Response to Anonymous Referee #2

We would like to thank the referee #2 for the comments and suggestions which help us improve the manuscript. Our response and the corresponding changes are listed below.

General Comments:

This paper presents WRF/Chem model simulations to assess the impacts of the heterogeneous hydrolysis of N2O5 on atmospheric chemistry for southern China, a region where high concentrations of N2O5 and ClNO2 were recently observed. A chlorine chemistry module was added to WRF/Chem to not only include HNO3 as a product of N2O5 hydrolysis, but also ClNO2, which in known to impact the oxidizing capability of the atmosphere by chlorine activation. The results show that for the chosen model domain and a simulation period during winter, N2O5 heterogeneous hydrolysis contributes significantly to the formation of particulate nitrate and ozone.

The results further point towards major model uncertainties due to chlorine emission inventories, which is consistent with previous studies. The contribution of this work consists of WRF/Chem model development and the application of the extended model to a region where, so far, not much information on the importance of N2O5 hydrolysis has been available. Obtaining good agreement between simulation and observation of N2O5 and ClNO2 is challenging, so I commend the authors for their efforts. The study fits well within the scope of ACP, and it will be of interest for the community. I recommend the paper for publication after the authors address my questions and comments below.

Specific comments:

1. page 2, line 25: Saer is described as aerosol surface to volume ratio. This is confusing, it should rather be the aerosol surface area density, since it refers to the aerosol surface area per volume of air.

Response: The definition of Saer has been revised to 'aerosol surface area density'.

2. page 3, line 22: "1-minute value", what does that exactly mean? Were you sampling every minute or averaging over many samples for 1-minute intervals?

Response: '1-minute value' is the average of data points collected every 6 second in a 1-minute interval. Please refer to Wang et al. (2016) for further details on the CIMS measurement.

3. page 6, equation 2: The factor A in this equation is a function of the surface area to volume ratio for the particles in those experiments. It would be worth checking that this is comparable to (or valid for) the study here.

Response: The factor 'A' in the parameterization proposed by Bertram and Thornton (2009) refers to a pre-factor which includes the ratio of the *volume to surface area* of the particles used in their experiments which is $3.75*10^{-8}$ m**,** i.e. the ratio of the *surface area to volume* is $2.67*10^{7}$ m^{-1}.

The average simulated ratio of surface area to volume for the particles in southern China within the PBL is shown below (the interval is $0.5*10^{7}$ m^{-1}), from which we can see that the simulated ratio is practically within the range of 0.5 to 2.5 $*10^{7}$ m^{-1} in southern China, which is very close to the value used in the parameterization.

We have added the comparison of observed and simulated ratio of the surface area to volume to the manuscript.

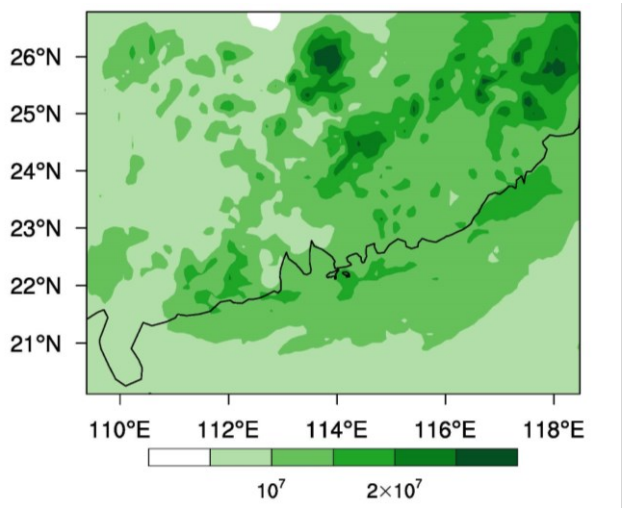

Figure R1. Average simulated ratio of surface area to volume (m^{-1}) for the particles within PBL

4. How was the liquid water content of the aerosol determined? Are both inorganic and organic species contributing to aerosol water uptake, or is it only the inorganic species that determine the aerosol liquid water content?

Response: The liquid water content was predicted using the thermodynamic module, ISORROPIA. Only the inorganic species have been considered in determining the aerosol liquid water content.

5. Related to point 4, what is the liquid water content of the aerosols for the simulations presented here? Is the RH high enough that water uptake is predicted? For example, Lowe et al. (2015) and Chang et al. (2016) have shown that using the Bertram and Thornton parameterization can lead to problems in low RH environments — not because there is a problem with this parameterization, but rather with the way aerosol water uptake is handled in CTMs. It would be interesting to see how this study compares in this regard.

Response: The spatial plot of aerosol liquid water content is shown below.

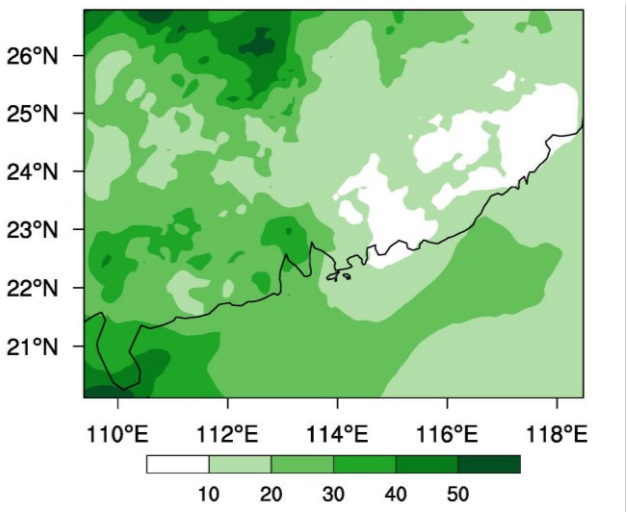

Figure R2. The average aerosol liquid water content (μg m^{-3}) in southern China during the simulation period within the PBL.

We had validated RH simulation performance, and the RH was well predicted during the simulation period (Wang et al., 2016). The mean bias between simulated and observed RH was only 3.54, and the correlation coefficient was 0.89, and the root mean square error was only 11.29.

We have noticed the conclusions of Lowe et al. (2015) and Chang et al. (2016), but it seems that our model performed relatively well to predict the uptake of N_2O_5 on aerosol surface in the Hong Kong – Pearl River Delta region, given that the simulated uptake at TMS (in the range of 0.008 to 0.031) is only a little higher than the observed uptake (in the range of 0.004 to 0.029), see section 3.2.1 (p9) for details.

6. Were clouds present during the simulation period and were they simulated? How is heterogeneous hydrolysis on cloud droplets handled?

Response: During the observation campaign at TMS (957 a.s.l.), there were clouds events sometimes. The N_2O_5 and $ClNO_2$ concentrations were below or near detection limit during such events. Therefore, we did not focus on the cloud simulation in our study. The heterogeneous processes on cloud droplets were not considered in our model.

7. page 7, line 3: Please add some information on the vertical model resolution. Many studies exist in the last 15 years that show pronounced gradient in N2O5 and NO3 mixing ratios, and the vertical resolution of the model is important. (e.g. Brown et al., 2007a, 2007b; Geyer and Stutz, 2004; Stutz et al., 2004, Riemer et al. 2003.)

Response: We used 30 model layers, and the vertical model resolution was determined using eta levels, which are shown below:

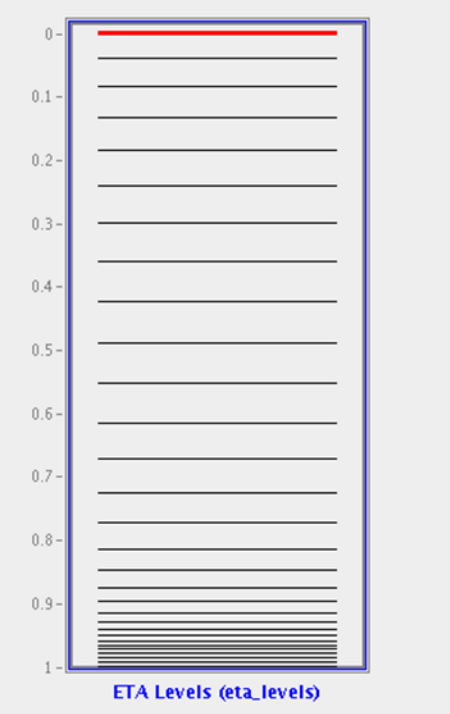

Figure R3. The setting of eta levels in WRF model.

The eta levels used in our study have 8 levels in the lowest 1 km or so (approximately the height of planetary boundary layer at noon), to provide more detailed information within the boundary layer.

We have added information on the vertical model resolution in the manuscript.

8. Table 3: Explain "Fac2"

Response: Fac2 is defined as the fraction of the simulations that are within a factor of two of the observations. The definition has been added to the manuscript.

9. Table 3 and Figure S1: It sounds like the observations of PM2.5, NO2, and O3 are available for the entire period, not only for the nights when N2O5 and ClNO2 were observed. I suggest, for figure S1, to show the entire time series, which will convey better the information if the temporal variation of the pollutant is captured. With the gaps in the time series it's hard to tell.

Response: The observations for the entire period at TMS along with the times series of $PM_{2.5}$, NO_2, and O_3 concentrations at environmental monitoring stations have been added to the supplement. And the temporal variations of these pollutants were not simulated as well as we had stated. We have revised the manuscript accordingly.

10. What is the rationale for choosing the base case for the comparison to observations in section 3.1? This seems strange to me. I would assume that the HET+Cl case is the "best effort" to capture the processes that are occurring in the real atmosphere. So, what conclusion can be

drawn from the comparison of observations to the base case? If the hydrolysis has an impact as the paper states, should we not expect a disagreement of base case and observations?

Response: We followed Sarwar et al. (2012) to firstly validate the performance of Base case in order to establish a reasonably good basis before we could further develop the model to include the heterogeneous chemistry of N_2O_5, and to evaluate the impacts of the model development.

But we agree with the reviewer that the HET+Cl case should be the 'best effort' logically, therefore, we have added model performance statistics of HET+Cl case in the manuscript. And the model performance of O_3 simulation in Hong Kong – Pearl River Delta region was improved in HET+Cl case, while the performance of $PM_{2.5}$ and NO_2 simulation did not show improvement, which could be due to many reasons, e.g. emission inventory.

11. page 8, line 29: calculations of averages: which hours count as "night" for the presented case?

Response: The time period used to calculate the nighttime average was mostly 18:00-07:00 local time, depending on the availability of the observations.

12. Figure 2: It would be interesting to add the "HET" case to this graph.

Response: The simulated N_2O_5 and $ClNO_2$ concentrations form 'HET' case have been added to the Figure 2 as suggested.

13. page 9, line 5, the statement: "the HET+Cl case captured the temporal evolution of the two compounds well". From Figure S2, I'm not sure if one can make such a statement. For some nights the peaks are roughly coinciding, for other nights not. I realize that it is very difficult to obtain good agreement with these species. There can be many reasons why there are differences between a point measurement of ClNO2 and N2O5 and a model simulation, but I'd rather suggest not making such statements in a case like this.

Response: We agree with the reviewer that it is a rather challenging task to well reproduce the N_2O_5 and $ClNO_2$ concentrations. So we have changed the statement into "the HET+Cl case generally captured the temporal variations of these two compounds."

14. To enhance the process-level analysis of this paper I suggest to comment on the spatial distribution of the yield ϕ. Where in the model domain is it that ClNO2 is produced?

Response: The spatial plot of the simulated yield in southern China has been added to the manuscript. We have also added a comparison of the simulated yields in our study with the ones reported previously. The following sentence has been added to the manuscript.

"The simulated yield of $ClNO_2$ during night-time within PBL ranged within 0.1-0.7, which is consistent with previous observation study (0.1-0.65) (Osthoff et al., 2008) and modelling study (0-0.9) (Sarwar et al., 2012)."

15. The terms "under-simulated" and "over-simulated" appear frequently in the manuscript. These are not the appropriate English terms. I suggest changing this to "underpredicted" and "overpredicted".

Response: Corrected. Thanks for the suggestion.

16. page 9, line 7: the overprediction of ClNO2 can also be due to an underestimation of the sinks.

Response: This is a very good suggestion. We have added this possible reason. The following sentence has been added to page 9.

'Besides, the overpredicted $ClNO_2$ could also be due to the underestimation of $ClNO_2$ sink (e.g. Roberts et al, 2008).'

17. General comments about the figures: They are very low resolution. I suggest to submit better-quality figures for the revised version.

Response: Higher quality figures have been used in the revised version paper.

18. page 9, line 26: "within the lowest 1000 m": Does this mean that the mixing ratios were averaged over the lowest 1000 m, or is one particular layer shown in Figure 3a and c? Please clarify.

Response: We referred to 'the averaged mixing ratios over the lowest 8 layers (approximately 1000m)' when we used the term 'within the lowest 1000m'.

19. page 9, line 10: Simulated uptake coefficients higher than observed ones: From the description in section 2.2.2 it appears that organic coatings are not taken into account even though it has been shown in several studies that the presence of these can lower the uptake coefficient notably. Could the presence of organics, which is not accounted for in the simulation, explain this discrepancy and consequently also the underprediction of N2O5 and overprediction of ClNO2? Please add some discussion.

Response: We agree with the reviewer that the organic inhibition effect could be part of the reason that N_2O_5 was underpredicted and $ClNO_2$ was overpredicted.

The following sentence has been added to the manuscript "The reactive uptake coefficient could be overestimated because the parameterization used in this study (Bertram and Thornton, 2009) didn't consider the inhibition of organic coating to the uptake coefficient." in section 3.2.1 (p9).

20. page 10, line 5: change "suppression" to "reaction". NO3 also reacts with VOC. Does this also contribute to low NO3 concentrations near the ground?

Response: Corrected. The effect of VOCs to the NO_3 (and N_2O_5) concentration has been added to the manuscript.

21. page 10, line 9: reference to Sarwar et al (2012): Many studies have shown evidence for pronounced vertical gradients in the profiles of N2O5 before that study, see my comment 7 above.

Response: Several previous studies on the vertical gradients of N_2O_5 have been added.

22. page 14, line 2: "average meteorological conditions": Remind the reader what this means (average in the sense of what?)

Response: To demonstrate the spatial distribution of simulated N_2O_5 and $ClNO_2$ under general conditions or average conditions, we calculated the average concentrations of N_2O_5 and $ClNO_2$ in the sense of time. The word 'meteorological' in the term 'average meteorological conditions' might be a little confusing, therefore, after consideration, we deleted the word 'meteorological'.

Reference:

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Lowe, D., Archer-Nicholls, S., Morgan, W., Allan, J., Utembe, S., Ouyang, B., Aruffo, E., Le Breton, M., Zaveri, R.A., Di Carlo, P., Percival, C., Coe, H., Jones, R. and McFiggans, G.: WRF-Chem model predictions of the regional impacts of N_2O_5 heterogeneous processes on night-time chemistry over north-western Europe, Atmos. Chem. Phys., 15, 1385-1409, 2015.

Roberts, J. M., Osthoff, H. D., Brown, S. S., & Ravishankara, A. R.: N2O5 oxidizes chloride to Cl2 in acidic atmospheric aerosol, Science,321, 1059-1059, 2008,

Sarwar, G., Simon, H., Bhave, P. and Yarwood, G.: Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, Atmos. Chem. Phys., 12, 6455-6473, 2012.

Wang, T., Tham, Y.J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S.C.N., Dubé, W.P., Blake, D.R., Louie, P.K.K., Luk, C.W.Y., Tsui, W. and Brown, S.S.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res. Atmos., 121, doi: 10.1002/2015JD024556, 2016.