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.

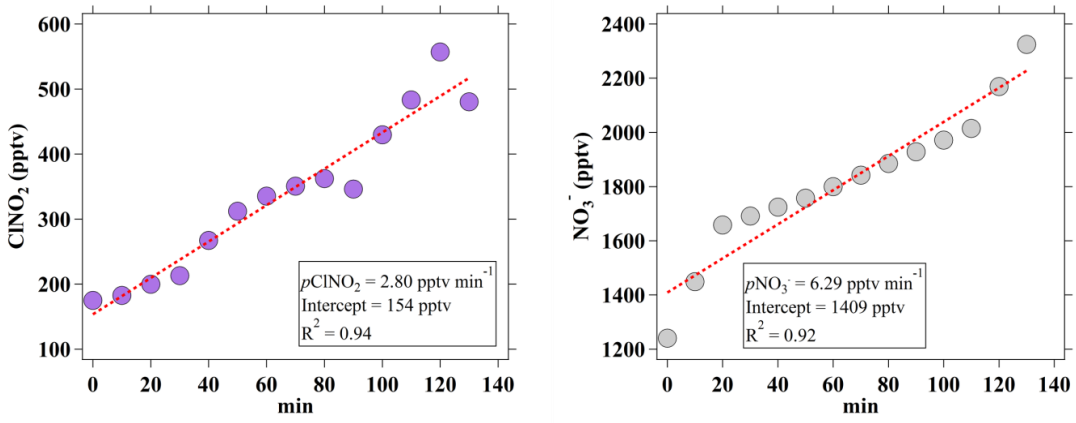
Page 5, lines 25-26: Are the quoted average production rates of NO3 for nighttime only for nighttime and daytime?

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$_2$O$_5$, which can bias the estimation of γ(N$_2$O$_5$)."

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.

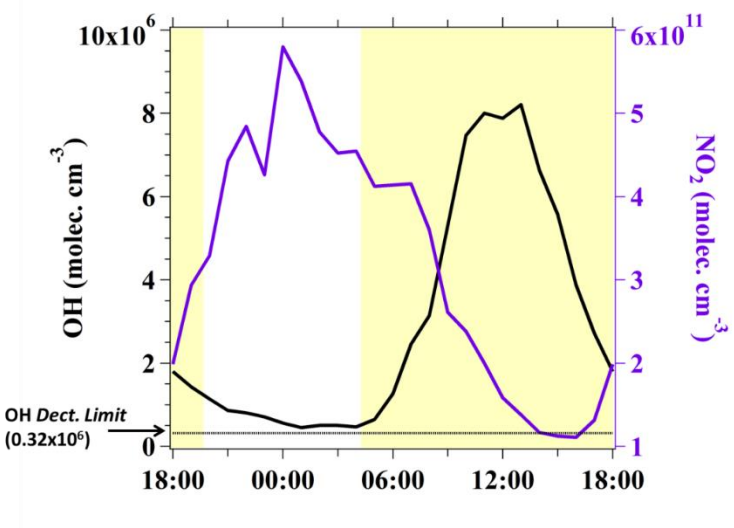
Response: Yes, we agree with the reviewer that the photochemical soluble nitrate production may not affect the results. As for the partitioning, the gas-phase HNO_3 measurement showed that it is only 7% (on average) of the total NO_3^- during the nighttime (see Figure 3b in the main text), suggesting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

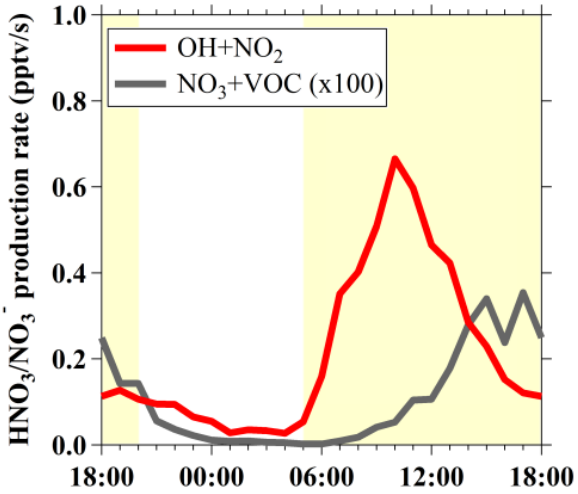
Reaction	**Products**	***k* (cm^3 molecule^{-1} s^{-1} at 25° C)**
$NO_3 + C_2H_6$	$\cdot C_2H_5 + HNO_3$	1.0×10^{-17} [a]
$NO3 + C_3H_6$	$\cdot CH_2CH{=}CH_2 + HNO_3$	4.8×10^{-16} [b]
$NO3 + C_3H_8$	$\cdot CH_3CH_2CH + HNO_3$ $\cdot CH_3CHCH_3 + HNO_3$	7.0×10^{-17} [a]
$NO_3 + HCHO$	$\cdot HCO + HNO_3$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

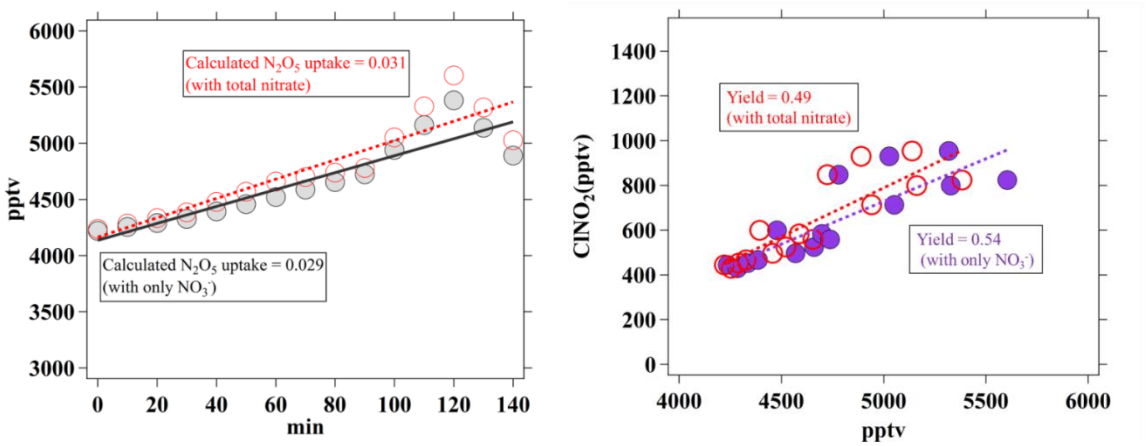
The revised Figure 3c as below:



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.