac{1}{\gamma_{B\&T+Org}} = \frac{1}{\gamma_{B\&T}} + \frac{1}{\gamma_{Org}} \qquad \text{(Eq 8)}$$

Here, the H_{org} is the Henry's Law constant of N_2O_5 for organic coating; D_{org} is the solubility and diffusivity of N_2O_5 in the organic coating of thickness L; and R_c and R_p are the radii of the aqueous core and particle, respectively. 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. The $H_{org}D_{org}$ is equal to $0.03 \times H_{aq}D_{aq}$, where $H_{aq} = 5000$ M atm^{-1} and $D_{aq} = 10^{-9}$ m^2 s^{-1} (Chang et al., 2011 and references therein). In addition, Evan and Jacob (2005) proposed a simpler parameterization of N_2O_5 uptake on sulfate aerosol ($\gamma_{E\&J}$) as a function of temperature and RH, as given by equation (9).

$$\gamma_{E\&J} = (2.79\times10^{-4}+1.3\times10^{-4}\times RH - 3.43\times10^{-6}\times RH^2 + 7.52\times10^{-8}\times RH^3)\times10^{(4\times10^{-2}\times(T-294))} \qquad \text{(Eq 9)}$$

Figure 5 illustrates a comparison of field-derived N_2O_5 uptake coefficients with the values computed from the above parameterizations. The computed $\gamma_{B\&T}$ (red circle) ranged from 0.046 to 0.094 and was consistently higher than the field-derived $\gamma(N_2O_5)$ by up to a factor of 9. By accounting for the effects of organic coating on the N_2O_5 uptake coefficient via equations (7) and (8), the calculated N_2O_5 uptake coefficients (green circle in Figure 5) are significantly underestimated. Note that only six cases were available to compute the $\gamma_{B\&T+Org}$ due to the limited organic aerosols data for the study period. The N_2O_5 uptake coefficients computed from the parameterization suggested by Evan and Jacob (2005) are generally consistent with the field-derived $\gamma(N_2O_5)$ (as shown by blue circles). The different results from these parameterizations may suggest more complex aerosol composition, mixing states ~~or~~and other physical-chemical properties in the real ambient atmosphere than in the aerosol sample used in the laboratory study.

We then examine the relationships of the field-derived $\gamma(N_2O_5)$ with RH, water content, and aerosol compositions, as illustrated in Figure 6. It can be seen in Figure 6a that the $\gamma(N_2O_5)$ has a clear correlation with the aerosol water content (r^2 =

0.~~86~~88; $p < 0.01$, *t*-test). The strong dependence of $\gamma(N_2O_5)$ on the aerosol water content was observed at RH lower than 80% or $[H_2O]$ lower than 40 mol L^{-1}. The $\gamma(N_2O_5)$ then plateaus at about 0.~~032~~ 035 when the RH exceeds 80%. This pattern is similar to the trends observed in laboratory studies for N_2O_5 uptake onto aqueous sulfate and malonic acid aerosols, in which the $\gamma(N_2O_5)$ strongly increases with humidity at RH below 40-50% but becomes insensitive above this threshold (e.g., Hallquist et al., 2003; Thornton et al., 2003). The $\gamma(N_2O_5)$ at Wangdu shows a trend of decreasing with the concentration of NO_3^- per volume of aerosol (see Figure 5b), which is similar to the results from the previous laboratory studies (Bertram and Thornton, 2009; Griffiths et al., 2009). However, we do not think that $[NO_3^-]$ is the dominant limiting factor for N_2O_5 uptake at this site, as seen in the consistency of the $\gamma(N_2O_5)$ data points with the change in RH (in the color code of Figure 6b), the increasing trend of $\gamma(N_2O_5)$ with the concentration of particulate nitrate in the air (c.f. Figure 6c), and the positive dependency of $\gamma(N_2O_5)$ on the molar ratio of $[H_2O]/[NO_3^-]$ (c.f. Figure 6d), which reflect that the N_2O_5 uptake is more sensitive to the aerosol water content than to the NO_3^-, at least up to $[H_2O]:[NO_3^-]$ of 20. The increase in ambient particulate nitrate is probably due to the faster N_2O_5 heterogeneous reaction. The N_2O_5 uptake does not show an increasing trend with the chloride-to-nitrate molar ratio, a pattern demonstrated in the laboratory result (Bertram and Thornton, 2009), but rather a decrease for high $[Cl^-]/[NO_3^-]$ ratios, and it also correlates with differences in RH (c.f. Figure 6e). There is a lack of correlation of $\gamma(N_2O_5)$ with the $[Org]:[SO_4^{2-}]$ observed in the ratio range of 0.5–1.2, indicating that the suppression of organics on the N_2O_5 uptake may be insignificant at Wangdu. These results are in line with the parameterization comparison results shown in Figure 5, reveal that the variation in the N_2O_5 uptake at Wangdu is not driven by the chemical properties of aerosols like NO_3^-, Cl^-, and organics, but rather that the RH or the aerosol water content plays a defining role in the N_2O_5 heterogeneous uptake.

The response of N_2O_5 uptake~~ on~~ to the changes in RH is consistent with the changes in the sulfate (SO_4^{2-}) concentrations (see Figure 6g), which mainly determine the hygroscopicity of the aerosols and were found to be responsible for the particle growth at Wangdu (Wu et al., 2017). The hygroscopic growth of aerosols inferred by the RH (water uptake) can affect the amount of water in the aerosol and the volume-to-surface area ratio ($[H_2O]V/S_a$). The good positive correlation of $\gamma(N_2O_5)$ with $[H_2O]V/S_a$ (see Figure 6h) suggests that the increased volume of aerosol, in particular the layer of aerosol water content, could allow efficient diffusion of N_2O_5 and solvation of N_2O_5 into $H_2ONO_2^+$ and NO_3^- for further aqueous reactions, whereas a smaller volume of aerosol (less water content) may be easily saturated by N_2O_5 and then diffuse the N_2O_5 out of the aerosol, limiting the solvation of the N_2O_5 process and restricting N_2O_5 uptake. These results are consistent with ~~Several~~ several laboratory studies which have demonstrated that an increase in RH enhanced the particle aqueous volume and increased the bulk reactive N_2O_5 uptake on aqueous ~~acids~~ sulfate and organic acids (~~i.~~e.g., malonic, succinic, and glutaric acid) ~~and aqueous sulfate~~ containing aerosols (Thornton et al., 2003; Hallquist et al., 2003). The increase in RH can also lower the viscosity of the aqueous layer in organic-containing aerosols, leading to greater diffusivity of N_2O_5 within the aerosol water layer, which ultimately increases the N_2O_5 uptake (Gržinic et al., 2015).

The strong dependency of N_2O_5 uptake upon the RH has not been clearly demonstrated in other field measurements. Field observations of $\gamma(N_2O_5)$ in North America and Europe show any significant direct dependence of $\gamma(N_2O_5)$ on RH but were strongly influenced by the aerosol composition (refer to the descriptions in Table 2). For instance, the flight measurements in Texas and London showed the independence of $\gamma(N_2O_5)$ at RH from 34% to 90%, but the $\gamma(N_2O_5)$ were generally controlled by the amount of NO_3^- and/or organic compounds (Brown et al., 2009; Morgan et al., 2015). A comparison of ground measurements in Seattle and Boulder showed variations in $\gamma(N_2O_5)$ at various $H_2O(l)$ levels in the two places, but the RH alone was insufficient to describe their observed $\gamma(N_2O_5)$ variability, and the organic composition of the aerosols was determined to have a dominant influences on $\gamma(N_2O_5)$ (Bertram et al., 2009). Another study from a mountainous site in Germany reported no significant correlation of $\gamma(N_2O_5)$ with aerosol compositions and only a weak dependence on humidity (Phillips et al., 2016). However, field measurements at Jinan and Mt. Tai in northern China during the same season also showed a positive relationship of $\gamma(N_2O_5)$ with an RH between 43% and 72% and aerosol water content of 31–65 mol L^{-1}, respectively (Wang X. et al., 2017; Wang Z. et al., 2017). The results of this study and previous reported results in the region may suggest that RH and aerosol water content are the important limiting factors for the N_2O_5 heterogeneous process in the polluted northern China. In summary, the more complex parameterizations considering nitrate, chloride, and the organic coating cannot fully represent the variation of $\gamma(N_2O_5)$ at Wangdu; instead, a simple parameterization that accounts only for temperature and RH appears to explain the variation in $\gamma(N_2O_5)$ at Wangdu. It would be of great interest to determine whether such a phenomenon can be found in other places.

3.4 Factors that affect the $ClNO_2$ production yield

In addition to the uptake coefficients, the factors that influence the branching yield of $ClNO_2$ from the N_2O_5 heterogeneous uptake were also assessed. Figure 7a shows the scatter plot of the ϕ calculated from equation (3) versus the $ClNO_2$ yield derived from the Wangdu field data from equation (5) in Section 3.2. Generally, the $\phi_{param.}$ shows less variability but was obviously overestimated ~~in~~ relative to the field-determined ϕ. Such a discrepancy has also been observed elsewhere (Thonton et al., 2010; Mielke et al., 2013; Riedel et al., 2013), including our recent observations in an urban site (Jinan) and a mountaintop site (Mt. Tai) in northern China, where the parameterized ϕ would be overestimated by up to two orders of magnitude (Wang X. et al., 2017; Wang Z. et al., 2017). Further analysis by linking the field-derived $ClNO_2$ yields with the aerosol water content (Figure 7b) and the Cl^- content (Figure 7c) show a weak positive correlation (r^2 = 0.~~34~~36) and a weak negative trend (r^2 = 0.~~25~~20), respectively (from quadratic fitting). The weak correlations reflect that the $ClNO_2$ yield is not solely controlled by the amount of water and chloride in the aerosol, as defined in the parameterization (see Eq. 3), and/or the existence of other nucleophiles that can compete with Cl^- in reactions R3 and R4. 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.

An interesting observation from Wangdu is that the field-derived ϕ shows a ~~good~~ decreasing trend (r^2 = 0.~~65~~ 58 from quadratic data fitting) with the ratio of acetonitrile to carbon monoxide (CH_3CN/CO), which is an indicator of biomass burning emission (Christian et al., 2003; Akagi et al., 2011), as illustrated in Figure 7d. The ϕ decreased at larger CH_3CN/CO ratios, which corresponds to higher $[Cl^-]$ concentrations per volume of aerosols (c.f. Figure 7c) because biomass burning emits a significant level of chloride particles. The observations here may suggest that the ϕ is likely "suppressed" in air masses influenced by biomass burning, which were frequently observed during the study period (Tham et al., 2016), and is consistent with the recent field observation of much lower concentrations of $ClNO_2$ during the bonfire event in Manchester compared to that after the event (Reyes-Villegas et al., 2017) and with a laboratory experiment which demonstrated that only a small amount (~10%) of reacted N_2O_5 was converted to $ClNO_2$ on the biomass-burning aerosols (Ahern et al., 2017). Another laboratory study showed that the $ClNO_2$ yield can be reduced by as much as 80% in the presence of aromatic organic compounds like phenol and humic acid in the aerosol (Ryder et al., 2015), and previous studies in China reported abundant humic-like substances (e.g., aromatic organic compounds) in aerosols with a large contribution from biomass burning (Fu et al., 2008). Therefore, the frequently observed influence of biomass burning at the Wangdu site during the campaign could in part explain the lower ϕ values and the discrepancy between observation and parameterization. ~~Other factors, such as the nonuniform distribution of chloride within the aerosol, might also contribute to the overestimation of ϕ from the parameterization (Riedel et al., 2013).~~ More studies are needed to investigate the effects of biomass burning emissions on the heterogeneous process.

4 Summary and conclusions

We present an in-depth analysis of the N_2O_5 uptake coefficient and $ClNO_2$ yield in a polluted northern China environment during the summer of 2014. Large variations in the levels of $\gamma(N_2O_5)$ and ϕ were observed during the study, ranging from ~~0.006~~ 0.005 to 0.039~~0.034~~ and from ~~0.07~~ 0.06 to 1.04, respectively. A comparison between the $\gamma(N_2O_5)$ values derived from the field and the parameterizations that considered the nitrate and chloride levels and the hydrophobic organic coating showed poor agreement, suggesting more complex influences of ambient aerosol properties at the site than with the pure or mixed samples used in the laboratory. The $\gamma(N_2O_5)$ values at Wangdu were found to have a clear dependence on the RH and the aerosol water content, a phenomenon that was found in laboratory experiments but has not been ~~reported~~ observed in previous field studies in the United States or Europe. The parameterization that explicitly considers the dependence on RH showed better agreement with the field-derived $\gamma(N_2O_5)$ compared to the more complex formulation that considers the aerosol composition. The $ClNO_2$ yield estimated from the parameterization is generally overestimated when compared to the field derived values. The observed ϕ was found to be "suppressed" in the air masses influenced by biomass burning even though abundant aerosol chloride was present. The results of this study point to the need for more field and laboratory studies to obtain realistic parameterization of the heterogeneous processes of N_2O_5 and $ClNO_2$ to better simulate the ozone and aerosol production in air quality models in regions of China with high NO_x emissions.

Acknowledgment. The authors thank Steven Poon, Qiaozhi Zha, Zheng Xu and Hao Wang for the logistics support, to Liming Cao and Lingyan He for providing the aerosol mass spectrometer data and to Li Zhang for scientific discussion. This work was funded by the National Natural Science Foundation of China (91544213, 41505103 and 41275123), National Key Research and Development Program of China (2016YFC0200500), Research Grants Council of Hong Kong (15265516), PolyU Project of Strategic Importance (1-ZE13) and Research Institute for Sustainable Urban Development (RISUD). The Peking University team acknowledges support from the National Natural Science Foundation of China (21190052) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05010500). The Leibniz Institute for Tropospheric Research team acknowledges funding from the Sino German Science Center (No. GZ663).

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Table 1: N_2O_5 uptake coefficients and $ClNO_2$ production yields from 10 selected plumes at Wangdu during the summer of 2014. The uncertainty (±) of the $\gamma(N_2O_5)$ and ϕ was estimated by the geometric mean of uncertainty from the scattering of the data plots and uncertainty from measurement of N_2O_5, $ClNO_2$, aerosol surface area, and ~~particulate~~ total NO_3^-.

~~Plume~~	~~Date (Time)~~	~~$\gamma(N_2O_5)$~~	~~$\phi(ClNO_2)$~~
~~1~~	~~20 June (23:00) – 21 June (01:20)~~	~~0.029 ± 0.011~~	~~0.54 ± 0.19~~
~~2~~	~~21 June (03:30 – 05:00)~~	~~0.032 ± 0.015~~	~~1.04 ± 0.35~~
~~3~~	~~24 June (20:30 – 22:10)~~	~~0.014 ± 0.008~~	~~0.10 ± 0.05~~
~~4~~	~~24 June (22:30) – 25 June (00:00)~~	~~0.027 ± 0.009~~	~~0.38 ± 0.12~~
~~5~~	~~27 June (20:40) – 28 June (00:00)~~	~~0.011 ± 0.007~~	~~0.15 ± 0.09~~
~~6~~	~~28 June (22:30) – 29 June (00:40)~~	~~0.006 ± 0.002~~	~~0.20 ± 0.06~~
~~7~~	~~29 June (22:00) – 30 June (01:20)~~	~~0.015 ± 0.005~~	~~0.28 ± 0.12~~
~~8~~	~~30 June (21:10) – 1 July (00:10)~~	~~0.019 ± 0.007~~	~~0.18 ± 0.06~~
~~9~~	~~5 July (00:30) – 5 July (02:30)~~	~~0.032 ± 0.019~~	~~0.45 ± 0.27~~
~~10~~	~~5 July (23:40) – 6 July (02:00)~~	~~0.034 ± 0.014~~	~~0.07 ± 0.03~~

Plume	Date (Time)	$\gamma(N_2O_5)$	$\phi(ClNO_2)$
1	20 June (23:00) – 21 June (01:20)	0.032 ± 0.011	0.48 ± 0.17
2	21 June (03:30 – 05:00)	0.030 ± 0.015	1.04 ± 0.35
3	24 June (20:30 – 22:10)	0.013 ± 0.006	0.09 ± 0.05
4	24 June (22:30) – 25 June (00:00)	0.025 ± 0.008	0.44 ± 0.13
5	27 June (20:40) – 28 June (00:00)	0.012 ± 0.007	0.14 ± 0.08
6	28 June (22:30) – 29 June (00:40)	0.005 ± 0.002	0.20 ± 0.06
7	29 June (22:00) – 30 June (01:20)	0.012 ± 0.004	0.36 ± 0.15
8	30 June (21:10) – 1 July (00:10)	0.015 ± 0.006	0.21 ± 0.07
9	5 July (00:30) – 5 July (02:30)	0.039 ± 0.020	0.43 ± 0.26
10	5 July (23:40) – 6 July (02:00)	0.033 ± 0.015	0.06 ± 0.03

Table 2: Summary of field-observed N_2O_5 uptake coefficient and $ClNO_2$ yield from previous studies.

Location	Environment	$\gamma(N_2O_5)$	ϕ	Descriptions	Reference
North America					
New England, US	Coastal + Inland	0.001–0.017	*n.a*	Aircraft measurement (below 1500 m). $\gamma(N_2O_5)$ is higher in elevated sulfate region.	Brown et al., 2006
Coast of Texas, US	Coastal	*n.a*	0.10–0.65	Shipborne measurement. Influenced by urban outflow.	Osthoff et al., 2008
Texas, US	Coastal + Inland	0.0005–0.006	*n.a*	Aircraft measurement (below 1000 m). $\gamma(N_2O_5)$ was independent of humidity (RH, 34% to 85%) and aerosol compositions.	Brown et al., 2009
Seattle, US	Coastal	0.005–0.04	*n.a*	Urban/suburban environment. $\gamma(N_2O_5)$ was enhanced with higher RH but has strong correlation with organic-to-sulfate ratio.	Bertram et al., 2009
Calgary, Canada	Inland	0.02	0.15	Ground urban area. Influenced by anthropogenic activities within the urban area.	Mielke et al., 2011
La Jolla, US	Coastal	0.001–0.029	*n.a*	Polluted coastal site. $\gamma(N_2O_5)$ was suppressed by nitrate.	Riedel et al., 2012b
Coast of Los Angeles, US	Coastal	*n.a*	0.15–0.62	Shipborne measurement. Influenced by land-sea breeze.	Wagner et al., 2012
Pasadena, US	Coastal	$\gamma\phi = 0.008$ (average)		Ground measurement during the California Nexus 2010 campaign. $\gamma\phi$ was enhanced by submicron chloride, but suppressed by organic matter and liquid water content.	Mielke et al., 2013
Boulder, US	Inland	0.002–0.1	0.01–0.98	Tower measurement (0-300 m) downwind of urban city. $\gamma(N_2O_5)$ dependence on nitrate. Higher ϕ in coal combustion plume.	Wagner et al., 2013 Riedel et al., 2013
Europe					
London	Coastal + Inland	0.01–0.03	*n.a*	Aircraft measurement (500-1000 m). $\gamma(N_2O_5)$ was independent of humidity (RH, 50% to 90%) but dependent on nitrate loading.	Morgan et al., 2015
Kleiner Feldberg	Inland	0.004–0.11	0.029–1.38	Semirural mountain-top site in SW Germany (825 m above sea level). $\gamma(N_2O_5)$ was independent of aerosol compositions but has a weak dependence on humidity.	Phillips et al., 2016
China					

Hong Kong	Coastal	0.004–0.021	0.02–0.98	Rural mountain-top site in southern China (957 m above sea level). Influenced by pollution from urban area.	Brown et al., 2016 Yun et al., 2018
Jinan	Inland	0.042–0.092	0.01–0.08	Urban-surface in polluted urban area of northern China. $\gamma(N_2O_5)$ showed positive dependence on RH.	Wang X. et al., 2017
Mt. Tai	Inland	0.021–0.103	0.17–0.90	Mountaintop site in northern China (1465 m above sea level). Elevated $\gamma(N_2O_5)$ for high humidity (>80%) condition. Higher ϕ in coal-fired power plant plumes.	Wang Z. et al., 2017
Beijing-urban	Inland	0.025−0.072	*n.a*	Polluted urban surface-site in northern China during early autumn. High $\gamma(N_2O_5)$ was related to high aerosol liquid water content.	Wang H. et al., 2017
Beijing-rural	Inland	0.012–0.055	0.50–1.00	Rural surface site in northern of Beijing. Influenced by the outflow of the urban Beijing.	Wang H. et al., 2018
Wangdu	Inland	~~0.006~~0.005–~~0.034~~0.039	~~0.07~~0.06–1.04	Semirural and surface site in northern China. $\gamma(N_2O_5)$ has strong dependence on humidity and aerosol water content. Variable ϕ and lower values for cases influenced by biomass burning activities.	This study

n.a = no information available

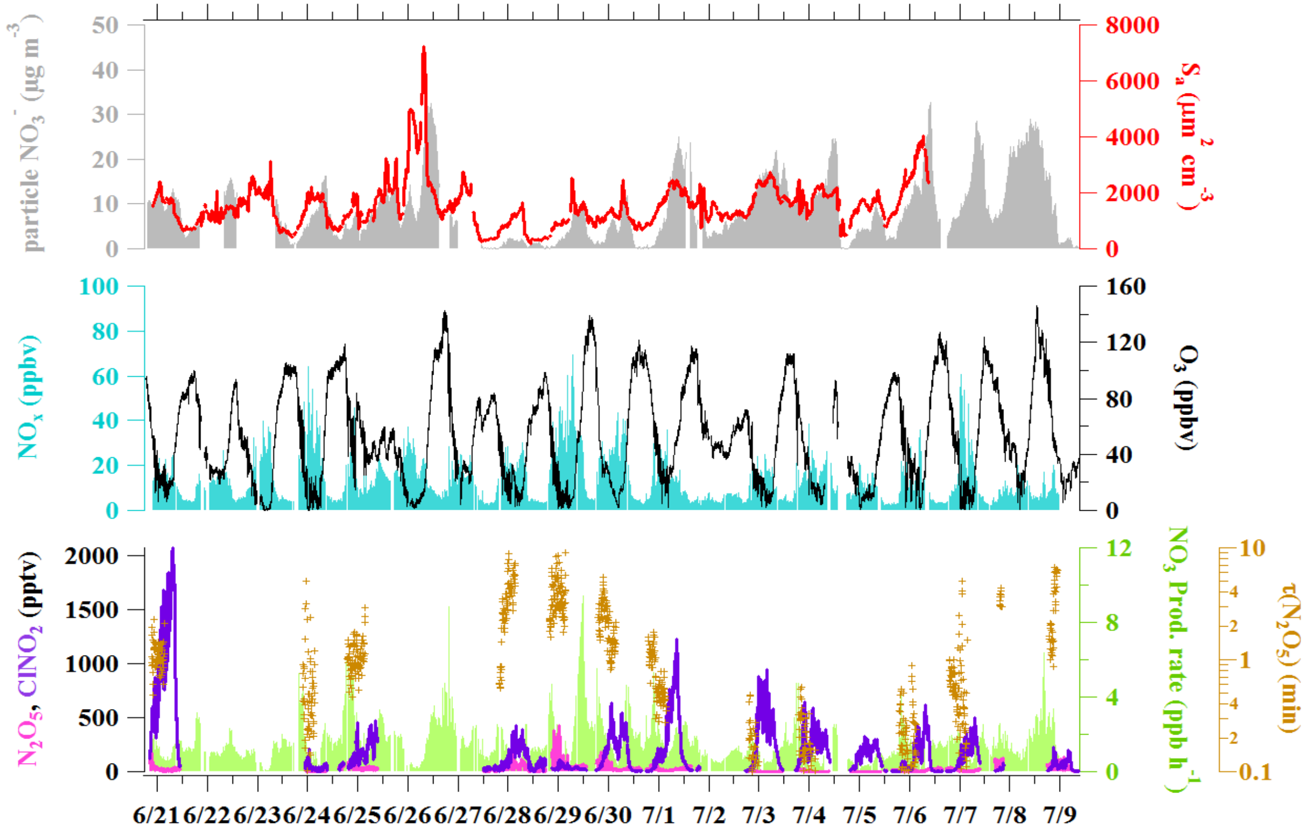
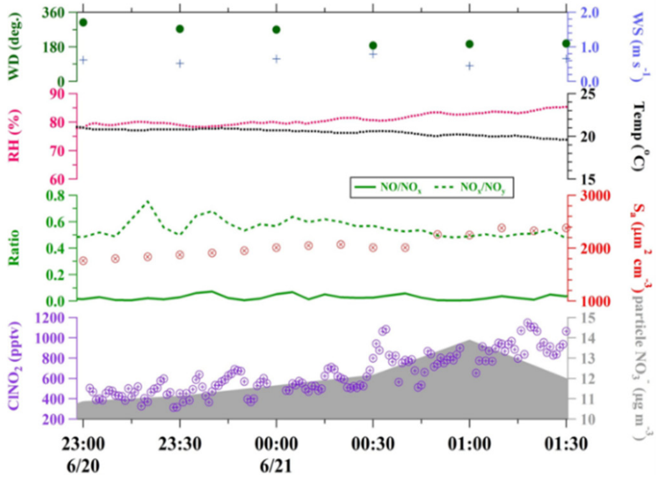
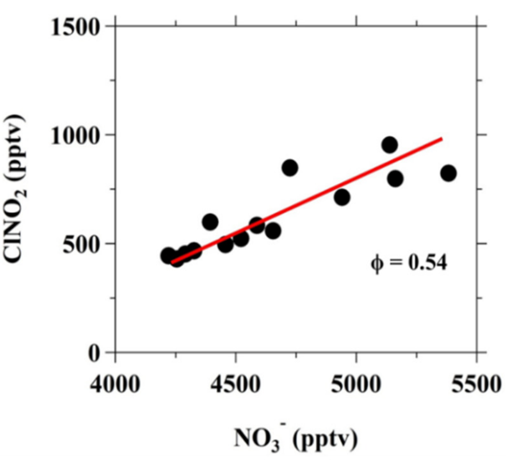


Figure 1: Time series of N_2O_5, $ClNO_2$, NO_3 production rate, the steady-state lifetime of N_2O_5, O_3, NO_x, fine particulate NO_3^-, and S_a data at Wangdu from 21 June to 9 July 2014. N_2O_5 and $ClNO_2$ are 1-min data, whereas the NO_x, O_3, NO_3 production rate and $\tau(N_2O_5)$ are given as 5-min averages. The data for S_a and fine particulate NO_3^- are in 10-min and 30-min time resolutions, respectively. The data gaps were caused by technical problems, calibrations, or instrument maintenance.

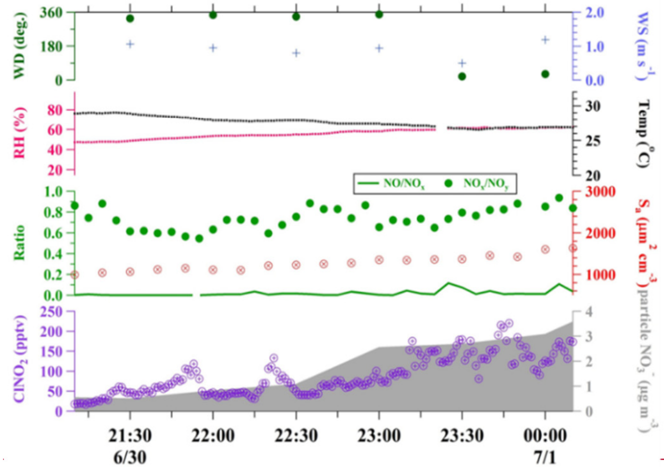
(a)


WD (deg.)
360
180
0
WS (m s-1)
2.0
1.0
0.0
RH (%)
90
80
70
60
Temp (°C)
25
20
15
NO/NOx
NO2/NOy
Ratio
0.8
0.6
0.4
0.2
0.0
Sa (μm2 cm-3)
3000
2000
1000
ClNO2 (pptv)
1200
1000
800
600
400
200
particle NO3- (μg m-3)
15
14
13
12
11
10
23:00
6/20
23:30
00:00
6/21
00:30
01:00
01:30

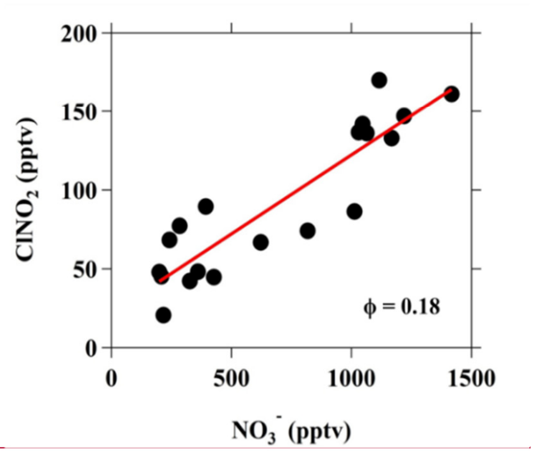
(b)


ClNO2 (pptv)
1500
1000
500
0
NO3- (pptv)
4000
4500
5000
5500
ϕ = 0.54

(c)


WD (deg.)
360
180
0
WS (m s-1)
2.0
1.0
0.0
RH (%)
80
60
40
20
Temp (°C)
30
25
20
NO/NOx
NO2/NOy
Ratio
1.0
0.8
0.6
0.4
0.2
0.0
Sa (μm2 cm-3)
3000
2000
1000
ClNO2 (pptv)
250
200
150
100
50
0
particle NO3- (μg m-3)
4
3
2
1
0
21:30
6/30
22:00
22:30
23:00
23:30
00:00
7/1

(d)


ClNO2 (pptv)
200
150
100
50
0
NO3- (pptv)
0
500
1000
1500
ϕ = 0.18

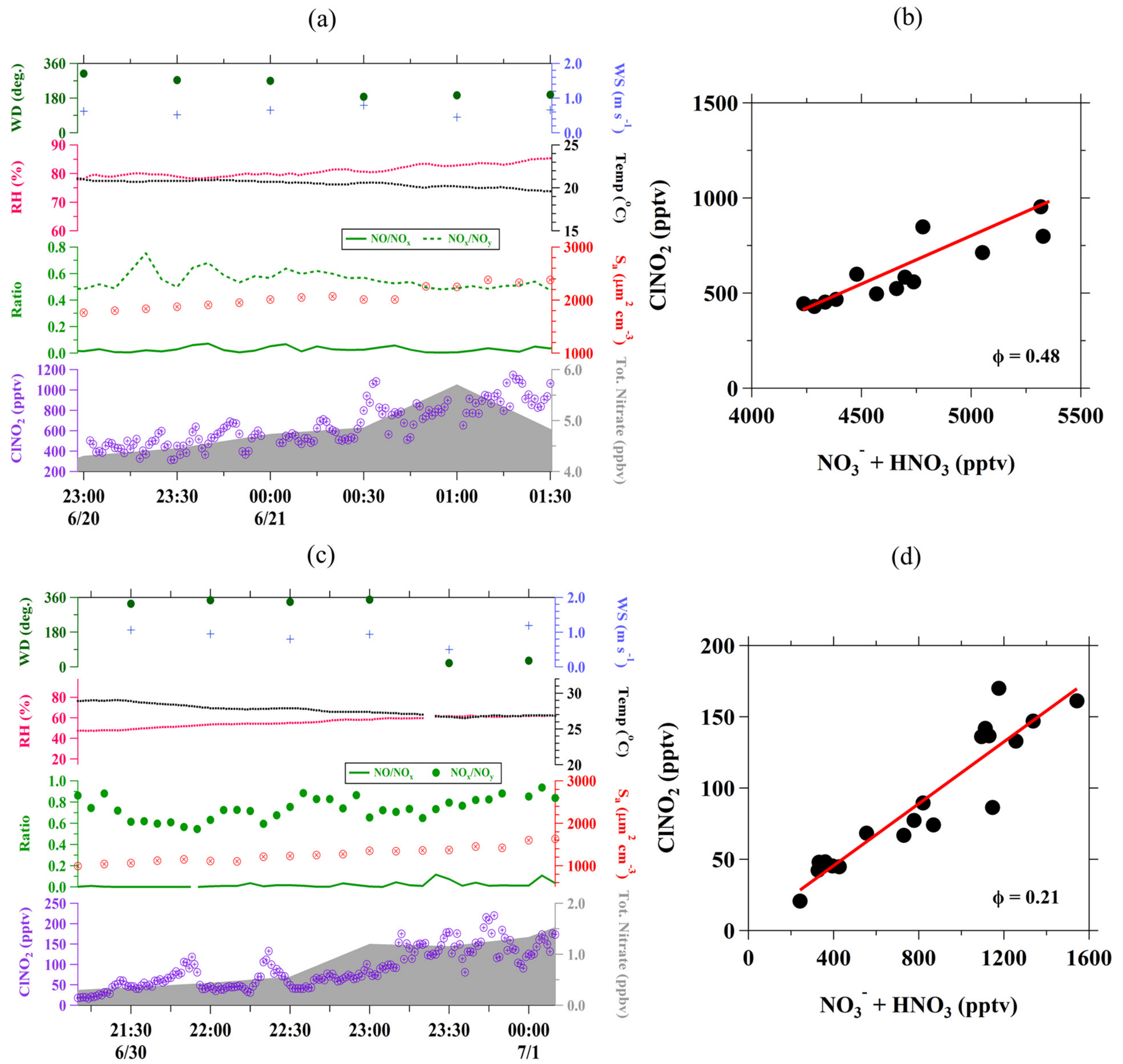
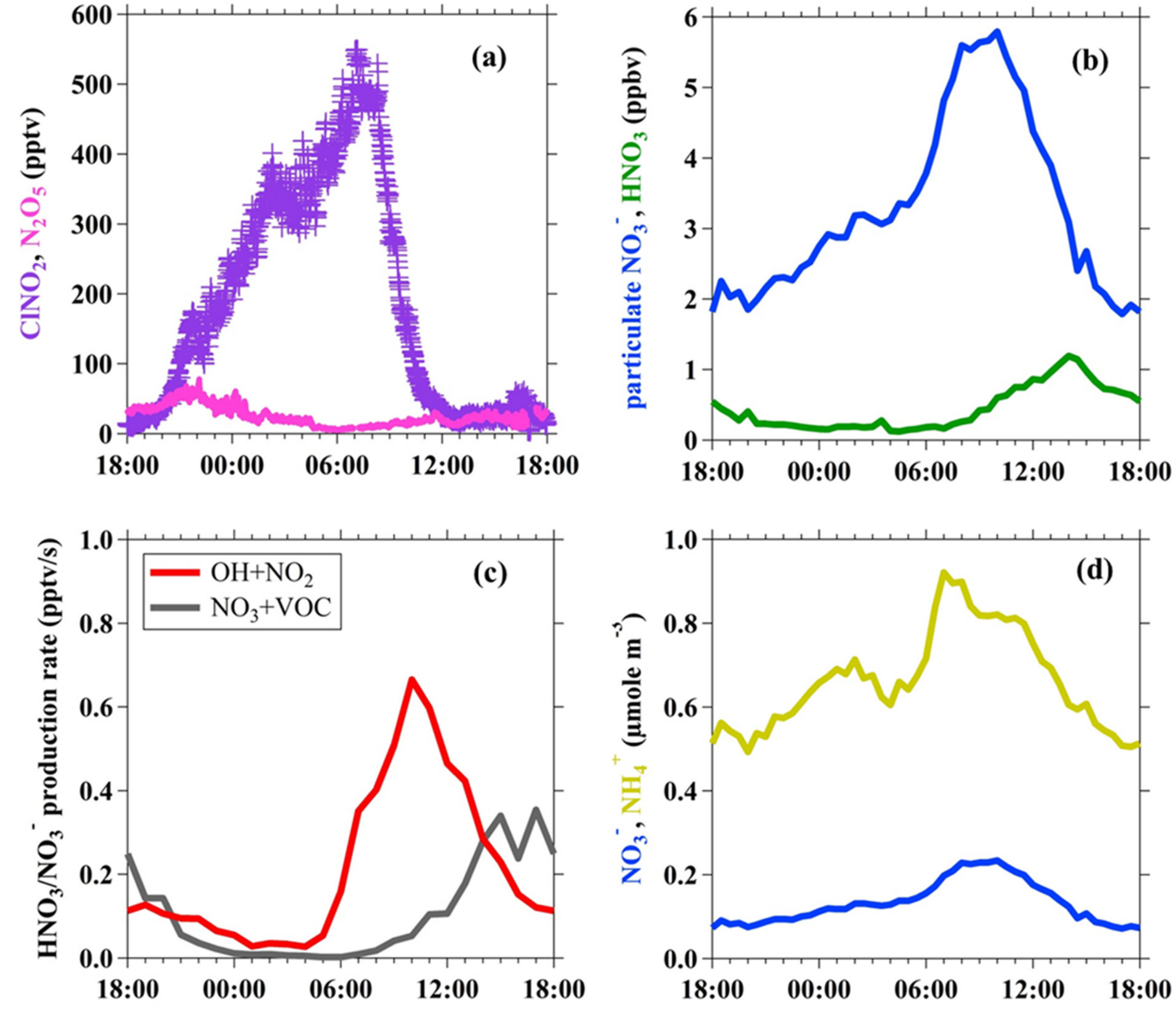


Figure 2: Example of the accumulation of $ClNO_2$ and total nitrate (particulate NO_3^- + HNO_3) concentrations during the relatively constant condition of relevant chemical compositions and environmental variables observed for (a) Plume 1 on 20-21 June 2014 and (c) Plume 7 on 29-30 June 2014. Scatter plots of $ClNO_2$ versus particulate NO_3^- + HNO_3 to estimate the $ClNO_2$ yield (ϕ) for these two cases are shown in (c) and (d).


(a)
$ClNO_2$, N_2O_5 (pptv)
600
500
400
300
200
100
0
18:00
00:00
06:00
12:00
18:00
(b)
particulate NO_3^-, HNO_3 (ppbv)
6
5
4
3
2
1
0
18:00
00:00
06:00
12:00
18:00
(c)
$OH+NO_2$
NO_3+VOC
HNO_3/NO_3^- production rate (pptv/s)
1.0
0.8
0.6
0.4
0.2
0.0
18:00
00:00
06:00
12:00
18:00
(d)
NO_3^-, NH_4^+ (µmole m^{-3})
1.0
0.8
0.6
0.4
0.2
0.0
18:00
00:00
06:00
12:00
18:00

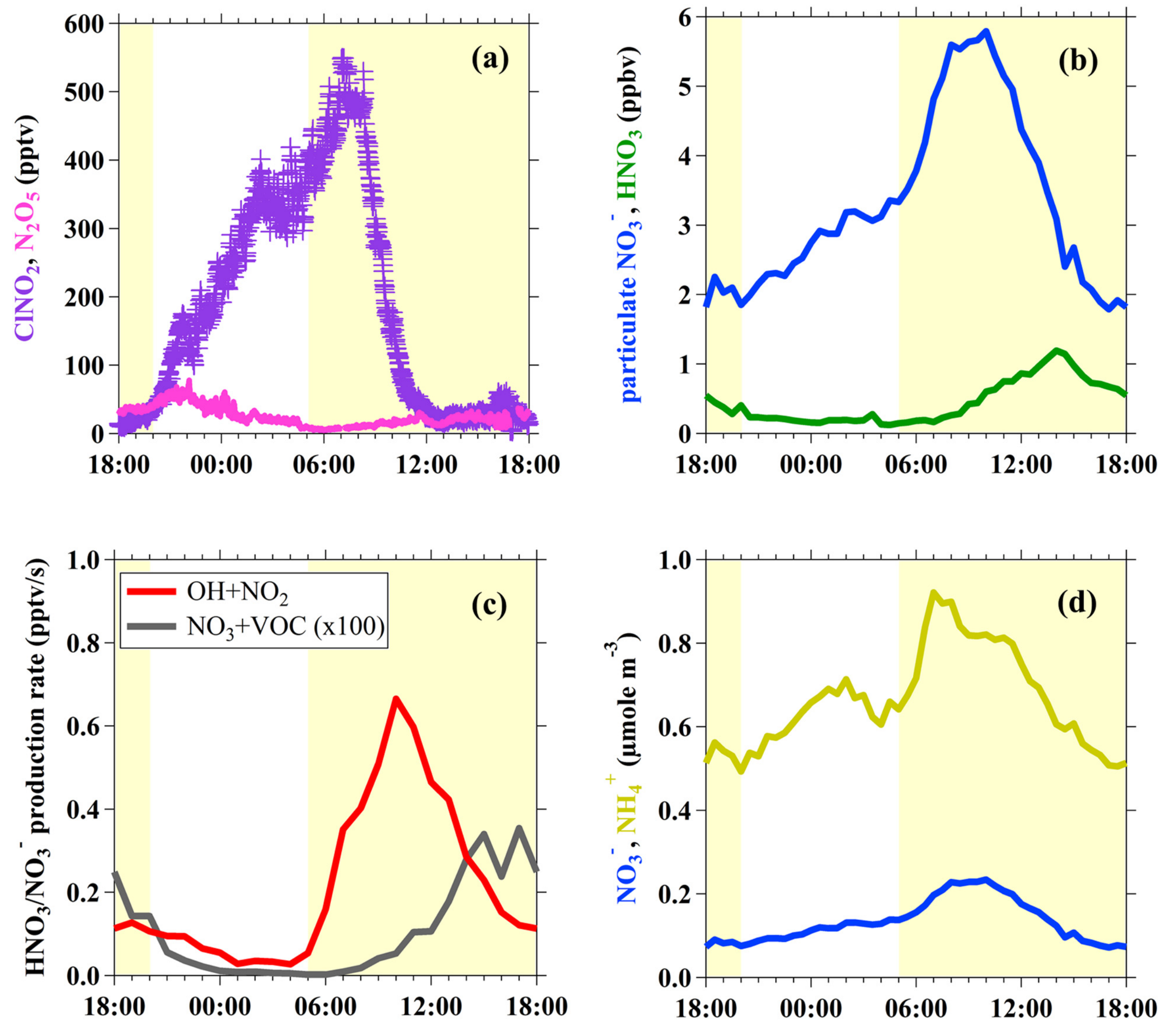
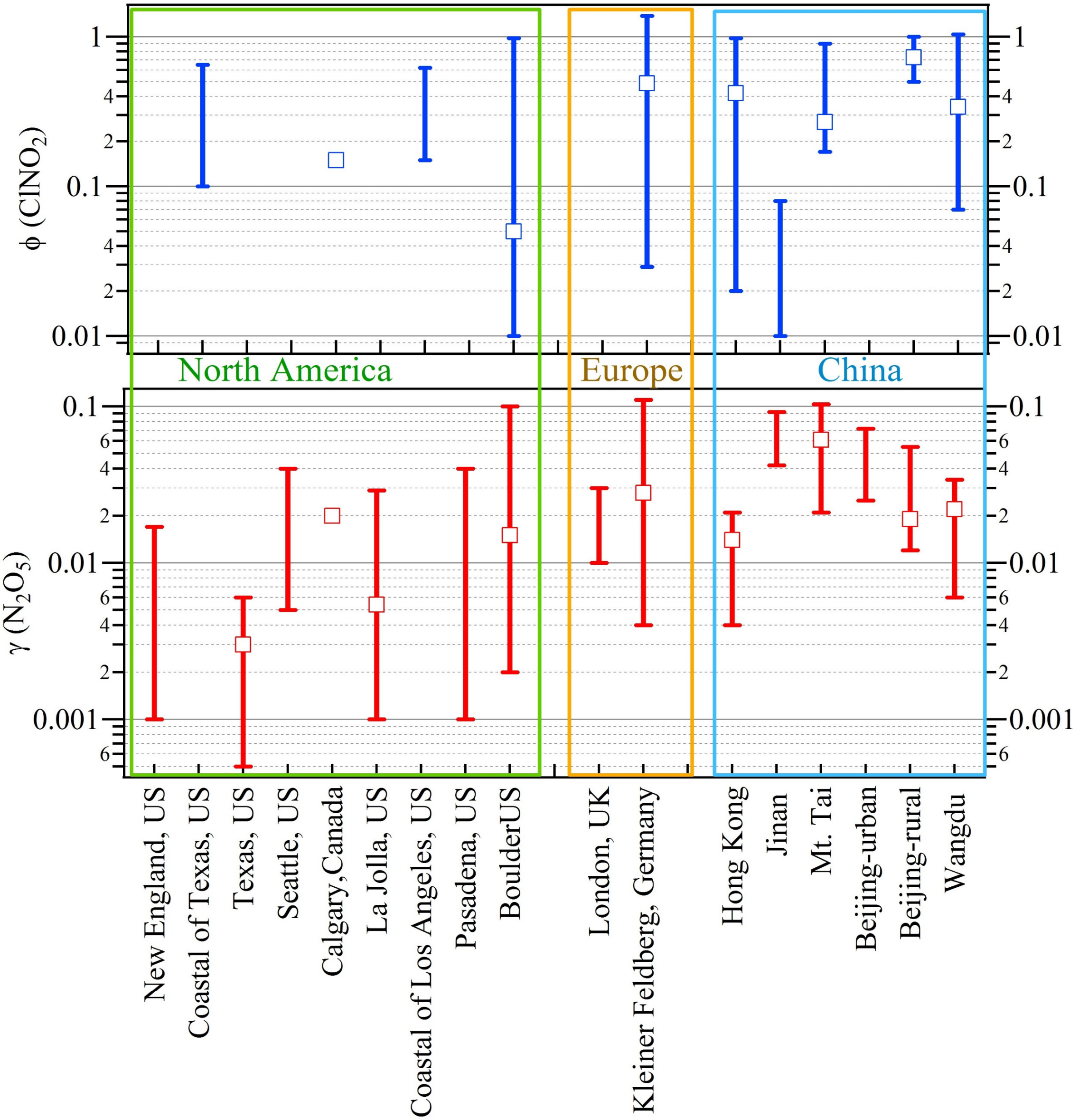


Figure 3: Diurnal variations of (a) N_2O_5 and $ClNO_2$; b) particulate NO_3^- and gas-phase HNO_3 (c) gas-phase production rate of NO_3^-/HNO_3 via reaction of $OH+NO_2$ and NO_3+VOC; and (d) concentrations of NH_4^+ in relation to particulate NO_3^-. The time indicated in x-axis is the local time and the shaded area (yellow) represent the daytime.


ϕ (ClNO$_2$)
1
4
2
0.1
4
2
0.01
North America
Europe
China
γ (N$_2$O$_5$)
0.1
6
4
2
0.01
6
4
2
0.001
6
New England, US
Coastal of Texas, US
Texas, US
Seattle, US
Calgary,Canada
La Jolla, US
Coastal of Los Angeles, US
Pasadena, US
BoulderUS
London, UK
Kleiner Feldberg, Germany
Hong Kong
Jinan
Mt. Tai
Beijing-urban
Beijing-rural
Wangdu

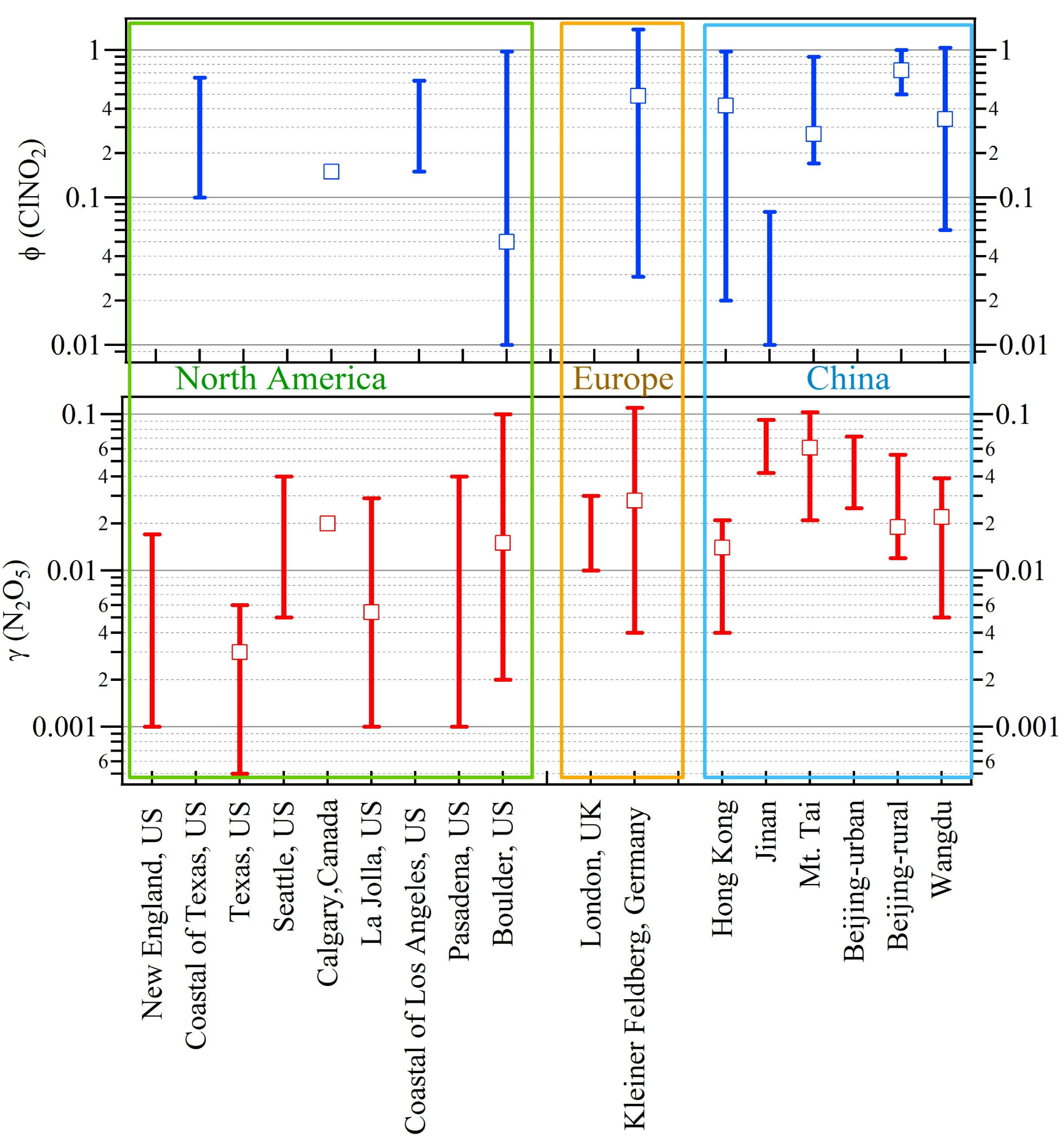
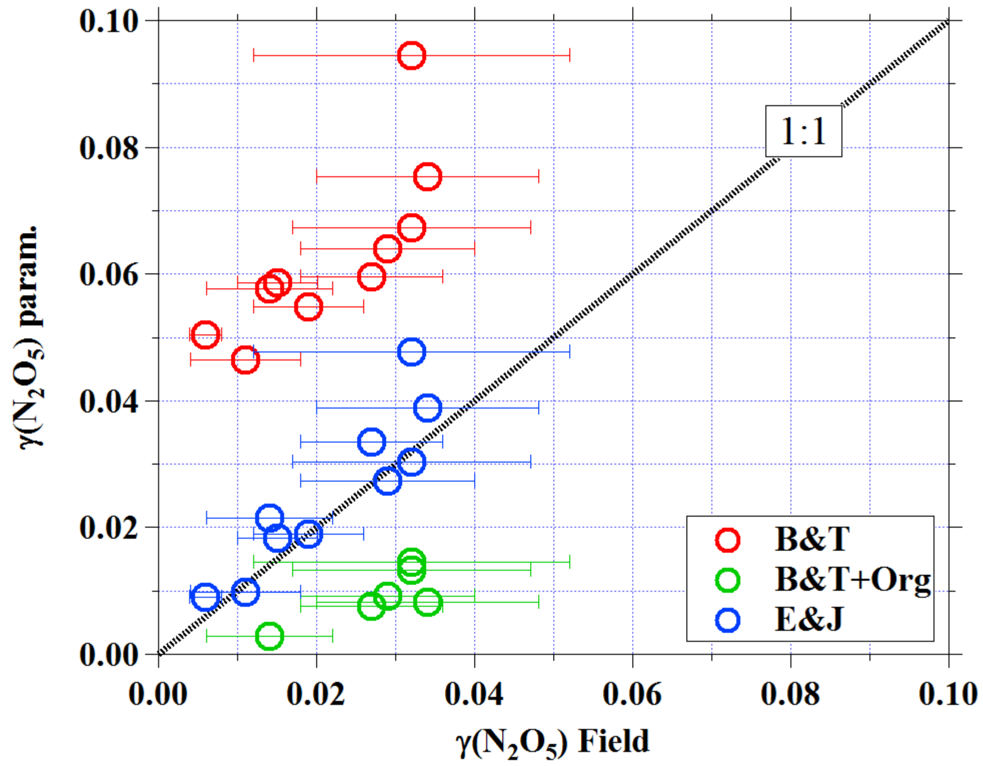


Figure 4: Comparison of field-observed N_2O_5 uptake coefficient and $ClNO_2$ yield from previous studies. Sticks represent the range of the reported values, and cubes represent the median or average values reported in these measurements. The corresponding references are listed in Table 2.


0.10
0.08
0.06
0.04
0.02
0.00
γ(N₂O₅) param.
0.00
0.02
0.04
0.06
0.08
0.10
γ(N₂O₅) Field
1:1
B&T
B&T+Org
E&J

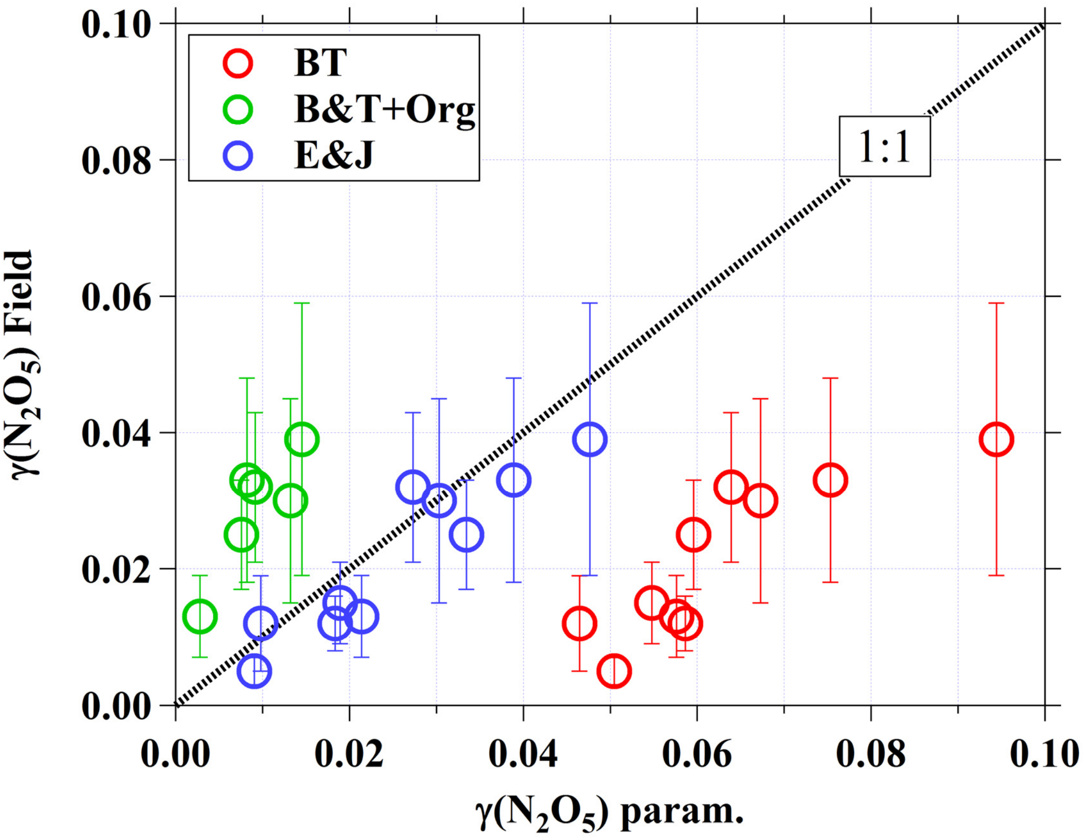
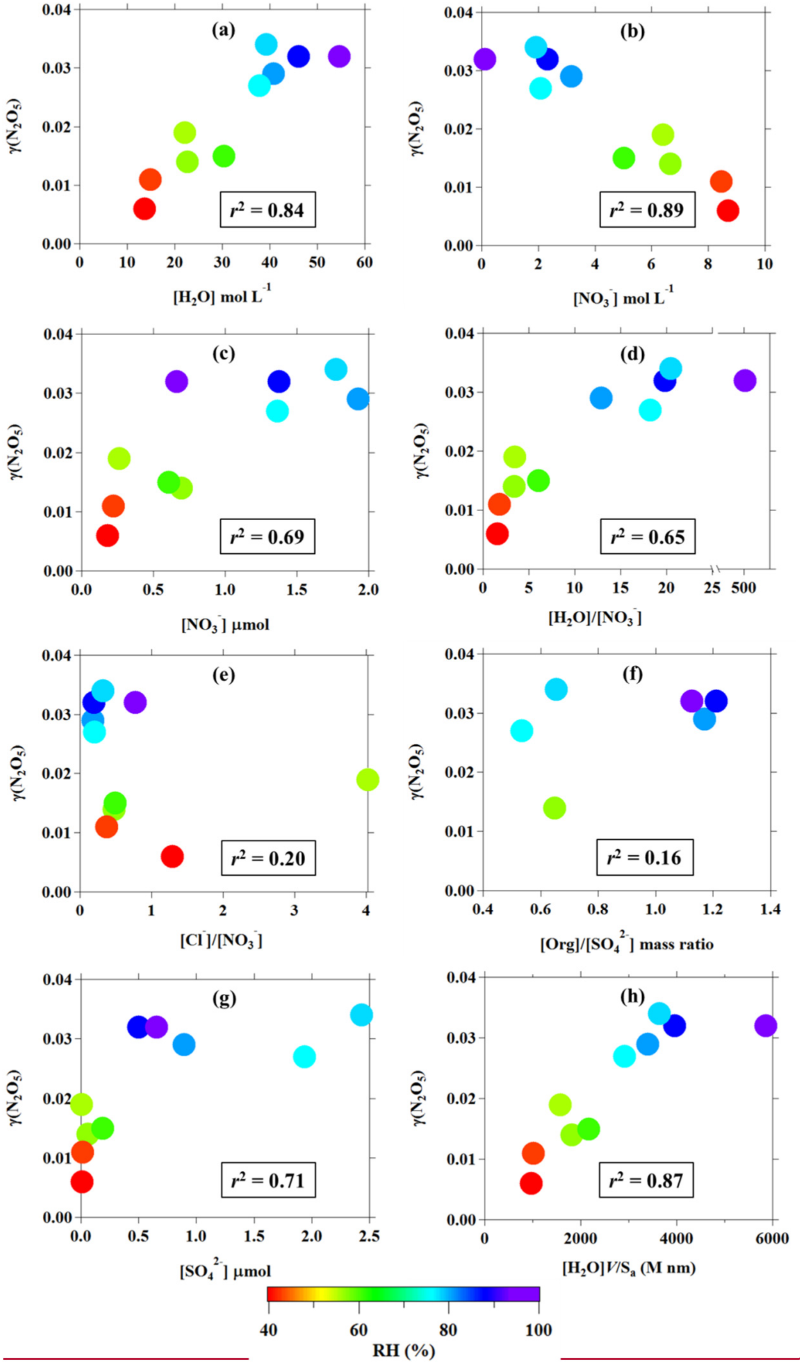


Figure 5: Comparison of field-derived N_2O_5 uptake coefficients with values computed from different parameterizations. The dashed line represents 1:1, and the error bars show the uncertainty of γ(N_2O_5) derived from the field.


(a)
$\gamma(N_2O_5)$
$[H_2O]$ mol L^{-1}
$r^2 = 0.84$
(b)
$[NO_3^-]$ mol L^{-1}
$r^2 = 0.89$
(c)
$[NO_3^-]$ µmol
$r^2 = 0.69$
(d)
$[H_2O]/[NO_3^-]$
$r^2 = 0.65$
(e)
$[Cl^-]/[NO_3^-]$
$r^2 = 0.20$
(f)
$[Org]/[SO_4^{2-}]$ mass ratio
$r^2 = 0.16$
(g)
$[SO_4^{2-}]$ µmol
$r^2 = 0.71$
(h)
$[H_2O]V/S_a$ (M nm)
$r^2 = 0.87$
40
60
80
100
RH (%)

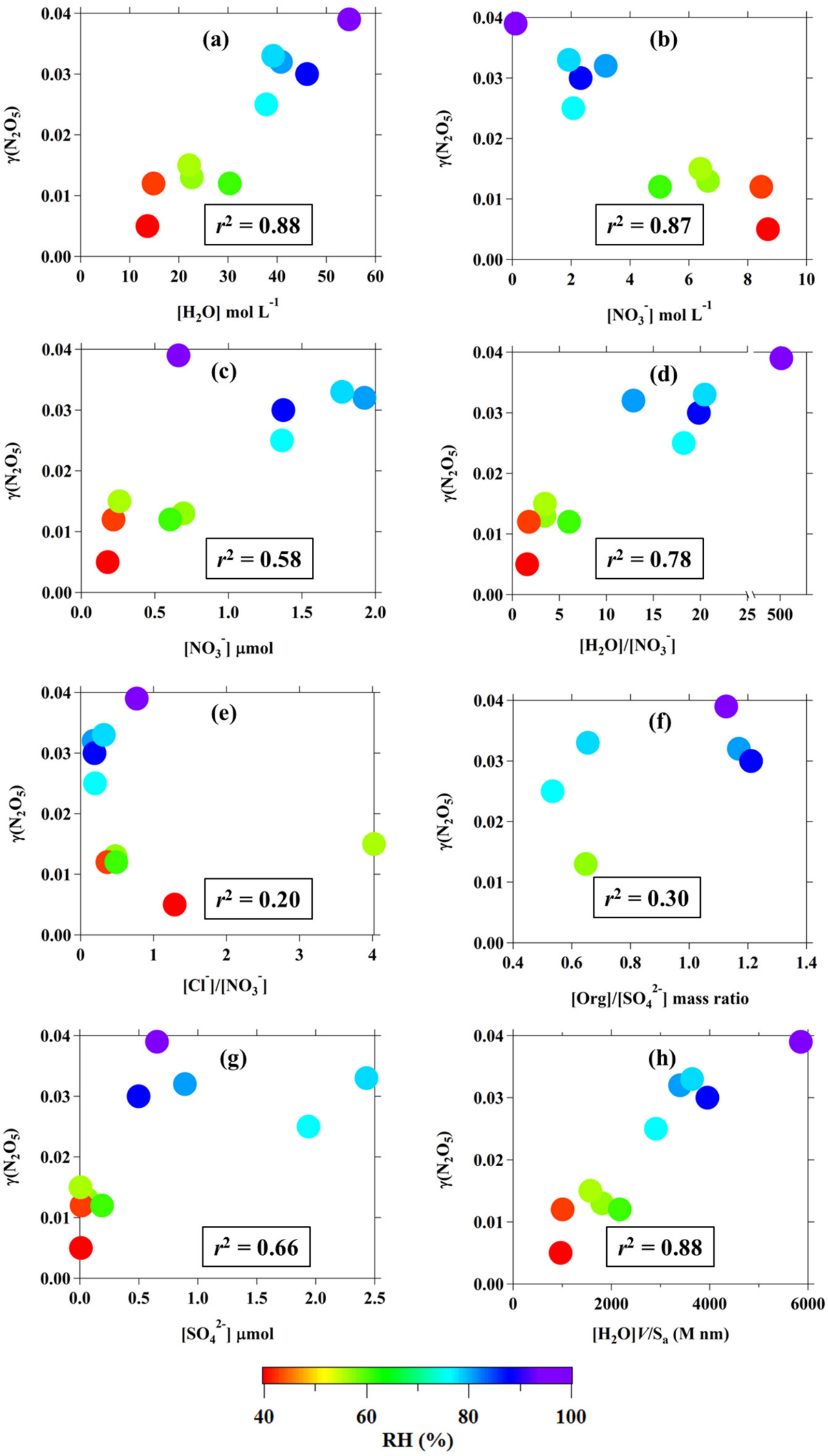
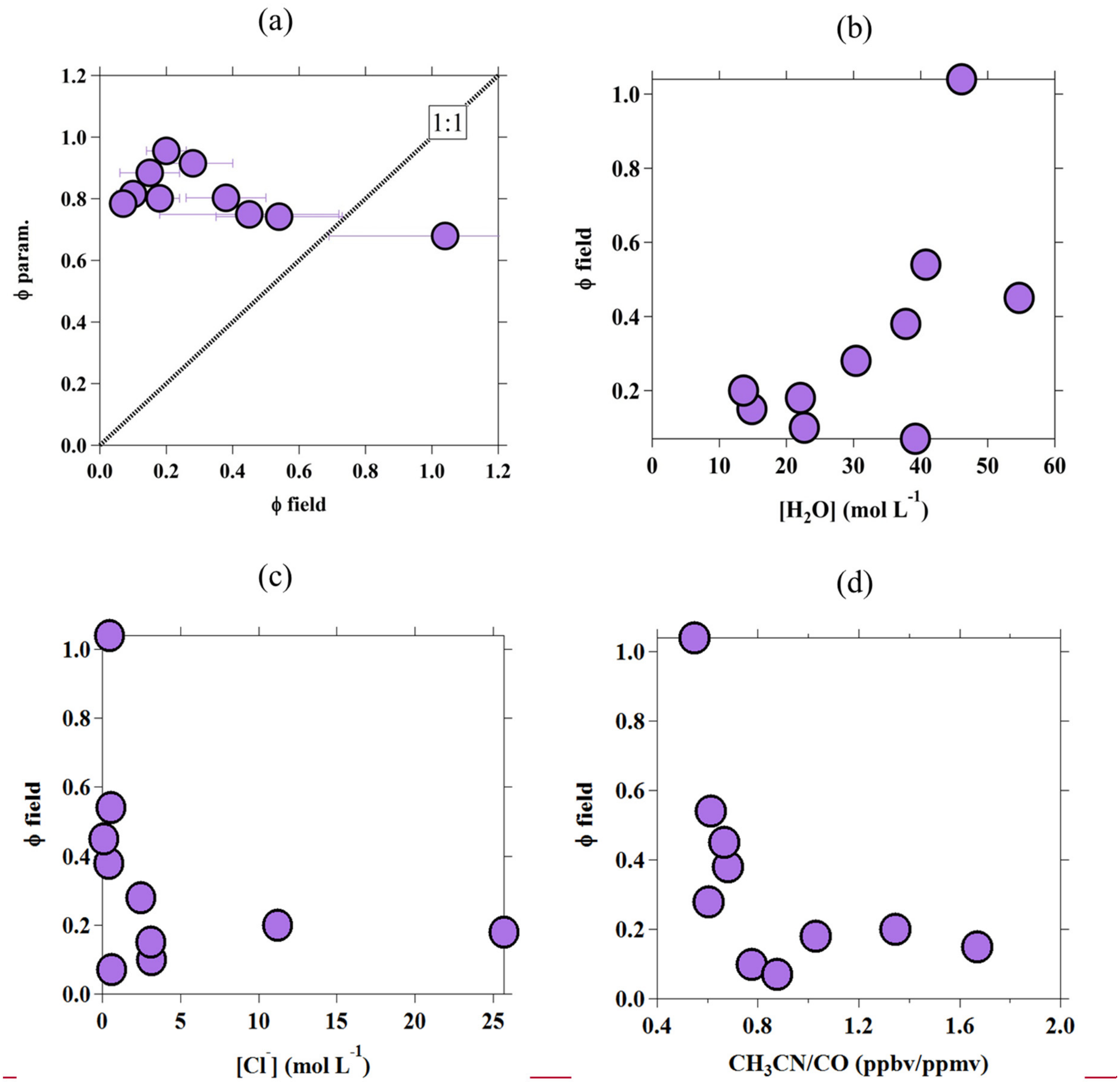

(a)
$r^2 = 0.88$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0
10
20
30
40
50
60
$[H_2O]$ mol L^{-1}
(b)
$r^2 = 0.87$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0
2
4
6
8
10
$[NO_3^-]$ mol L^{-1}
(c)
$r^2 = 0.58$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0.0
0.5
1.0
1.5
2.0
$[NO_3^-]$ µmol
(d)
$r^2 = 0.78$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0
5
10
15
20
25
500
$[H_2O]/[NO_3^-]$
(e)
$r^2 = 0.20$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0
1
2
3
4
$[Cl^-]/[NO_3^-]$
(f)
$r^2 = 0.30$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0.4
0.6
0.8
1.0
1.2
1.4
$[Org]/[SO_4^{2-}]$ mass ratio
(g)
$r^2 = 0.66$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0.0
0.5
1.0
1.5
2.0
2.5
$[SO_4^{2-}]$ µmol
(h)
$r^2 = 0.88$
$\gamma(N_2O_5)$
0.00
0.01
0.02
0.03
0.04
0
2000
4000
6000
$[H_2O]V/S_a$ (M nm)
40
60
80
100
RH (%)

Figure 6: **Relationship between field-derived γ(N_2O_5) and a) aerosol water content (mol per volume of aerosol); b) nitrate concentration per volume of aerosol; c) particulate nitrate concentration (μmol m^{-3} of air); d) H_2O to NO_3^- molar ratio; e) Cl^- to NO_3^- molar ratio; f) organic-to-sulfate mass ratio (data from aerosol mass spectrometer); g) concentration of SO_4^{2-} (μmol m^{-3} of air); and h) amount of water in aerosol multiplied by the volume-to-surface area ratio. Color code represents the ambient RH, and the value in the box is the best correlation coefficient obtained from curve fittings.**



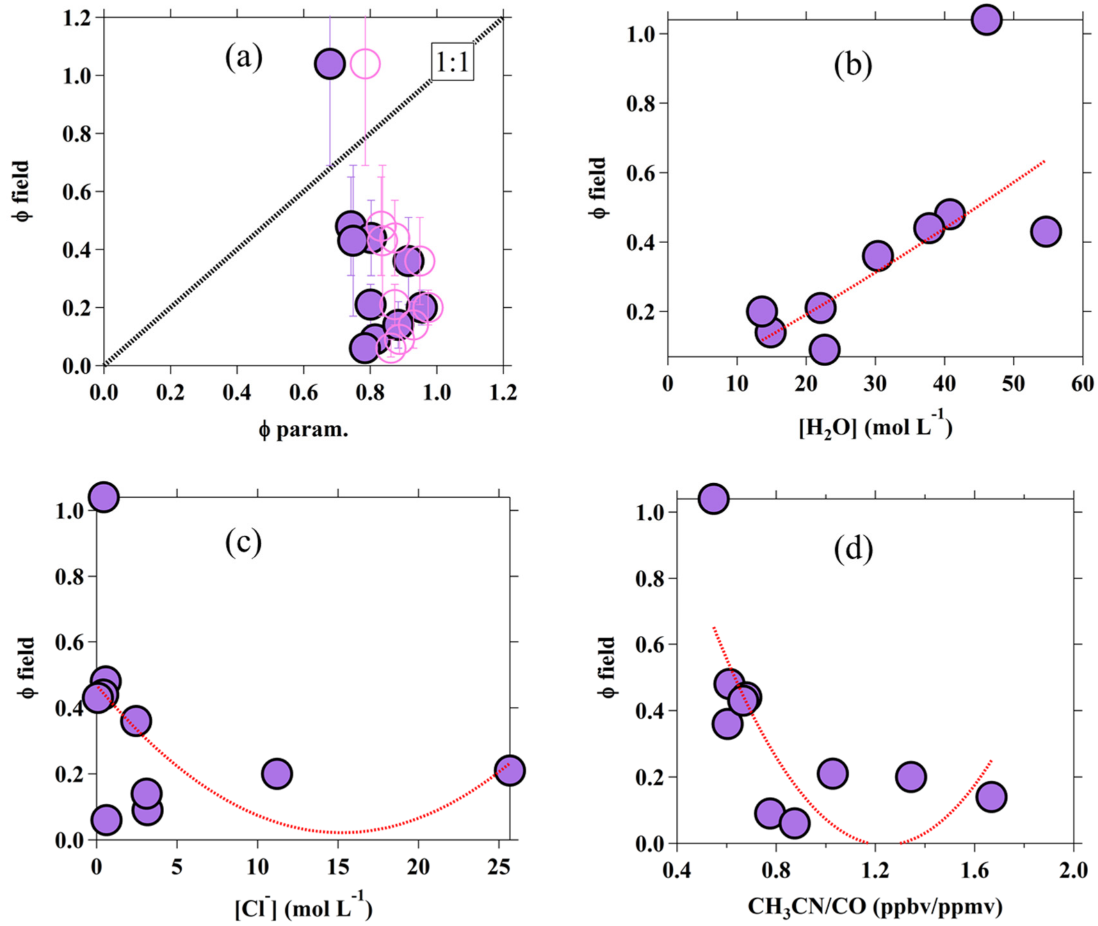


Figure 7: Scatter plots for (a) yield derived from the field versus yield calculated from the parameterization, using k_{R4}/k_{R3} of 483 (recommended by Bertram and Thornton, 2009; solid circle) and 836 (recommended by Behnke et al., 1997; pink open circle). ~~(e~~Error bars represent the uncertainty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