Anonymous Referee #2

The paper reports on measurements of N2O5 and ClNO2 on a mountain top site in the North China Plane (NCP), and examines the chemistry of N2O5 to ClNO2 conversion in power plant plumes that were observed during the project. This study is a very useful addition to the growing literature on this important chlorine activation pathway. In general the paper is clear and very well written and should be publishable pending the handling of the following comments and questions.

We thank the reviewer for the valuable feedback, and we have revised the manuscript according to the comments. Our responses, including changes made to the manuscript, are listed below.

Reviewer comments are in italics. Author responses are in plain face. Changes to the text are in blue.

General Comments

1. *I would like to see a better description of the aerosol particle characteristics and chemistry. For example, surface area, organic fraction, in addition to nitrate and chloride could be included in Figure 1. This would be particularly useful since this is likely the major difference between the environment in this study relative to the studies in Europe or North America.*

Response: We thank the reviewer for the valuable suggestion. Additional description and discussion of the aerosol characteristic are included in the revised text. The time series of measured aerosol nitrate, sulfate, chloride and surface area was also added in the revised Figure 2, as follows:

"The average nighttime mixing ratios of O_3 and NO_2 were 77 and 3.0 ppbv, respectively, with an average nitrate radical production rate $p(NO_3)$ of 0.45 ± 0.40 ppb h^{-1}, which is indicative of potentially active NO_3 and N_2O_5 chemistry during the study period. However, the low N_2O_5 mixing ratios observed during most of the nights suggest a rapid loss of N_2O_5, which is consistent with the observed high aerosol surface area (Sa), varied from ~100 to 7800 μm^2 cm^{-3} with a mean value of 1440 μm^2 cm^{-3}."

"The elevated $ClNO_2$ levels observed at Mt. Tai are similar to recent measurements at a surface rural site (Wangdu) in northern China (Tham et al., 2016) and a mountain site (Tai Mo Shan) in southern China (Wang et al., 2016), but are slightly higher than previous measurements conducted in coastal (e.g., Osthoff et al., 2008; Riedel et al., 2012; Mielke et al., 2013) and inland sites (e.g., Thornton et al., 2010; Phillips et al., 2012; Riedel et al., 2013) in other regions of the world. During the campaign at Mt. Tai, the average concentrations of aerosol sulfate and nitrate were 14.8 ± 9.0 and 6.0 ± 4.7 μg m^{-3}, accounting for 29.5% and 12.0% of $PM_{2.5}$ mass, respectively. The aerosol organic-to-sulfate ratio, a parameter that potentially affects the uptake process (Bertram et al., 2009b), was 0.74 on average and much lower than those from studies mentioned above in Europe and US. Moreover, the nighttime averaged Cl^- concentration was 0.89 ± 0.86 μg cm^{-3}, and was an order of magnitude higher than Na^+, indicating abundant non-oceanic sources of chloride (e.g., from coal combustion and biomass burning in the NCP) (Tham et al., 2016), which could enhance the production of $ClNO_2$."

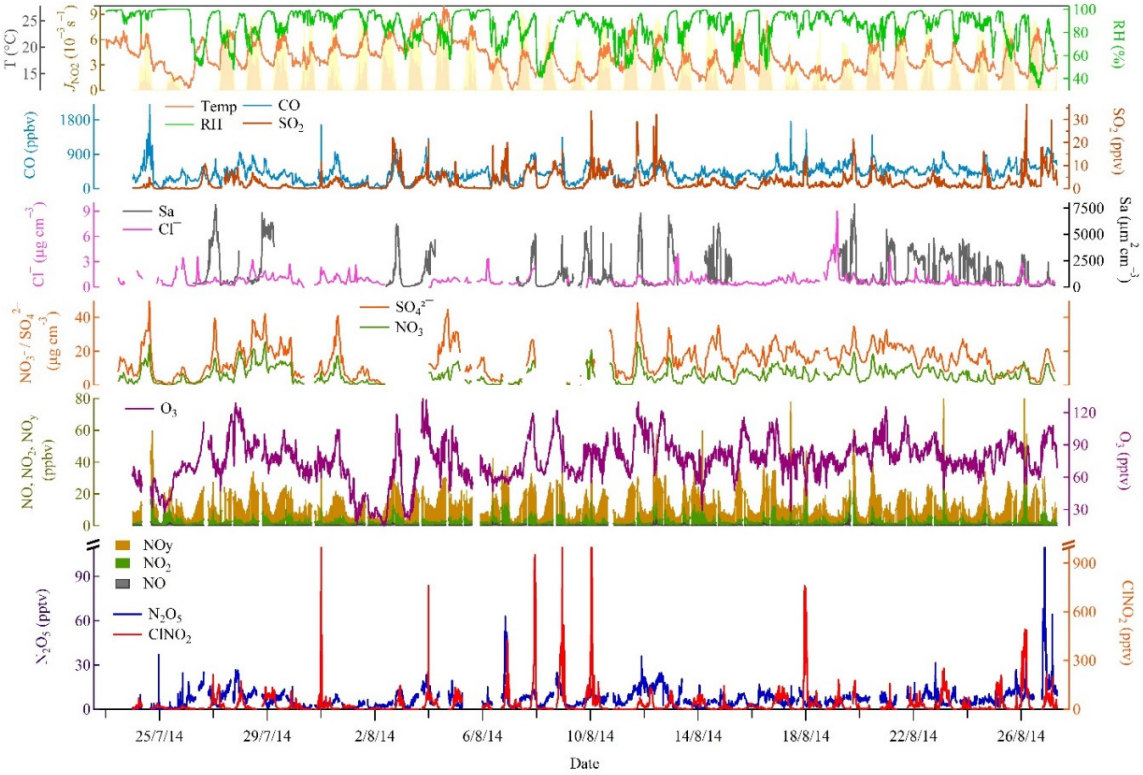

Figure 2 : Time series for N_2O_5, $ClNO_2$, related trace gases, aerosol properties, and meteorological data measured at Mt. Tai from July 24 to August 27, 2014.

References:

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, 2016.

2. *It would also be helpful if instead of mass concentration, some of the correlations in figures (Figure 11, Figure S1) could be also done with molar concentration, which is how the lab studies (Bertram and Thornton,2009, Roberts et al, 2009) were parameterized.*

Response: We changed the aerosol nitrate and chloride concentrations in the supplement figures to molar concentrations, as shown below. For the Figure 11, it was intended to compare the predicted nitrate concentration with the measured increase of nitrate concentration, so we think the comparison in mass concentration is straightforward and just keep it as before.

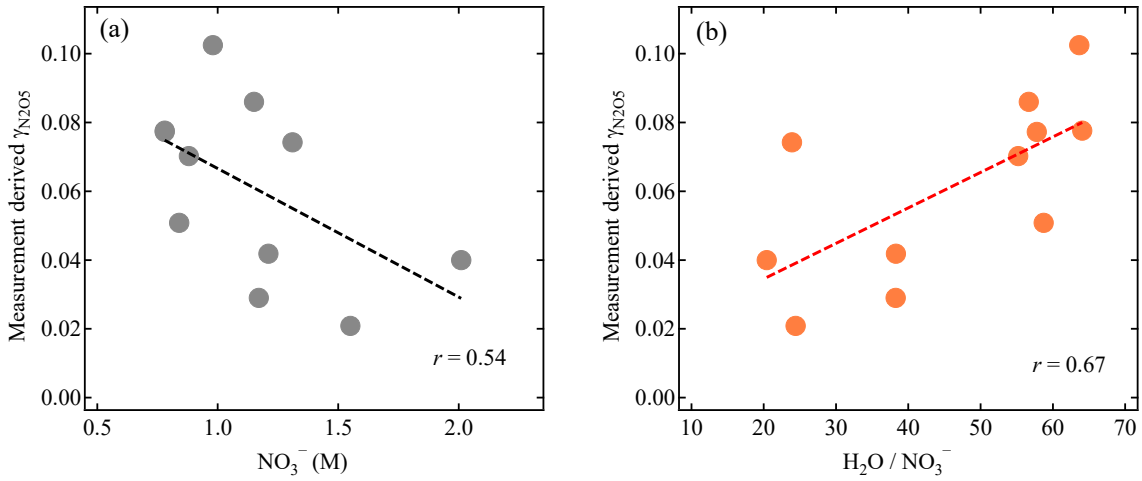

Figure S2: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol nitrate and (b) the molar ratio of aerosol water to nitrate during the study period.

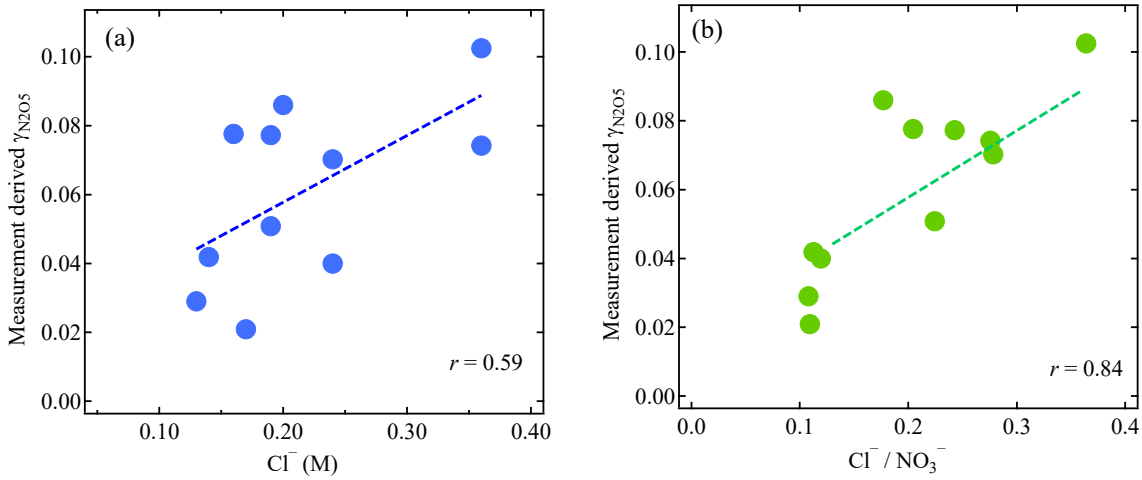

Figure S3: Relationship between derived γ_{N2O5} from the measurements with (a) the molar concentration of aerosol chloride and (b) the molar ratio of aerosol chloride to nitrate during the study period.

Specific Comments

3. *Abstract, Line 12. I know what you mean when you say effect the next day's photochemistry, but someone not familiar with ClNO2 would first need to know that it photolyzes to yield chlorine atoms, so some additional explanation would be good here.*

Response: We revised the abstract to clarify the effects as follows:

"Dinitrogen pentoxide (N_2O_5) and nitryl chloride ($ClNO_2$) are key species in nocturnal tropospheric chemistry, and have significant effects on particulate nitrate formation and the following day's photochemistry through chlorine radical production and NO_x recycling upon photolysis of $ClNO_2$."

4. *Abstract Line 18. A brief phrase describing how you got the uptake coefficient and yield would be good here.*

Response: As the reviewer suggested, we added the methodology information in the abstract to clarify it as follows:

"The heterogeneous N_2O_5 uptake coefficient (γ) and $ClNO_2$ yield (ϕ) were estimated from steady-state analysis and observed growth rate of $ClNO_2$. The derived γ and ϕ exhibited high variability, with means of 0.061 ± 0.025 and 0.27 ± 0.24, respectively."

5. *Abstract, Line 22. When you use the word "determined" it sounds like a measurement. It would more accurate to say 'estimated' or 'modeled'.*

Response: We changed the word of 'determined' to 'estimated'.

6. *Page 3, Line 2. Not sure what is meant when you say "the field determination of (phi) is limited". Do you mean that there are not very many reported determinations of (phi) from field measurements?*

Response: The reviewer's understanding is correct. To clarify, we revised the text as follows:

"There are only a few studies on the determination of ϕ from field measurement, and the possible effects of real atmospheric aerosols (including organic composition, mixing state, and chloride partitioning between particle sizes, etc.) have not been well characterized (Mielke et al., 2013; Phillips et al., 2016)."

7. *Page 3, Line 13. The Thornton et al., 2010 reference should be included in this list.*

Response: The suggested reference is added to the list.

8. *Page 4, Line 19. It would be more proper to say 'iodide ion chemical ionization mass spectrometry with a quadrupole mass spectrometer'.*

Response: We corrected it according to the suggestion.

9. *Page 11, Eq. 6. The term dN2O5/dt should really be the loss rate of N2O5, which are corrected shown in the next two terms in the equation.*

Response: We agree with the reviewer's suggestion, and the equation was corrected by removing the first two terms.

10. *Page 11, Lines 15-20. The big problem with this analysis is that it assumes that the growth rates that are inferred from Figure 9 correspond to the actual kinetic time within the plume. There is no way to know if that is true. The features in Figure 9 could be due to something completely different, e.g. a gradual shift in wind direction so that the plume as gradually influencing the site, starting with the dilute edge. There is simply no way to know what the*

physical circumstances were, with the evidence at hand. Another approach needs to be found, or the analysis should be abandoned.

Response: We agree with the reviewer that the growth rate estimation could be biased due to the potential variation of the plume, and simplified estimation would result in some uncertainties. We were aware of these limitations in the estimation, and therefore had carefully inspected the time series to choose the data during a period when related parameters in the air mass were relatively constant. It is likely that the assumptions are reasonable during the short time periods, usually around 2 to 3 hours. In addition, we have applied an alternative approach to derive the $ClNO_2$ yields from the ratio of observed enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- and HNO_3), according to the method suggested by Riedel et al. (2013). The derived ϕ values from this approach exhibit reasonable agreement with the original analysis, and most of the differences between two groups of data are within 40% (see figure below). Although either approach requires assumptions and would introduce some uncertainties, the general consistency can serve as a check to corroborate the yield analysis.

To clarify, we have revised the text by elaborating these assumptions in the estimation and the criteria for selecting cases, and also added the comparison results between two different approaches in the revised version, as follows:

"For regional diffuse pollution cases, the ϕ defined in R3 can be estimated from the ratio between $ClNO_2$ production rate and N_2O_5 loss rate, as the first term in below equation:

$$\phi = \frac{d\mathrm{ClNO_2}/dt}{k(\mathrm{N_2O_5})_{het}[\mathrm{N_2O_5}]} = \frac{[\mathrm{ClNO_2}]}{\int k(\mathrm{N_2O_5})_{het}[\mathrm{N_2O_5}]\,dt} \qquad (6)$$

$k(N_2O_5)$ values can be determined using the inverse steady-state lifetime analysis described above in Eq. 3, and the production rate of $ClNO_2$ can be derived from the near-linear increase in $ClNO_2$ mixing ratio observed during a period, when the related species (e.g., NO_x, SO_2) and environmental variables (e.g., temperature, RH) were roughly constant. The approach here assumes that the relevant properties of the nocturnal air mass are conserved, and neglects other possible sources and sinks of $ClNO_2$ in the air mass history. For the intercepted coal-fired plumes exhibiting sharp $ClNO_2$ peaks, the $ClNO_2$ yield can be estimated from the ratio of the observed $ClNO_2$ mixing ratio to the integrated N_2O_5 uptake loss over the plume age (i.e., the second term in Eq. 6). The analysis assumes that no $ClNO_2$ was present at the point of plume emission from the combustion sources and no $ClNO_2$ formation before sunset, and that the γ and ϕ within the plumes did not change during the transport from the source to the measurement site. The potential variability in these quantities likely bias the estimates, but these assumptions are a necessary simplification to represent the averaged values that best describe the observations. It should be noted that the steady-state N_2O_5 loss rate is crucial in the yield estimation, which could be underestimated by potentially overestimating the loss rate in some cases with large uncertainties in N_2O_5 measurement and NO_3 reactivity analysis. Therefore, an alternative approach suggested by Riedel et al. (2013) was also applied to derive the $ClNO_2$ yield from the ratio of enhancements of $ClNO_2$ and total nitrate (aerosol NO_3^- + HNO_3) in the cases. Given the low time resolution of nitrate data that could potentially introduce large uncertainties, this approach will only be used as a reference to validate the former analysis based on Eq. 6."

"The determined ϕ for the seven coal-fired plumes are also listed in Table 1. During the measurement period, ϕ varied from 0.02 to 0.90, with an average of 0.28 ± 0.24 and a median of 0.22. In comparison, the ϕ derived from the production ratio approach showed comparable results with an average of 0.25 ± 0.17, and the ϕ values from two different approaches match reasonably well with a Reduced Major Axis Regression (RMA) slope of 0.78 ± 0.08 and r^2 of 0.73 (cf Figure S4), which corroborates the yield analysis and indicates that the differences are within the overall uncertainty of 40%."

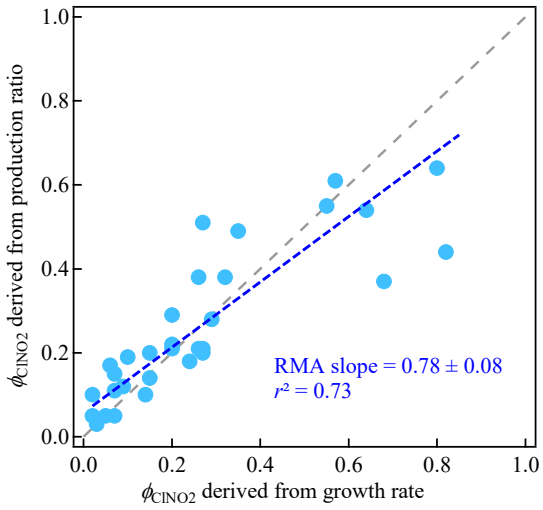

Figure S4: Comparison of estimated $ClNO_2$ yields from two different approaches: approach A using the ratio of the observed $ClNO_2$ growth rate to steady-state N_2O_5 loss rate based on Eq. 6; approach B using the production ratio of observed enhancements of $ClNO_2$ and total nitrate, $\phi = 2/(\Delta NO_3^-/\Delta ClNO_2 + 1)$ according to Riedel et al., 2013.

References:

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, J. Geophys. Res. -Atmos., 118, 8702-8715, 10.1002/jgrd.50637, 2013.

11. Page 11-12, Eq.7 and Lines 1-2. With the equation written as is, k' would then be 1/450, not 450 as stated, to match the parameterization of Roberts et al., 2009. I believe the correct expression was used to generate the points in Figure 10a since Eq. 7 as written would generate phi's that were quite a bit <1.

Response: We corrected the typo in the revised version.

12. Page 12, Eq. 8. Same problem as Eq. 6, dN2O5/dt is not the proper term here.

Response: The equation is corrected by removing the first term.