Response to Anonymous Referee #1

We thank the referee for the comments and suggestions which help us improve the quality of the paper. Our response and the corresponding changes are listed below.

General Comments:

Li et al. present a set of regional photochemical modeling runs that simulate ClNO2 formation and impacts corresponding to recent field measurements in China. The field study reported the highest ever measured ambient concentration of ClNO2 indicating that this region of the world may be uniquely impacted by the chemistry associated with this compound. This study represents the first regional modeling study of ClNO2 impacts in Asia and is important for characterizing these impacts in a region with severe air pollution. The model is uniquely situated to provide a full spatial and temporal characterization of this chemistry which is not feasible with measurements alone.

One major comment is that the model performance was not great and the authors often overstate the accuracy of the performance based on the comparisons provided. Rather than gloss over the poor model performance, the authors should acknowledge this limitation and discuss how those model inaccuracies might impact their results (for instance large under-estimates of PM2.5 might lead to underestimates of the ClNO2 formation). Despite the often poor model performance, this study is valuable since it is the first application of its kind in China and provides new insights into times and locations where ClNO2 impacts are predicted to be most important. This type of characterization of spatial and temporal patterns is not possible with measurements alone.

Another major comment is that all results (figs 3-10) are given as episode averages (all hours). Since many of the pollutants modeled have distinct diurnal profiles (i.e. O3, N2O5, ClNO2) these averages are hard to interpret. For N2O5 and ClNO2, the daytime values are essentially zero so these averages include high nighttime values averaged with many zeros during daytime hours. The reader does not get a good sense of the maximum magnitude of these pollutants at night. For ozone, many areas are titrated at night so again this doesn't give any sense of how high daytime ozone values are impacted. This averaging leads the authors to make statements like "elevated levels of . . . O3 (up to 44.5 ppb)" (p 11). 44.5 ppb of ozone is generally not considered an elevated level! I suggest that the authors add some results which either show diurnal averages of changes, time series of changes, or spatial plots of max values (and maximum changes) in addition to average values. This will provide a more complete picture of the modeled impacts of this chemistry.

Overall, this analysis used the best technical information currently available to complete this modeling and I think this paper will be of interest to ACP readers. I recommend publication after the authors address general comments above and specific comments below.

Response: We agree with the reviewer that the model performance was not as great as we stated. We have revised the sentence describing model performance in the abstract to be 'The updated model can generally capture the temporal variation of N_2O_5 and $ClNO_2$ observed at a mountain-top site in Hong Kong, but overestimates N_2O_5 uptake and $ClNO_2$ production.' We also deleted the word 'satisfactorily' in section 3.1 (p8), and deleted a sentence in section 3.1 (p8) 'The capture of the temporal variations of these pollutants at the TMS site provides a good basis for simulation of the N_2O_5 and $ClNO_2$ temporal patterns (see Section 3.2.1).'

We had discussed the potential effects of the discrepancy between the simulated and observed concentrations of $PM_{2.5}$, NO_2 and O_3 in Hong Kong – Pearl River Delta region on the N_2O_5 and $ClNO_2$ simulation in section 3.2.1.

We have replaced the Figure 3 with the average $ClNO_2$ and N_2O_5 concentrations during nighttime (18:00-07:00). We have added the spatial plots of average maximum values and maximum changes of NO, NO_2, total nitrate and O_3 in the supplement to provide extra information on the impacts of the N_2O_5 and $ClNO_2$ chemistry in southern China.

Specific comments:

1. Figs 3-7, and text throughout results section: Are heights given as above ground level (agl) or above sea level (asl)? The text repeatedly says "agl" but figures indicate terrain features in black which suggests that these heights are actually "asl". Please clarify and also add text to the caption which describes the black shaded regions in the figures.

Response: The statement used in text, 'agl', is correct. We calculated the 'agl' based on the 'asl' and the 'terrain height' (black shaded features in cross-section figures). We have added the description of the terrain features in figures.

2. Page 2, Line 16: hydrolysis of NO5 is "A" major loss pathway of NOx but perhaps not "THE" major loss pathway. What about reactions of NO3 with VOCs?

Response: Indeed, the loss of NOx through the N_2O_5 heterogeneous reaction and through the reaction between NO_3 with VOCs can be both important. The word 'the' has been changed to 'a'.

3. Page 2, Line 26: It would be good to clarify that gamma, the reactive uptake coefficient, represents the probability that a collision between N2O5 and a particle will result in uptake and chemical reaction.

Response: The following explanation of the reactive uptake coefficient has been added to the manuscript 'the possibility that a colliding of N_2O_5 molecule with a particle will lead to uptake and chemical reaction (Sarwar, et al. 2012).' in section 1 (p2).

4. Page 2, line 7 – Page 3, line 5: In the discussion of previous parameterizations for gamma, you should also mention that gamma has been measured by various field campaigns (Brown et al, 2006; Brown et al, 2009; Osthoff et al, 2008) which showed very different values for marine versus inland aerosols.

Response: Previous measurement studies on uptake coefficients have been added to the manuscript.

5. Page 3, lines 6-20: You missed several important earlier studies in your summary of modeled impacts of N2O5 and ClNO2 chemistry on air pollution concentrations/ chemistry: Dentener and Crutzen, 1993; Riemer et al., 2003; Evans and Jacob, 2005; Simon et al, 2009

Response: These previous studies of the impacts of N2O5 and ClNO2, including Dentener and Crutzen, 1993; Riemer et al., 2003; Evans and Jacob, 2005; Simon et al, 2009, have been added to the manuscript as suggested.

6. Page 3, line 20: change "biomass burning" to "biomass burning and sea salt"

Response: Corrected.

7. Page 4, lines 18-24 and section 3.1: Comparisons with some additional measurements would be valuable if these measurements were made. For instance, if aerosol size distribution was measured that would allow for calculation of ambient surface area which could be directly compared with model results. Since surface area, not PM2.5 mass, drives this chemistry that would be a useful comparison. Also, were there any speciated PM2.5 measurements available to compare with the model (specifically aerosol nitrate and particulate chloride)? Were HCl and HNO3 measured? These could all provide better constraints and characterization of model performance if they are available. In addition, a more complete model evaluation would be useful. For instance, the authors might include time series of model performance, r2 values, maps of MB etc. There are several places in section 3.1 where the authors' characterization of the model performance is overly favorable and not supported by the figures provided. Statements that the model performed "reasonably well", "satisfactorily" etc are probably not warranted given that Figure S1 shows consistent under-predictions of ozone and PM2.5 of 20-40 ppb and 10-30 ug/m3 respectively.

Response: The comparison of measured and simulated surface area at TMS site has been added in section 3.1. The comparison of aerosol nitrate at TMS site has been added in section 3.1. The comparison of observed and simulated chloride had been conducted in section 3.1. No gas-phase HCl and HNO_3 were measured.

Time series of the comparison of measured and simulated $PM_{2.5}$, NO_2, and O_3 at the environmental monitoring stations and at TMS site have been added to the supplement.

We have revised the description of the model performance, see our response to the general comment.

8. Page 5, lines 5-15: Please specify if these are gas-phase or particle-phase chlorine emissions? Previous work on gas-phase chlorine emissions in the U.S. (Sarwar and Bhave, 2007; Chang et al, 2002) could be used as a starting point for deriving gas-phase chlorine emissions in China. Also, speciation profiles of PM2.5 emissions sources by Reff et al. (2009) could be used to derive particulate chloride emissions by applying fractional Cl contributions from all sources to the PM2.5 emissions in the current inventory. I am not suggesting that work needs to be done for this study, but the authors might discuss these past efforts as a basis for improving Chinese Cl emissions going forward.

Response: These are both gas and particle phase. For biomass burning, it is aerosol phase chlorine emission. For anthropogenic emission, it is gas phase chlorine (HCl) emission.

We have added a short description on the methodology that could be used to develop the chloride emission inventory in China.

9. Section 2.3.1: Please add information about which days were modeled. Was the modeled period Nov 15-Dec 5 to match measurements? Also, please state whether a spin-up period was included and, if so, how many days were used.

Response: The simulation period was November 15 to December 5, 2013, which had been stated in Section 2.3.2 (p7). The reviewer's understanding is correct. The simulation period was chosen according to the measurement period. One-day spin-up period was used.

10. Page 9, lines 4-5: I don't think Fig S2 supports the contention that temporal variations of N2O5 and ClNO2 are "well captured". The model does predict that these pollutants build up at night and are close to 0 during daytime but other than that modeled peaks often appear at different hours and nights than observed peaks.

Response: We agree with the reviewer that the temporal variation of N_2O_5 and $ClNO_2$ was not well captured in our simulation. The words 'well' in 'well captured' has been revised to 'generally' in section 3.2.1 (p9).

11. Page 9, lines 6-15: The reactive uptake coefficient could be too high in the model because the Bertram and Thornton parameterization does not account of organic inhibition of uptake that has been previously described by Riemer et al, 2009.

Response: We agree the reviewer's suggestion. In fact, in page 9, we had stated that in Sarwar et al. (2012), the authors attributed the parameterization (Bertram and Thornton, 2009) to be a possible reason that $ClNO_2$ was overestimated.

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) does not consider the inhibition of organic coating to the uptake coefficient." in section 3.2.1 (p9).

12. Page 12, line 13-14: The difference between HET and HET+Cl also shows the impact of lower levels of N2O5 conversion to HNO3.

Response: Indeed, the difference of HET and HET+Cl, i.e. the impacts of $ClNO_2$ production, showed that less N_2O_5 were transformed into HNO_3 (and nitrate aerosol). And in the manuscript, we used total nitrate (HNO_3+nitrate aerosol) to avoid redundant description.

13. Page 12, line 19: The decreases in O3 appear to only occur over a very small area, not over rural and coastal regions generally.

Response: We agree. The sentence has been modified accordingly.

14. Page 12, line 22-23: This is confusing to me. If I understand the HET run correctly, it simply set the yield value to zero for the ClNO2 pathway which should mean that more N2O5 is converted to HNO3 and less is conserved in the ClNO2 reservoir. Therefore, the HET+CL simulation should increase NOx everywhere. What would cause broad decreases in NO and NO2 across the domain with the addition of the ClNO2 formation?

Response: The reviewer's understanding is correct. In HET case, the $ClNO_2$ yield was set to be zero, and all N_2O_5 loss was transformed into total nitrate.

The possible causes for the changes of NO and NO_2 from HET to HET+Cl case are discussed below. The produced $ClNO_2$ *(1) releases NO_2* and Cl radical after sunrise, and both of them increase the formation of O_3. The increased O_3 enhances the reaction of NO with O_3, which leads to the *(2) loss of NO*, and the *(3) formation of NO_2*. The increased O_3 also increases the level of OH radicals, which enhances the reaction of NO_2 with OH and then results in the *(4) loss of NO_2*. The combination of the effects *(1), (2), (3) and (4)* mentioned above are the net effects of the $ClNO_2$ production on NO and NO_2. Our study showed that the NO was reduced across the domain. And for the NO_2, the enhanced production outweighed the loss in urban areas, while in other regions, the NO_2 was decreased.

We have added a short discussion of the possible causes in the manuscript.

15. Page 12, line 23: Consider rephrasing, I don't consider a decrease of 2.35 ug/m3 "slight".

Response: The word 'slight' has been deleted.

16. Page 12, line 25: What fraction of N2O5 produced ClNO2? It would be useful to report what yield values were predicted by the model for equation 5. How do these yields compare to previously reported observed yields (Osthoff et al., 2008) or modeled yields (Sarwar et al. 2012)? It might be useful to provide a map of yield values during nighttime hours.

Response: The spatial distribution of simulated yield during nighttime has been added to the manuscript. And the comparison of the yields with previous reported observed and simulated has been added to the manuscript. 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)."

17. Page 12, line 26-27: Simon et al. (2009) reported that half of the O3 impact from ClNO2 chemistry came from Cl activation while half came from the recycling of NO2.

Response: The conclusion from Simon et al. (2009) has been added to explain our results.

18. Table 3: The authors should consider including O3 performance for daytime values (8-hr daily max or 1-hr daily max) as well as all hours averages. Also what is "fac2"? This is not defined anywhere in the paper. How is it calculated?

Response: We have added 1-h daily maximum O_3 as the indicator of model performance.

FAC2 is defined as the fraction of simulated results that are within a factor of two of the observations. The calculation of FAC2 is as follows.

FAC2 = (the number of simulations that are within a factor of two of the observations) / (the number of observations).

The definition of FAC2 has been added to the manuscript.

19. Table 4: The authors should state the time period used to calculated average simulated concentrations.

Response: The time period used to calculate the average simulated concentration is the entire simulation period (November 15 to December 5, 2013). It has been added to the manuscript.

20. Figures 4 and 5: Consider using the same scale for the horizontal and vertical plots. The concentrations don't look different enough to warrant different scales.

Response: The scales have been revised as suggested.

21. Figure 6: The choice of the log scale makes variations in the O3 concentrations harder to see. Consider using a linear scale.

Response: A linear scale has been applied to the O_3 concentration figure.

Reference:

Dentener, F.J. and Crutzen, P.J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x, O_3, and OH, J. Geophys. Res. Atmos., 98, 7149-7163, 1993.

Evans, M.J. and Jacob, D.J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophys. Res. Lett., 32, doi: 10.1029/2005GL022469, 2005.

Riemer, N., Vogel, H., Vogel, B., Schell, B., Ackermann, I., Kessler, C. and Hass, H.: Impact of the heterogeneous hydrolysis of N_2O_5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions, J. Geophys. Res. Atmos., 108, doi: 10.1029/2002JD002436, 2003.

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.

Simon, H., Y. Kimura, G. McGaughey, D. T. Allen, S. S. Brown, H. D. Osthoff, J. M. Roberts, D. Byun, and D. Lee: Modeling the impact of $ClNO_2$ on ozone formation in the Houston area, J. Geophys. Res., 114, doi:10.1029/2008JD010732, 2009.

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.

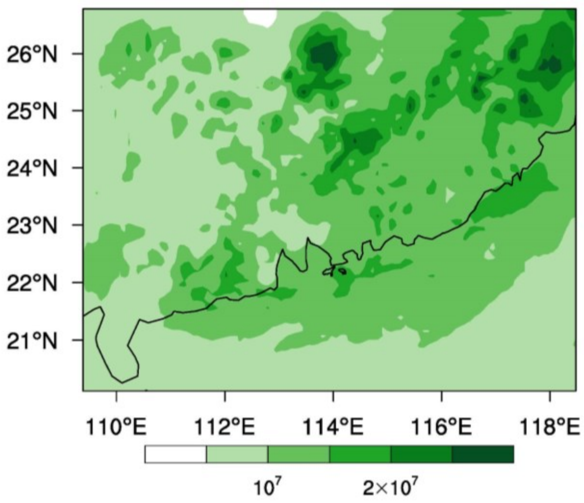

Figure R1. Average simulated ratio of surface area to volume (m^{-1}) for the particles within PBL

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.

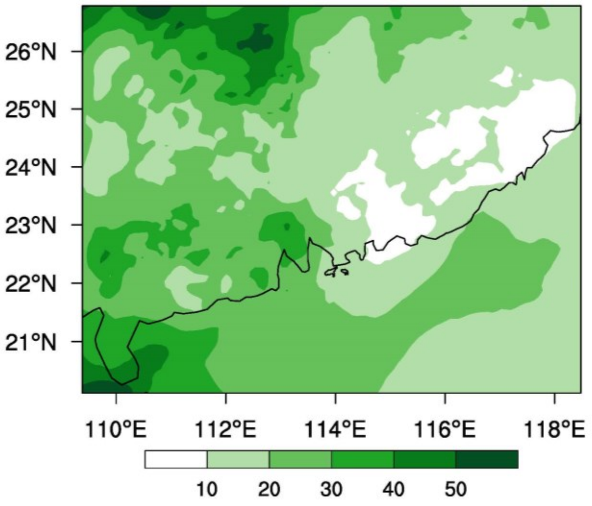

Figure R2. The average aerosol liquid water content (μg m^{-3}) in southern China during the simulation period within the PBL.

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:

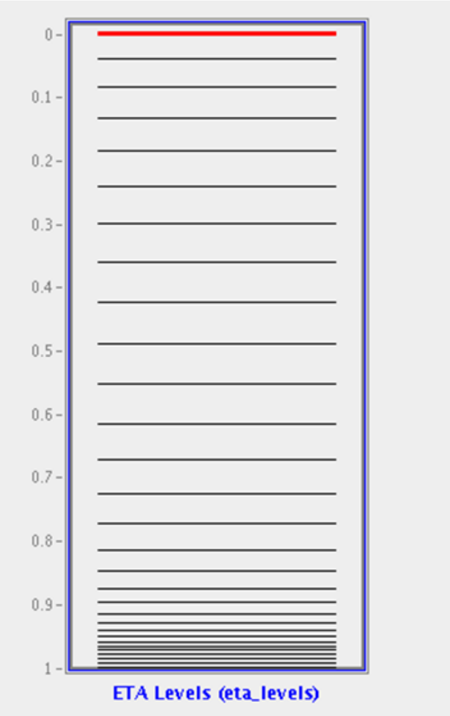

Figure R3. The setting of eta levels in WRF model.

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:

Chang, W. L., S. S. Brown, J. Stutz, A. M. Middlebrook, R. Bahreini, N. L. Wagner, W. P. Dubé, I. B. Pollack, T. B. Ryerson, and N. Riemer: Evaluating N_2O_5 heterogeneous hydrolysis parameterizations for CalNex 2010, J. Geophys. Res. Atmos., 121, doi:10.1002/2015JD024737, 2016.

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.

Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: Improvement and application of the WRF-Chem model in southern China

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Abstract: The uptake of dinitrogen pentoxide (N_2O_5) on aerosol surfaces and the subsequent production of nitryl chloride ($ClNO_2$) can have significant impact on the oxidising capability and thus on secondary pollutants such as ozone. The range of such impact, however, has not well been quantified in different geographical regions. In this study, we applied the Weather Research and Forecasting coupled with Chemistry (WRF-Chem) model to investigate the impact of the N_2O_5 uptake processes in the Hong Kong-Pearl River Delta (HK-PRD) region, where the highest ever-reported N_2O_5 and $ClNO_2$ concentrations were observed in our recent field study. We first incorporated into the WRF-Chem an aerosol thermodynamics model (ISORROPIA II), recent parameterisations for N_2O_5 heterogeneous uptake and $ClNO_2$ production and gas-phase chlorine chemistry. The revised model was then used to simulate the spatiotemporal distribution of N_2O_5 and $ClNO_2$ over the HK-PRD region and the impact of N_2O_5 uptake and Cl activation on ozone and reactive nitrogen in the planetary boundary layer (PBL). The updated model can generally capture the temporal variation ~~is capable of reproducing the temporal patterns~~ of N_2O_5 and $ClNO_2$ observed at a mountain-top site in Hong Kong, but overestimates N_2O_5 uptake and $ClNO_2$ production. The model results suggest that under average ~~meteorological~~ conditions, elevated levels of $ClNO_2$ (>0.25 ppb within the PBL) are present in the south-western PRD, with the highest values (>1.00 ppb) predicted near the ground surface (0-200 m above ground level (a.g.l.)). In contrast, during the night when very high levels of $ClNO_2$ and N_2O_5 were measured in well-processed plumes from the PRD, $ClNO_2$ is mostly concentrated within the residual layer (~300 m a.g.l.). The addition of N_2O_5 heterogeneous uptake and Cl activation reduces the NO and NO_2 levels by as much as 1.93 ppb (~7.4%) and 4.73 ppb (~16.2%), respectively, increases the total nitrate and ozone concentrations by up to 13.45 μg m^{-3} (~ 57.4%) and 7.23 ppb (~16.3%), respectively, in the PBL. Sensitivity tests show that the simulated chloride and $ClNO_2$ concentrations are highly sensitive to chlorine emission. Our study suggests the need to measure the vertical profiles of N_2O_5/$ClNO_2$ under various meteorological conditions, to consider

the chemistry of N_2O_5/$ClNO_2$ in the chemical transport model, and to develop an updated chlorine emission inventory over China.

1 Introduction

Dinitrogen pentoxide (N_2O_5) is mostly produced by chemical reactions involving ozone (O_3) and nitrogen dioxide (NO_2).

$$O_3 + NO_2 \longrightarrow NO_3 \qquad (1)$$

$$NO_3 + NO_2 \longrightarrow N_2O_5 \qquad (2)$$

The subsequent heterogeneous uptake of N_2O_5 produces nitrate on water-containing aerosol surfaces via reaction 3 (hydrolysis) and produces both nitrate and gaseous nitryl chloride ($ClNO_2$) on chloride-containing aerosol surfaces via reaction 4 (Finlayson-Pitts et al., 1989; Osthoff et al., 2008). The net reaction of reactions 3 and 4 could be treated as reaction 5, in which the $ClNO_2$ yield, i.e. parameter ϕ, represents the fraction of N_2O_5 that reacts via reaction 4. The produced $ClNO_2$ can be further photolysed into Cl radical and NO_2 (via reaction 6).

$$N_2O_5(g) + H_2O(aq) \longrightarrow 2\ HNO_3(aq) \qquad (3)$$

$$N_2O_5(g) + HCl(aq) \longrightarrow HNO_3(aq) + ClNO_2(g) \qquad (4)$$

$$N_2O_5(g) + (1\text{-}\phi)H_2O(aq) + \phi\ HCl(aq) \longrightarrow (1\text{-}\phi)\times 2\ HNO_3(aq) + \phi\times(HNO_3(aq) + ClNO_2(g)) \qquad (5)$$

$$ClNO_2(g) + h\nu \longrightarrow Cl\ (g) + NO_2(g) \qquad (6)$$

The above processes affect the fate and composition of the total reactive nitrogen (NO_y), which is the sum of NO, NO_2, HNO_3 (g), 2*N_2O_5, NO_3, $ClNO_2$, PAN, HONO, HNO_4, aerosol nitrate, and various organic nitrates. The hydrolysis of N_2O_5 is ~~the~~ a major loss pathway for NO_x (=NO+NO_2) at night, reducing the amount of NO_x for daytime photochemistry in the following day, while producing nitrate aerosol contributing to secondary aerosol (Brown and Stutz, 2012). When $ClNO_2$ is produced, it serves as a reservoir for reactive nitrogen at night and is photolysed to recycle NO_2 and release highly reactive chlorine radicals (Cl activation), both of which can significantly affect the daytime photochemistry, such as O_3 formation via reactions with volatile organic compounds (VOCs) (Atkinson, 2000; Thornton et al., 2010; Riedel et al., 2014).

The critical parameters required to determine the impacts of the N_2O_5 uptake processes are the rate constant of reaction 5, k_5, and the yield of $ClNO_2$, ϕ. k_5 can be calculated from Eq. (1) by treating the N_2O_5 heterogeneous uptake reaction as a first order reaction (Chang et al., 2011),

$$k_5 = \frac{V_{N_2O_5} \times S_{aer} \times \gamma}{4}, \qquad \text{(Equation 1)}$$

where $V_{N_2O_5}$ denotes the mean molecular velocity of N_2O_5, S_{aer} is the aerosol surface area density ~~surface to volume ratio~~, and γ represents the heterogeneous uptake coefficient of N_2O_5 which is the possibility that a colliding of N_2O_5 molecule with a particle will lead to uptake and chemical reaction (Sarwar, et al. 2012). $V_{N_2O_5}$ and S_{aer} are relatively well determined; therefore, the treatments of γ and ϕ are crucial for the prediction of the impacts of N_2O_5 uptake and Cl activation. In terms of γ, a fixed value of 0.1 was first proposed (Dentener and Crutzen, 1993). Highly variable γ were then derived from observational campaigns which showed distinguished values on inland and marine aerosols (e.g. Brown et al., 2006; Osthoff et al., 2008; Brown et al., 2009). Later laboratory and modelling studies considered dependence of γ on the aerosol species/compositions (sea salt, black carbon, sulfate, nitrate, chloride, organic matter and water), temperature and/or relative humidity (Evans and Jacob, 2005 and the reference therein; Davis et al., 2008; Anttila et al., 2006; Riemer et al., 2009; Bertram and Thornton, 2009). Several parameterisations have been proposed for the yield of $ClNO_2$. Simon et al. (2010) applied a constant value of 0.75 for the fraction of N_2O_5 involved in the production of $ClNO_2$. More detailed parameterisations of ϕ considering the effects of aerosol compositions were proposed by Roberts et al. (2009) and by Bertram and Thornton (2009).

Several studies ~~have been conducted to~~ examined the impacts of N_2O_5 uptake *or* $ClNO_2$ production with the use of the chemical transport model. Dentener and Crutzen (1993) evaluated the impacts of the N_2O_5 uptake on tropospheric aerosol by using a constant γ (0.1), and their results showed a substantial decrease of NOx (50%) and a slight reduction of O_3 (9%) globally. Riemer et al. (2003) utilized a weighting factor on a constant γ (0.02) to study the N_2O_5 heterogeneous hydrolysis, and their research showed small impacts on O_3 and remarkable influences on nitrate formation in Europe. By applying parameterizations of γ for various aerosol compositions and meteorological conditions, Evans and Jacob (2005) showed higher levels of O_3 and NOx compared to simulations with 0.1 as γ. Lowe et al. (2015) and Archer-Nicholls et al. (2014) incorporated the heterogeneous uptake of N_2O_5 on particles into the MOSAIC aerosol module in WRF-Chem based on the methods suggested by Bertram and Thornton (2009), Anttila et al. (2006) and Riemer et al. (2009). Their results suggested that N_2O_5 uptake suppressed VOC oxidation (by OH and NO_3) by a factor of 1.5 and significantly enhanced nitrate formation during nighttime (an increase from 3.5 to 4.6 μg Kg^{-1}) over north-western Europe. Simon et al. (2009) used a gas-phase reaction to represent the heterogeneous production process of $ClNO_2$, and their study predicted modest increases in O_3 due to the $ClNO_2$ production in Houston. Sarwar et al. (2012) implemented the heterogeneous production of $ClNO_2$ based on the parameterisation proposed by Bertram and Thornton (2009) and additional gas-phase chlorine reactions in CMAQ and examined the impacts of Cl activation due to $ClNO_2$ production and Cl chemistry on air quality. Their results showed that $ClNO_2$ production reduced the total nitrate level (up to 0.8-2.0 μg m^{-3} or 11-21%) and had modest impacts on the 8-h O_3 level (up to 1-2 ppb or 3-4%) in the United States. Sarwar et al. (2014) expanded the study region used in Sarwar et al. (2012) to the entire northern hemisphere and suggested that $ClNO_2$ production had remarkable impacts on the air quality in China and western Europe with enhancements of the 8-h O_3 level up to 7.0 ppb. Most previous studies focused on investigating the effects of N_2O_5 uptake or $ClNO_2$ production in North America and Europe; however, little is known about Asia. The only study that covered Asia was performed by Sarwar et al. (2014); it used a coarse model resolution (>100 Km) and considered only biomass burning and sea salt as the source of chloride ~~over land~~.

Previous studies in Asia (Hong Kong) have revealed the existence and significance of $ClNO_2$ in this region (Wang et al., 2014; Tham et al., 2014; Xue et al., 2015). In a recent field study, we observed the highest ever-reported mixing ratios of N_2O_5 (1-minute average value up to 7.7 ppbv) and $ClNO_2$ (4.7 ppbv) at a mountain top site (957m above sea level) in Hong Kong (Brown et al., 2016; Wang et al., 2016). This result indicates rapid production of N_2O_5 and $ClNO_2$ in the Hong Kong-Pearl River delta (HK-PRD) region which has long suffered O_3 and NO_x pollution (Wang et al., 2009). Meteorological analysis and chemical data revealed highly inhomogeneous dynamic and chemical processes and considerable impacts of the $ClNO_2$ chemistry on the radical budget (up to 77% increase of OH) and daytime O_3 production (up to 41%) in the high $ClNO_2$ air mass as it transported to downwind locations above the ocean (Wang et al., 2016). It was also suggested in that study that other locations downwind of major urban areas under prevailing conditions may experience more frequent events with high levels of $ClNO_2/N_2O_5$ than the site in Hong Kong. It is therefore of great interest to investigate the regional distribution of $N_2O_5/ClNO_2$ and the impact of N_2O_5 uptake and subsequent chemistry.

This study was conducted to investigate (1) the spatial (horizontal and vertical) distribution of the N_2O_5 and $ClNO_2$ concentrations in the HK-PRD region and (2) the spatial extent of the impact of N_2O_5 uptake processes on the formation of O_3 and the partitioning of reactive nitrogen in this region. The latest version of a widely used aerosol thermodynamics model, ISORROPIA II (Fountoukis and Nenes, 2007), was incorporated into the MADE/VBS aerosol model. ISORROPIA II has the ability to simulate the equilibrium between hydrogen chloride (HCl) and chloride which is critical for the simulation of N_2O_5 heterogeneous uptake and Cl activation. But this capacity is not considered in the current MADE/VBS model in WRF-Chem (Grell et al., 2005; Ahmadov et al., 2012). Up-to-date parameterisation for N_2O_5 uptake and $ClNO_2$ production and Cl radical initiated chemistry were implemented into WRF-Chem. The revised WRF-Chem was then applied to southern China to investigate the spatial distribution of N_2O_5 and $ClNO_2$ and the impacts of these processes on O_3 and NO_y. We start with a description of the data used to run and validate the simulations, the amendments to the WRF-Chem model, and the model setup in Section 2. In Section 3, we show the performance of the WRF-Chem model in the simulation of several air pollutants without N_2O_5 uptake processes, and the simulation results of N_2O_5 and $ClNO_2$ with N_2O_5 uptake and Cl activation processes; we then evaluate the impacts of N_2O_5 uptake and Cl activation on NO_x, total nitrate, O_3 and NO_y partitioning, and test the sensitivity of the $ClNO_2$ concentration to chlorine emissions. A summary is given in Section 4.

2 Methodology

2.1 Data

2.1.1 Field measurement data

N_2O_5 and $ClNO_2$ concentrations were measured at Tai Mo Shan (TMS) in Hong Kong with a chemical ionization mass spectrometer between November 15 and December 5, 2013 (refer to Wang et al., 2016 for more details). The measurements were made on a mountain top in the south-eastern PRD at an altitude of 957m. Other major air pollutants, including $PM_{2.5}$, NO_2, and O_3, were also measured at the TMS site and at 11 general (non-roadside) monitoring stations of the Hong Kong Environmental Protection Department (HKEPD; available at: http://epic.epd.gov.hk/EPICDI/air/station/). Hourly measurement data were used to validate the performance of the WRF-Chem simulations.

2.1.2 Emission data

Four sets of anthropogenic emission inventories (EIs) covering different areas were adopted in this study. For mainland China, we used the Multi-resolution Emission Inventory for China (MEIC; available at http://meicmodel.org), developed by Tsinghua University for year 2010. For the PRD, the anthropogenic EI developed by the Southern China University of Technology was applied. The anthropogenic EI developed by HKEPD was used over Hong Kong. INTEX-B EI (Zhang et al., 2009) was adopted for other Asian regions. Readers are referred to Zhang et al. (2016) for the details of these anthropogenic EIs. For natural emissions, the biogenic emission parameterisation proposed by Guenther et al. (1994), the dust emission parameterisation proposed by Shaw et al. (2008) and the sea salt emission parameterisation proposed by Gong et al. (2002) were adopted in this study. The concentrations of sodium, chloride, calcium, magnesium and potassium in dust and sea salt follow those suggested by Millero (1996) and Wedepohl (1995), as shown in Table S1.

Chlorine emissions are not included in most EIs, but they are critical for the simulation of N_2O_5 uptake and Cl activation. In this study, the Reactive Chlorine Emission Inventory (RCEI) (Keene et al., 1999 and references therein, available at http://eccad.sedoo.fr/eccad_extract_interface/JSF/page_login.jsf) with a resolution of 1^ox1^o was adopted to provide chlorine emissions, including emissions from biomass burning (particulate phase) and anthropogenic activities (gas phase) (e.g. coal combustion). Global chlorine emissions from biomass burning and anthropogenic activities are estimated to be ~6.3 Tg Cl yr^{-1} and ~6.6 Tg Cl yr^{-1}, respectively. The RCEI inventory is the only available chlorine EI that currently covers China, and it is subject to some, probably large, uncertainties for representing Cl emissions in the HK-PRD region due to its low spatial resolution and the fact that it was compiled for year 1990. Coal consumption and SO_2 emissions from coal-fired power plants in China increased by 479% and 56% from 1990 to 2010, respectively (Liu et al., 2015); thus it is expected that chlorine emissions from coal combustion, which form a large proportion of anthropogenic chlorine (Keene et al., 1999), also increased significantly over that period. We conducted two sensitivity simulations by adjusting the chlorine emissions to test the dependence of the chloride and $ClNO_2$ concentrations on the varied chlorine emissions; the results are shown in Section 3.5.

2.1.3 Meteorological data

Three-hourly meteorological measurements, including atmospheric pressure, temperature, relative humidity, wind direction and wind speed, at ~2500 surface meteorological stations and twelve-hourly data at ~250 sounding stations, were obtained from the China Meteorological Agency (CMA) and Hong Kong Observatory and were adopted in Four-Dimensional Data Assimilation to improve the model performance of the meteorological fields using observational nudging techniques (Zhang et al., 2016). The FNL Operational Global Analysis dataset provided by the National Centers for Environmental Prediction (available at http://rda.ucar.edu/datasets/ds083.2/) was used for analysis nudging. Observational and analytical nudging techniques have been shown to improve the performance of meteorological simulation in both northern China (Zhang et al, 2015) and southern China (Zhang et al., 2016). Hourly datasets from ~500 surface meteorological observation stations obtained from the CMA were used to validate the meteorological simulations.

2.2 Model development

2.2.1 Incorporation of ISORROPIA II

ISORROPIA II, an aerosol thermodynamics model developed by Nenes et al. (1998) and Fountoukis and Nenes (2007), was incorporated to replace the aerosol thermodynamics module in the MADE/VBS aerosol model in the original WRF-Chem v3.5 so as to extend the capacity of simulation of the equilibrium between $PM_{2.5}$ compositions and their corresponding gaseous species. The MADE/VBS model adopts volatility basis set model to simulate secondary organic aerosol (SOA) formation and provides improved simulations of SOA compared to the traditional MADE/SORGAM model (Ahmadov et al., 2012). The current MADE/VBS model only estimates the thermodynamic equilibrium between SO_4^{2-}, NO_3^-, NH_4^+, H_2O and corresponding gases, whereas ISORROPIA II simulates the equilibrium between SO_4^{2-}, NO_3^-, NH_4^+, H_2O, Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+ and associated gases.

2.2.2 N_2O_5 heterogeneous uptake, $ClNO_2$ production and Cl gaseous reaction

We adopted the parameterisations of N_2O_5 heterogeneous uptake and $ClNO_2$ production suggested by Bertram and Thornton (2009). According to the parameterisations, the N_2O_5 heterogeneous uptake coefficient, γ, can be calculated with the following equation:

$$\gamma=Ak\left(1-\frac{1}{\left(\frac{0.06[H_2O(l)]}{[NO_3^-]}\right)+1+\left(\frac{29[Cl^-]}{[NO_3^-]}\right)}\right) \qquad \text{(Equation 2)}$$

where $A=3.2\times10^{-8}$, $k=1.15\times10^{6}\times(1-e^{(-0.13[H_2O(l)])})$, and $[H_2O(1)]$, $[NO_3^-]$ and $[Cl^-]$ are the molarities of liquid water, nitrate, and chloride in aerosol volume. The yield of $ClNO_2$, ϕ, can be calculated with the following equation:

$$\phi = \left(1+\frac{[H_2O(l)]}{483[Cl^-]}\right)^{-1} \qquad \text{(Equation 3).}$$

The loss of N_2O_5 and the production of nitrate and $ClNO_2$ can be predicted with Eq. (1-3). The produced $ClNO_2$ is then photolysed, releasing a Cl atom, which further oxidises VOCs like an OH radical. The Cl-initiated gaseous chemistry used in this study was originally designed for CB05 mechanism by Sarwar et al. (2012), and was modified for RACM_ESRL mechanism (detail reactions are shown in Table S2). RACM_ESRL mechanism is the updated Regional Atmospheric Chemistry Mechanism in WRF-Chem based on the original version in Stockwell et al. (1997). The photolysis rates of Cl_2, HOCl, $ClNO_2$ and formyl chloride (FMCl) were calculated with the absorption cross section and quantum yield obtained from Atkinson et al. (2007) and Atkinson et al. (2008).

We implemented the N_2O_5 heterogeneous uptake, the $ClNO_2$ production, and the Cl-initiated reactions into the MADE/VBS aerosol model, RACM_ESRL gas-phase mechanism and Madronich photolysis model (Madronich, 1987) in the 'RACM_SOA_VBS_KPP' chemistry option in WRF-Chem v3.5.

2.3 Model setup

2.3.1 Model configuration

The model configurations of WRF-Chem used in this study are shown in Table 1. We used the Noah model to simulate the land surface process, the YSU module to simulate the PBL processes, the Purdue Lin scheme to predict the microphysics, the Grell 3-D ensemble module to simulate cumulus, the RRTMG model to predict shortwave and longwave radiation and the RACM_ESRL, MADE/VBS and Madronich modules to simulate gas-phase chemistry, aerosol processes and photolysis.

Model simulations were conducted in 4 domains covering East Asia, southern China, the PRD and Hong Kong, with spatial resolutions of 27, 9, 3, and 1 km, respectively (see Fig. 1a). High grid resolutions were adopted in this study to capture the extremely inhomogeneous terrain, with land and sea, mountain and plain, urban and forested areas, as shown in the terrain map of domain 2 (southern China) in Fig. 1b. The red dotted line in Fig. 1b represents the vertical cross-section domain that intercepts the most polluted part of the PRD and follows the prevailing (north-east) wind direction. The vertical domain is used to illustrate the vertical distribution of the N_2O_5 and $ClNO_2$ concentrations and the impacts of N_2O_5 uptake processes in southern China. Thirty vertical model layers were adopted, of which eight layers are below 1000m (approximately the height of PBL at noon) to provide more detailed information within the PBL.

2.3.2 Simulation cases

Three simulation cases, shown in Table 2, were conducted from November 15 to December 5, 2013, during which $ClNO_2$ and N_2O_5 levels were measured at the TMS site. All simulations used ISORROPIA II as the aerosol thermodynamics module. Note that the Base case did not include N_2O_5 heterogeneous uptake (or $ClNO_2$ chemistry). The HET+Cl case included the complete N_2O_5 uptake and Cl activation processes, i.e., N_2O_5 loss on aerosol, $ClNO_2$ production and gaseous chlorine reactions. Differences in chemical concentrations between the Base and HET+Cl cases, i.e., HET+Cl-Base, represent the impacts of N_2O_5 uptake and Cl activation. To estimate the relative contribution of N_2O_5 uptake versus Cl activation to O_3 and NO_y partitioning, the HET case was also conducted, which included N_2O_5 uptake but not $ClNO_2$ production (i.e. $ClNO_2$ yield, ϕ, was set to 0) and therefore producing only nitrate from N_2O_5 uptake. The changes from the Base case to the HET case (HET-Base) represent the impacts of N_2O_5 heterogeneous uptake, whereas the changes from the HET case to the HET+Cl case (HET+Cl-HET), represent the impacts of Cl activation.

3 Results and discussion

3.1 Model performance of WRF-Chem without N_2O_5 uptake and Cl activation

The meteorological simulation determines the simulations of the transport of the air pollutants and therefore is crucial to the simulations of the spatial distributions of the atmospheric chemical species and their impacts. The performance of the meteorological module during the study period has been validated in Wang et al. (2016), which showed that atmospheric flow and other meteorological parameters were satisfactorily simulated. The reader is referred to Wang et al. (2016) for further details.

The chemical simulation results of WRF-Chem without N_2O_5 heterogeneous uptake and Cl activation, i.e., the Base case, were validated against hourly observations of several major air pollutants measured at 11 HKEPD stations and at the TMS site. $PM_{2.5}$, NO_2 and O_3 were selected as the validation species because they act as the reaction surface ($PM_{2.5}$) or precursors (NO_2 and O_3) for N_2O_5 and $ClNO_2$ production. As shown in Table 3, the validation results for HKEPD stations indicate that Base case simulated the major air pollutants reasonably well in this region but overestimated $PM_{2.5}$, slightly underestimated NO_2 and underestimated O_3. The Base case also generally reproduced the observed temporal variations of $PM_{2.5}$, NO_2 and O_3 at the HKEPD stations and the TMS site (Fig. S1 a, 1b, 1c), and simulated the level of aerosol surface area density and particulate nitrate at TMS (Fig S1d, 1e). It should be noted that the technique for measuring NO_2 by the HKEPD, which is similar to that used in the regular air monitoring networks in North America and Europe, employs catalytic conversion which over-measures NO_2 (e.g., Xu et al., 2013). The discrepancy between the simulated and observed major air pollutants in this area is expected to affect the simulations of N_2O_5 and $ClNO_2$, which will be discussed in Section 3.2.1. ~~In the Base case, the model, in general, satisfactorily reproduced the observed $PM_{2.5}$, NO_2 and O_3 levels at the TMS site during the nights when N_2O_5 and $ClNO_2$ were measured (Fig. S1). The capture of the temporal variations of these pollutants at the TMS site provides a good basis for~~

~~simulation of the N_2O_5 and $ClNO_2$ temporal patterns (see Section 3.2.1).~~ The model performance of major air pollutants of Base case is within the acceptable range and is similar to our previous applications of WRF-Chem (Zhang et al., 2015; Zhang et al., 2016) and other WRF-Chem model studies (e.g., Li et al., 2011).

The simulated fine chloride concentrations in the Base case were compared with observations from several campaigns, as shown in Table 4. Tan et al. (2009) reported average concentrations of 1.19 µg m^{-3} and 8.37 µg m^{-3} at an urban site in Guangzhou (GZ) in the PRD on normal days and hazy days in winter, respectively; in comparison, the Base case simulated an average level of 2.51 µg m^{-3} at that location. Tao et al. (2014) reported an average level of 3.30 µg m^{-3} in winter at the station of South China Institute of Environmental Science (SCIES) in Guangzhou; Base case predicted 2.13 µg m^{-3} at this location. At the Tung Chung (TC) site in Hong Kong, we had previously measured an average level of 1.10 µg m^{-3} of chloride in $PM_{2.5}$ in late autumn and early winter, while the Base case simulated 0.32 µg m^{-3}. At the TMS site, an average level 0.37 µg m^{-3} of chloride was observed during the campaign (which was also the simulation period of this study), while the Base case predicted 0.14 µg m^{-3}. The simulated chloride level in the Base case was in order with observations over the PRD, but it still ~~under-simulated~~underpredicted the observed chloride level due to the expected underestimates of chlorine sources in the EI we applied (see Section 2.1.2).

The simulated ratio of aerosol surface area to volume ranges between $0.5*10^7$ m^{-1} and $2.5*10^7$ m^{-1} (Fig. S2), which is comparable with the value ($2.67*10^7$ m^{-1}) used in the parameterization of N_2O_5 uptake coefficient on aerosol proposed by Bertram and Thornton (2009).

Overall, the validations of the meteorological and chemical simulations suggest that the model is capable of capturing the general characteristics of air flow and key atmospheric chemical processes and hence can provide a basis for further simulation of the distributions of the N_2O_5 and $ClNO_2$ concentrations, and the impacts of N_2O_5 uptake and Cl activation on NO_y partitioning and O_3 production.

3.2 Simulation of N_2O_5 and $ClNO_2$ with N_2O_5 uptake and Cl activation

3.2.1 Comparison of simulated N_2O_5 and $ClNO_2$ with observation

The average observed and simulated (HET+Cl case) concentrations of N_2O_5 and $ClNO_2$ were calculated for each night, as shown in Fig. 2. The mean observed N_2O_5 concentrations for each night varied from 0.02 to 0.74 ppb during the study period, while the average simulated N_2O_5 values from the HET+Cl case were between 0.02 and 0.35 ppb. The HET+Cl case reproduced the order of N_2O_5 concentrations but underestimated them within a factor of three. Differences between the HET case and HET+Cl case in the simulated N_2O_5 were unnoticeable. For $ClNO_2$, the average observed concentrations varied from 0.01 to 0.39 ppb, whilst the mean simulated values for each night varied between 0.05 and 0.42 ppb. The HET+Cl case reproduced the order of $ClNO_2$ concentrations with an overestimate mostly within a factor of four. The simulated and observed hourly concentrations of N_2O_5 and $ClNO_2$ are shown in Fig. ~~S2~~S3, indicating that the HET and HET+Cl case ~~well~~ captured the temporal variations of these two compounds in general.

The ~~under-simulated~~underpredicted N_2O_5 and ~~over-simulated~~ overpredicted $ClNO_2$ values in the HET+Cl case point to the underestimation of the sources and/or the overestimation of the sink of N_2O_5 and the overestimation of the production of $ClNO_2$. As shown in section 3.1, the simulated NO_2 and O_3 levels in the HK-PRD region are lower than the observations, which results in lower production of N_2O_5; the simulated $PM_{2.5}$ concentrations are higher than the observed values which would lead to an overestimate of N_2O_5 heterogeneous loss. The observation-derived N_2O_5 uptake coefficients at the TMS site (Brown et al., 2016) varied from 0.004 to 0.029 with an average value of 0.014, whilst the simulated uptake coefficients ranged from 0.008 to 0.031 with an average of 0.019, which suggests that the HET+Cl simulation generally overestimates N_2O_5 uptake coefficients, which causes further overestimation of the loss of N_2O_5. The reactive uptake coefficient could be overestimated because the parameterization used in this study does not consider the inhibition of organic coating to the uptake coefficient (Bertram and Thornton, 2009). The overestimated loss of N_2O_5 on aerosol inherently overestimated the production of $ClNO_2$. The parameterisations used in this study are likely to overestimate the $ClNO_2$ yield (Kim et al., 2014; Ryder et al., 2015), which would further overestimate the production of $ClNO_2$. In addition, the overpredicted $ClNO_2$ could also be due to the ignorance of possible $ClNO_2$ sinks (e.g. Roberts et al, 2008).

Discrepancies between the measured and simulated N_2O_5 and $ClNO_2$ levels have also been reported in previous model studies. Lowe et al. (2015) used the same parameterisations for N_2O_5 uptake that we applied in our study and showed slightly higher average simulated N_2O_5 values along two flight tracks but a factor of 1-2 lower simulated N_2O_5 in another flight. They noted that the underestimated N_2O_5 could be attributed to inaccuracies in the meteorological simulation. Sarwar et al. (2012) used the parameterisation for N_2O_5 uptake proposed by Davis et al. (2008) and by Bertram and Thornton et al. (2009) and yielded a slightly higher simulated peak value of $ClNO_2$ than the observed value in field studies conducted at different times from the model simulations. The authors attributed the overestimate of $ClNO_2$ to the overestimated N_2O_5 uptake in the parameterisations. Sarwar et al. (2014) predicted lower peak values of $ClNO_2$ than the observations and suggested that the underestimated $ClNO_2$ could be attributed to a relatively low model resolution (108 km).

3.2.2 Spatial distribution of average simulated N_2O_5 and $ClNO_2$

Figure 3a and 3c show the average mixing ratios of N_2O_5 and $ClNO_2$ during the night-time (18:-00-07:00, LT) ~~the entire simulation period~~ within the lowest 1000 m (the approximate height of the PBL at noon) in southern China in the HET+Cl case. Elevated levels of N_2O_5 (>0.10 ppb) and $ClNO_2$ (>0.25 ppb) were predicted in the areas downwind of the PRD, as a result of the transport of pollutant enriched air masses towards the south-west of the PRD by the prevailing north-easterly winds. The areas with the highest simulated N_2O_5 and $ClNO_2$ values did not cover the TMS site at which the highest ever reported N_2O_5 and $ClNO_2$ values were observed (Brown et al., 2016; Wang et al., 2016), which supports our speculation that the locations downwind of the PRD under the dominant north-easterly winds may frequently have higher levels of $ClNO_2$. The simulated yield of $ClNO_2$ during the night-time ranged from 0.1 to 0.7 within PBL (Figure S4), which is consistent with previous observation study (0.1 to 0.65) (Osthoff et al., 2008) and modelling study (0.0 to 0.9) (Sarwar et al., 2012).

The vertical distributions of N_2O_5 and $ClNO_2$ in the vertical domain (as described in section 2.3.1) are shown in Fig. 3b and 3d. Elevated levels of N_2O_5 (> 0.10 ppb) were predicted up to around 1000 m a.g.l., with the highest N_2O_5 level (>0.25 ppb) mostly between 400-800m a.g.l., probably due to ~~suppression~~ the reactions of NO_3 ~~(and N_2O_5) by~~ with NO and VOCs in the lowest several hundred meters over the urban area, as shown in Fig. ~~S3~~S5. Elevated levels of $ClNO_2$ (>0.25 ppb) were simulated up to 1000 m a.g.l., with the highest $ClNO_2$ values (>1.00 ppb) mostly concentrated within the near-surface layer of 0-200 m a.g.l. The vertical distribution of $ClNO_2$ was consistent with the vertical profile of chloride, as shown in Fig. ~~S4~~S6. The simulated vertical distribution of N_2O_5 and $ClNO_2$ are similar to those from previous observation and modelling studies. Stutz et al. (2004) calculated the steady-state N_2O_5 concentrations based on the measured vertical profile of NO_2 and NO_3 and found elevated values (up to 300 ppt) aloft (~110m). Brown et al. (2007a) measured N_2O_5 vertical profile within the nocturnal boundary layer (<300 m) on a tower in Boulder, U.S. and found the peak value (~700 ppt) at ~200m a.g.l. Brown et al. (2007b) reported N_2O_5 vertical measurements from an aircraft in U.S. and the average results showed the peak concentrations (~160 ppt) at ~200m a.g.l. ~~those of~~ Sarwar et al. (2012)~~, which showed that~~ simulated the distributions of N_2O_5 and $ClNO_2$ with CMAQ, and found that N_2O_5 peaked at 200-400 m a.g.l., and ~~simulated~~ $ClNO_2$ peaked at the surface and stretched up to 400 m a.g.l. in several U.S. cities at dawn.

3.2.3 Dynamic evolutions in cases with typical and extreme meteorological conditions

We examine the time evolution of the spatial distribution of $ClNO_2$ in two cases. In the typical case (the night of December 1/2), southern China was dominated by consistent north-easterly winds which represented the average dynamic conditions during the study period, while in the extreme case (the night of December 3/4), the air-flow over the region abruptly changed. Note that in this extreme case, the highest ever-reported $ClNO_2$ levels were observed at the TMS site, and the back trajectories and observations of chemical species pointed to the transport to the site of well-processed plumes from the PRD with enriched anthropogenic chloride and other pollutants (Wang et al., 2016).

In the typical case, consistent north-easterly winds controlled southern China throughout the night (Fig. 4). At the beginning of the night (18:00, local time (LT)), $ClNO_2$ began to build up near the urban area (Fig. 4a) and near the surface (Fig. 4b); at midnight (00:00, LT), the air with an elevated level of $ClNO_2$ moved to coastal areas (Fig. 4c) and accumulated near the surface (Fig. 4d); at dawn (06:00, LT), the peak $ClNO_2$ level was predicted over the open sea (Fig. 4e), and pumped up to higher altitudes with the peak value near the surface (Fig. 4f), due to the higher boundary layer height over the ocean, as shown in Fig. ~~S5~~S7.

In the extreme case, at the beginning of the evening (18:00, LT), southern China had unfavourable dispersion conditions over the land, including inconsistent wind directions and low wind speeds. The air pollutants emitted from the PRD slowly swirled over it, as shown in Fig. 5a, resulting in a longer 'cooking' time for $ClNO_2$ production. The vertical distribution (Fig. 5b) shows that $ClNO_2$-enriched air stretched from the ground up to 800m a.g.l. The enhanced production of $ClNO_2$ is believed to be partially responsible for the highest $ClNO_2$ mixing ratios measured at the TMS site at this night. At midnight (00:00, LT), inconsistent wind directions presented between land and sea areas: northerly winds dominated over the land area, while north-easterly winds dominated over the sea, leading to relatively slow motion of the $ClNO_2$-enriched plume from the land towards the ocean (Fig. 5c). The vertical distribution (Fig. 5d) suggests that $ClNO_2$ built up within the residue layer. At dawn (06:00, LT), the north-easterly wind regained control over the land areas, and the air with the elevated level of $ClNO_2$ (>2.00 ppb) was driven towards the ocean, as shown in Fig. 5e. The vertical distribution (Fig. 5f) shows that the peak $ClNO_2$ concentration was predicted to be in the residue layer at ~300m a.g.l. The changes of wind flow over the region during this night resulted in abnormal changes in the history of the air masses that reached the TMS site and led to the abrupt changes in the air pollutants concentrations observed there (see Wang et al., 2016 for details).

From these results, it can be seen that the vertical distributions of $ClNO_2$ demonstrated distinct features in the two cases. To understand the underlying cause, it is of significance to measure the vertical profiles of $ClNO_2$ under various meteorological conditions. In addition, during the extreme event, the location with the highest predicted $ClNO_2$ (>2.00 ppb) was not at the TMS site (>1.00 ppb), but was located in the western parts of the PRD (i.e., the cites of Jiangmen and Zhaoqing), which supports the contention that the $ClNO_2$ concentrations at other locations could be even higher than those observed at the TMS site (Wang et al., 2016). It would be of great interest to conduct measurements at the areas where the highest $ClNO_2$ concentrations are predicted.

3.3 Impacts of N_2O_5 heterogeneous uptake and Cl activation on NO_x, total nitrate and O_3

3.3.1 Impacts on ~~in the~~ horizontal and vertical ~~domains~~ distributions of the species

Figure 6 shows the simulation results for the average NO, NO_2, total nitrate and O_3 concentrations within the PBL (<1000m) during the entire simulation period in the Base case, and the difference of the results between the HET+Cl and Base cases in the horizontal domain. ~~Elevated~~ Relatively high levels of NO (up to 26.18 ppb; Fig. 6a), NO_2 (up to 29.18 ppb; Fig. 6c), total nitrate (up to 23.43 μg m^{-3}; Fig. 6e), and O_3 (up to 44.50 ppb; Fig. 6g) were predicted in southern China in the Base case. The spatial distributions of maxima of NO (Fig. S8a), NO_2 (Fig. S8c) and total nitrate (Fig. S8e) were similar to those of their daily-averages, whereas the spatial distribution of 1-hr maxima O_3 ((higher in PRD and its downwind areas; Fig. S8g) was different from its daily average (higher in rural and remote region; Fig. 6g).With the prevailing north-easterly wind, the pollutants emitted from the PRD were transported towards the south-west, resulting in the most polluted regions being the PRD and its south-westerly downwind areas. After addition of the N_2O_5 uptake and Cl activation processes, the NO (Fig. 6b) and NO_2 (Fig. 6d) levels were significantly decreased in the entire domain by up to 1.93 ppb (~ 7.4%) and 4.73 ppb (~ 16.2%), respectively. The regions with greater impacts on the NO and NO_2 due to the added processes were mostly urban and suburban areas with large emissions of NO_x. A significant portion of NO_x was transformed into total nitrate, which increased by as much as 13.45 μg m^{-3} (~ 57.4%) through the heterogeneous uptake of N_2O_5 (see Fig. 6f). As can be seen in Fig. 6h, the N_2O_5 uptake and Cl activation noticeably increased O_3 levels across southern China, with a maximum increase up to 7.23 ppb (~16.3%). It is worth noting that in addition to the urban and suburban areas, the O_3 levels over the rural and coastal areas was also significantly affected by the added processes. The average impacts of N_2O_5 uptake and Cl activation on daily-maxima of NO, NO_2, total nitrate and O_3 were shown in Fig. S8b, S8d, S8f and S8h, which were with similar spatial patterns as the averaged results of the entire simulation period. The incorporation of N_2O_5 uptake and Cl activation improved the model performance for daily O_3 and 1-h maximum O_3 (Table 3), but did not improve the simulations of $PM_{2.5}$ and NO_2 which could be due to various reasons, e.g. emission inventory, etc.

Figure 7 shows the average simulated NO, NO_2, total nitrate and O_3 values in the Base case, and the difference in the results between the Base and HET+Cl cases in the vertical domain. NO and NO_2 were concentrated within 800 m a.g.l. over the PRD and in downwind areas (see Fig. 7a and 7c). Total nitrate accumulated near the ground and stretched up to 800 m a.g.l. (Fig. 7e). Due to the titration effect of NO, relatively low average values of O_3 were simulated over urban areas (Fig. 7g). As shown in Fig. 7b and 7d, the N_2O_5 uptake and Cl activation decreased the NO and NO_2 levels across the vertical domain, with the largest impacts seen in the near-surface layer (0-400 m a.g.l.) over the PRD. The lost NO and NO_2 were mostly transformed into total nitrate, which increased remarkably in the near-surface layer (Fig. 7f). The impacts of N_2O_5 uptake and Cl activation on the O_3 level varied with altitude: the O_3 increased throughout the lowest 800 m with the largest enhancement near the ground, whereas it decreased above 1000 m a.g.l. (Fig. 7h). The changes in the O_3 were attributed to the combined effects of NO_x loss due to N_2O_5 uptake and Cl atom production due to Cl activation, both of which have nonlinear impacts on O_3 production. The relative contribution of N_2O_5 uptake versus Cl activation on the NO, NO_2, total nitrate and O_3 concentrations will be discussed in the following section.

3.3.2 Relative contribution of N_2O_5 heterogeneous uptake versus Cl activation

To understand the relative contribution of N_2O_5 uptake and Cl activation, we conducted a sensitivity case (HET case as listed in Table 2) in which only nitrate was produced via N_2O_5 uptake. The differences in the simulations between the Base and HET cases represent the effects of N_2O_5 uptake, while those between the HET and HET+Cl cases represent the effects of Cl activation.

As shown in Fig. 8a and 8c, the mere consideration of nitrate production from N_2O_5 uptake led to decreases in NO and NO_2 by up to 1.11 ppb and 4.28 ppb, respectively. In addition, most of the lost NO_x was transformed into total nitrate which increased by as much as 14.92 μg m^{-3} (Fig. 8e). These results are similar to those of Lowe et al. (2015), who suggested that the nitrate in PM_{10} was enhanced by up to 31.4% (increasing from 3.5 μg Kg^{-1} to 4.6 μg kg^{-1} at night) after considering the heterogeneous uptake processes of N_2O_5. The N_2O_5 uptake increased the O_3 levels by as much as 3.10 ppb in ~~urban and suburban~~ both urban and rural areas in the PRD and decreased the O_3 by up to 1.47 ppb in remote areas~~rural and coastal areas~~ (Fig. 8g), ~~due to the nonlinearity of O_3 production,~~ which are similar to the findings of Riemer et al. (2003) indicating that the N_2O_5 uptake resulted in an increase in the O_3 level in high-NO_x areas and a decrease in low-NO_x areas.

~~The further addition of Cl activation led to decreases in the NO level by as much as 0.96 ppb, as shown in Fig. 8b, and increases in NO_2 by up to 0.72 ppb, as shown in Fig. 8d.~~ The Cl activation ~~slightly~~ decreased the total nitrate by up to 2.35 μg m^{-3} (Fig. 8f), because a fraction of N_2O_5 was consumed to produce $ClNO_2$ in competition with nitrate production. The simulated O_3 was significantly increased throughout the domain by as much as 4.54 ppb (Fig. 8h), which could be attributed to the release of NO_2 molecules that subsequently undergo photolysis and form O_3, and the effects of the activation of Cl radicals that initiate~~d~~ VOCs degradation and O_3 formation (Simon et al., 2009). The increase in the O_3 further enhanced the oxidation of NO into NO_2 which decreased NO by as much as 0.96 ppb (Fig. 8b), and increased NO_2 in urban areas by up to 0.72 ppb (Fig. 8d).~~, and the~~ The recycling of NO_2 via $ClNO_2$ photolysis also contributed to the increase in NO_2. The O_3 increase also elevated the OH radical levels which enhanced the loss of NO_2 through its reaction with OH, resulting in the decrease of NO_2 in suburban and rural regions by up to 0.53 ppb (Fig. 8d).

3.4 Impacts of N_2O_5 uptake and Cl activation on NO_y partitioning

The composition and partitioning of NO_y affect the spatial range that nitrogenous species can reach after emission, and are therefore of great importance in atmospheric chemistry (Bertram et al., 2013). The average concentration of NO_y altered modestly within the PBL over domain 2 with the addition of N_2O_5 uptake and Cl activation (12.24 ppb and 11.42 ppb in the Base and HET+Cl cases, respectively). The fractions of each species in NO_y, however, were substantially affected. The NO_y partition was calculated over domain 2 for the Base and HET+Cl cases (see Fig 9). The percentage of N_2O_5 in NO_y decreased from 7.80% in the Base case to 1.01% in the HET+Cl case, and that for NO_3 decreased from 0.38% to 0.09%. The N_2O_5 uptake and Cl activation reduced the fraction of NO from 9.59% to 6.84% and that of NO_2 from 51.07% to 35.17%. The percentage of total nitrate (nitrate + HNO_3) in NO_y was significantly increased from 27.5% (=9.6%+17.9%) to 48.6% (=16.0%+32.6%). The added processes also introduced a new NO_y species, $ClNO_2$, which accounted for 3.47% in the HET+Cl case. The decrease in the NO_3 level caused by N_2O_5 heterogeneous uptake would suppress the night-time chemistry of NO_3 and VOCs. The N_2O_5 uptake transferred a significant portion of NO_x to total nitrate, reducing the lifetime and reaching range of NO_x-enriched plumes and thus affecting the NO_x-VOCs-O_3 photochemistry. The new species in the HET+Cl case, $ClNO_2$, contributed a non-negligible part of NO_y, and extended the lifetime and reaching range of reactive nitrogen.

3.5 Sensitivity of $ClNO_2$ concentration to chlorine emission

The production of $ClNO_2$ depends on the chloride concentration in aerosol according to the parameterisation used in this study (Bertram and Thornton, 2009). The only available chlorine EI for China is taken from a global dataset with a relatively low resolution (1°x1°) and for the year of 1990 (Keene et al., 1999). To test the sensitivity of the $ClNO_2$ production to Cl emissions, we conducted two simulations in which the RCEI emission were reduced by half (HET+Cl+0.5RCEI) and doubled (HET+Cl+2.0RCEI). The simulations show that the ambient chloride concentrations responded almost linearly to the applied chlorine emissions (data not shown). The simulated $ClNO_2$ has a similar temporal pattern in different Cl emissions (Fig. ~~S6~~S9). The $ClNO_2$ concentrations have positive but not linear correlation to Cl emission changes. As shown in Fig. 10, halving the Cl emissions leads to a 31% reduction in the simulated $ClNO_2$ level, whereas doubling the Cl emissions results in an average 31% increase of $ClNO_2$. The results indicate that simulation of $ClNO_2$ production is sensitive to chlorine emission. Therefore, future studies are needed to develop an up-to-date anthropogenic chlorine EI in China to better model $ClNO_2$ production, and to quantify its impact on atmospheric chemistry and air quality. Previous research on chlorine emission could be used as reference to develop chlorine EI in China. Chang et al. (2002) compiled a chlorine EI for Houston including the emissions from cooling towers, sea salt, point sources and various water treatments. Sarwar and Bhave (2007) integrated a chlorine EI for eastern U.S. with sources of various industrial point sources, area sources, cooling towers and swimming pools.

4 Summary and conclusions

In this study, a state-of-the-art chemical transport model (WRF-Chem) was further developed by incorporation of a widely-used aerosol thermodynamics model (ISORROPIA II), parameterisation of heterogeneous uptake of N_2O_5 and $ClNO_2$ production, and gas-phase chlorine chemistry. The revised model was used to simulate the spatial distributions of N_2O_5 and $ClNO_2$ and the impacts on O_3 and NO_y partitioning over the HK-PRD region where high levels of N_2O_5 and $ClNO_2$ had been observed. The revised model was able to capture the temporal patterns and the magnitudes of the observed N_2O_5 and $ClNO_2$ at a mountain-top site in Hong Kong, but tended to underpredict~~under-simulate~~ N_2O_5 and ~~over-simulate~~ overpredict $ClNO_2$ because of the underestimates of N_2O_5 sources and overestimates of N_2O_5 sink and $ClNO_2$ production. Model simulations show that under average ~~meteorological~~ conditions, high values of N_2O_5 and $ClNO_2$ are concentrated in the south-west region to the urban areas of the PRD and vertically peak within the layer of 400-800 m a.g.l. and 0-200 m a.g.l, respectively. At the night of December 3/4 when the highest ever-reported $ClNO_2$ (4.7 ppb) was observed, the model suggested that the high levels of $ClNO_2$ were concentrated in the residue layer (~300m a.g.l.) above the study region. The model simulations suggested that the region downwind of the urban PRD may experience higher levels of $ClNO_2$ than that observed at the TMS site. N_2O_5 uptake and Cl activation significantly decreased the levels of NO and NO_2 by up to 1.93 ppb (~7.4%) and 4.73 ppb (~16.2%), respectively, but increased the total nitrate level by as much as 13.45 $\mu g\ m^{-3}$ (~ 57.4%) and the O_3 by up to 7.23 ppb (~16.3%) within the PBL. Our results demonstrate the significant impacts of N_2O_5 uptake and $ClNO_2$ production on NO_x lifetime, secondary nitrate production, and O_3 formation and underscore the necessity of considering these processes in air quality models. Our simulations of $ClNO_2$ levels over southern China are sensitive to chlorine emissions, which suggests the need to develop a more reliable emission inventory of chlorine for better quantification of the N_2O_5/$ClNO_2$ chemistry and their impacts over China.

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Table 1. Model configuration

WRF-Chem modules	Parameterization options	Reference
Land surface	Noah Land Surface Model	Chen and Dudhia (2001)
PBL scheme	YSU	Hong et al. (2006)
Microphysics	Purdue Lin Scheme	Lin et al. (1983)
Cumulus	Grell 3-D ensemble	Grell and Devenyi (2002)
Shortwave and longwave radiation	RRTMG	Iacono et al. (2008)
Gas chemistry	RACM_ESRL	Updated version based on Stockwell et al. (1997)
Aerosol	MADE/VBS	Ahmadov et al. (2012)
Photolysis	Madronich	Madronich (1987)

Table 2. Simulation cases

Cases	Aerosol thermodynamics module	N_2O_5 and $ClNO_2$ chemistry
Base	ISORROPIA II	None
HET	ISORROPIA II	N_2O_5 heterogeneous uptake, no $ClNO_2$ production
HET+Cl	ISORROPIA II	N_2O_5 heterogeneous uptake, $ClNO_2$ production and gas-phase Cl reactions

Table 3. Comparison of chemical simulation with observation for Base and HET+Cl case

	Base				HET+Cl			
	$PM_{2.5}$ (μg m^{-3})	NO_2 (ppb)	O_3 (ppb)	1-h daily maximum O_3 (ppb)	$PM_{2.5}$ (μg m^{-3})	NO_2 (ppb)	O_3 (ppb)	1-h daily maximum O_3 (ppb)
Observation Average	37.43	33.67	28.29	50.98	37.43	33.67	28.29	50.98
Simulation Average	48.08	28.81	15.06	34.04	49.63	26.48	17.30	38.34
Normalized Mean Bias	28.5%	-14.4%	-46.8%	-33.2%	32.6%	-21.4%	-38.8%	-24.8%
Fac2[a]	0.69	0.71	0.46	0.86	0.69	0.70	0.50	0.92

a: Fac2 is defined as the fraction of the simulations that are within a factor of two of the observations.

Table 4. Comparison of measured and simulated (Base) chloride

Location	Period	Average measured concentration (μg m^{-3})	Average simulated concentration (μg m^{-3}) [e]
GZ	2007/12/31 to 2008/1/12 normal day	1.19 [a]	2.51
GZ	2007/12/31 to 2008/1/12 haze day	8.37 [a]	2.51
SCIES, GZ	2009-2010 winter	3.30 [b]	2.13
TC, HK	2011/10/25 to 2011/12/7	1.10 [c]	0.32
TMS, HK	2013/11/15 to 2013/12/5	0.37 [d]	0.14

a: Tan et al., 2009; b: Tao et al., 2014; c: unpublished data; d: Wang et al., 2016. e: The time period used to calculate the average simulated concentration is the entire simulation period (November 15 to December 5, 2013).

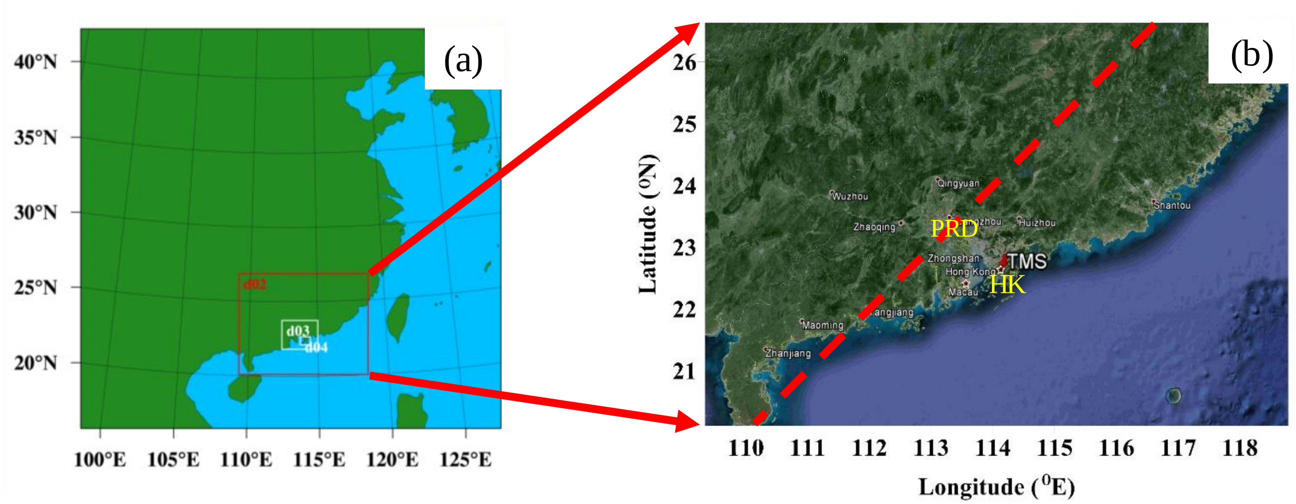

Figure 1. (a) Domain settings of WRF-chem simulations, and (b) the terrain in domain 2 (southern China). The red dotted line represents the vertical domain that intercepts the most polluted PRD region along the prevailing wind direction (north-east). TMS is the location of the site where N_2O_5 and $ClNO_2$ were measured. HK and PRD are the general locations of Hong Kong and Pearl River Delta region.

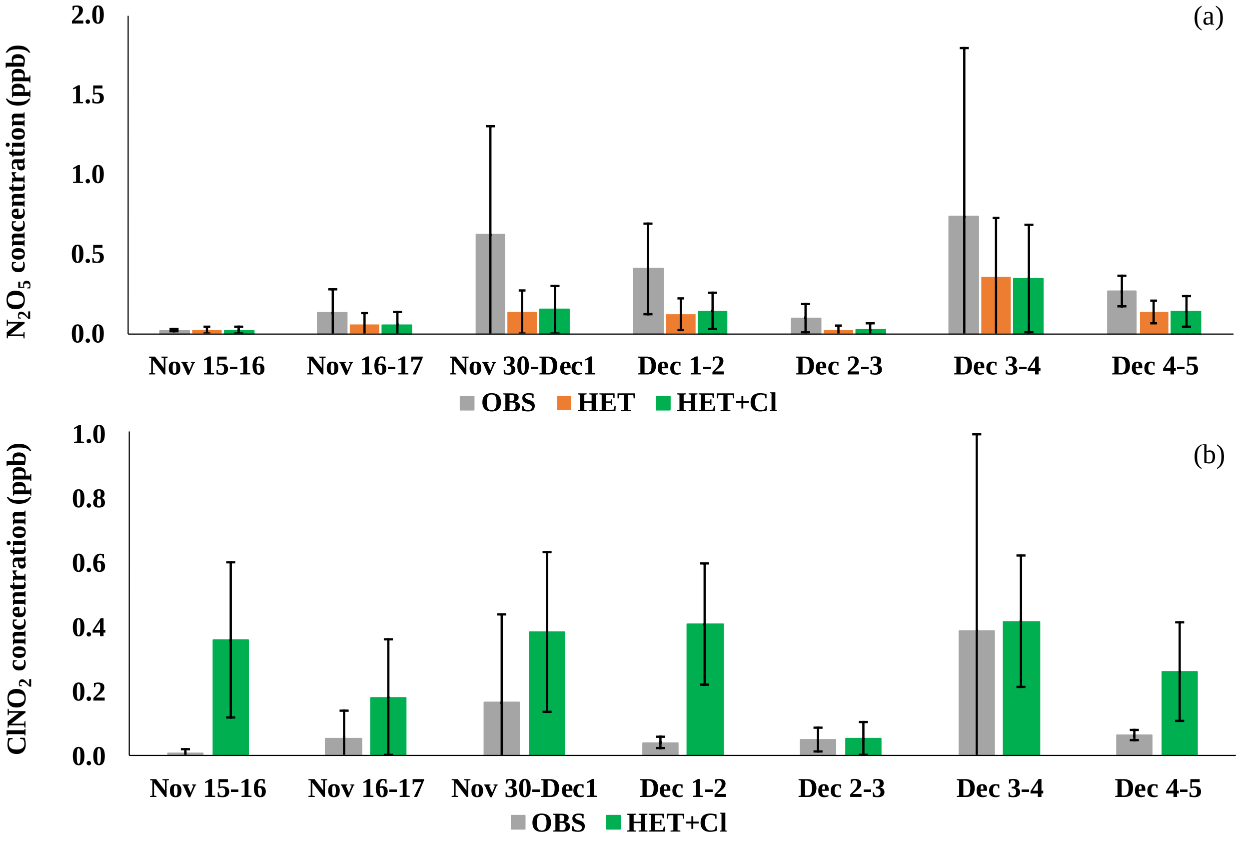

Figure 2. Comparison of simulated and observed average (a) N_2O_5 and (b) $ClNO_2$ concentrations at each night at TMS site. Error bars represent the standard deviation.

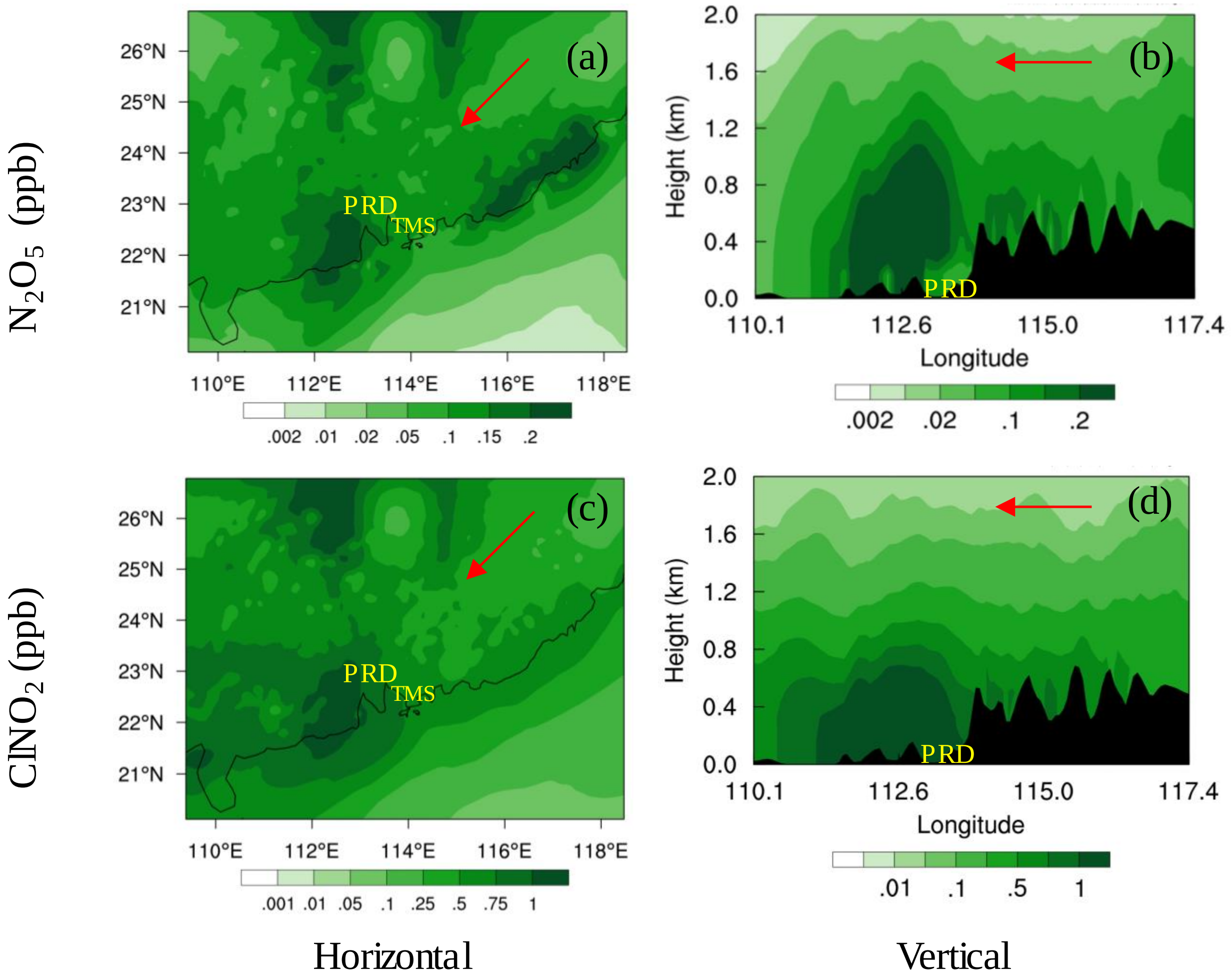

Figure 3. Horizontal distributions of (a) N_2O_5 and (c) $ClNO_2$ average mixing ratios (ppb) during ~~the study period~~night-time (18:00-07:00 LT) within the PBL from HET+Cl case; vertical distributions of (b) N_2O_5 and (d) $ClNO_2$ average mixing ratios (ppb) during ~~the study period~~night-time (18:00-07:00 LT) in the domain intercepting PRD and along the prevailing wind direction from HET+Cl case. Red arrows represent the prevailing wind direction. The black shades in vertical plots represent terrain features.

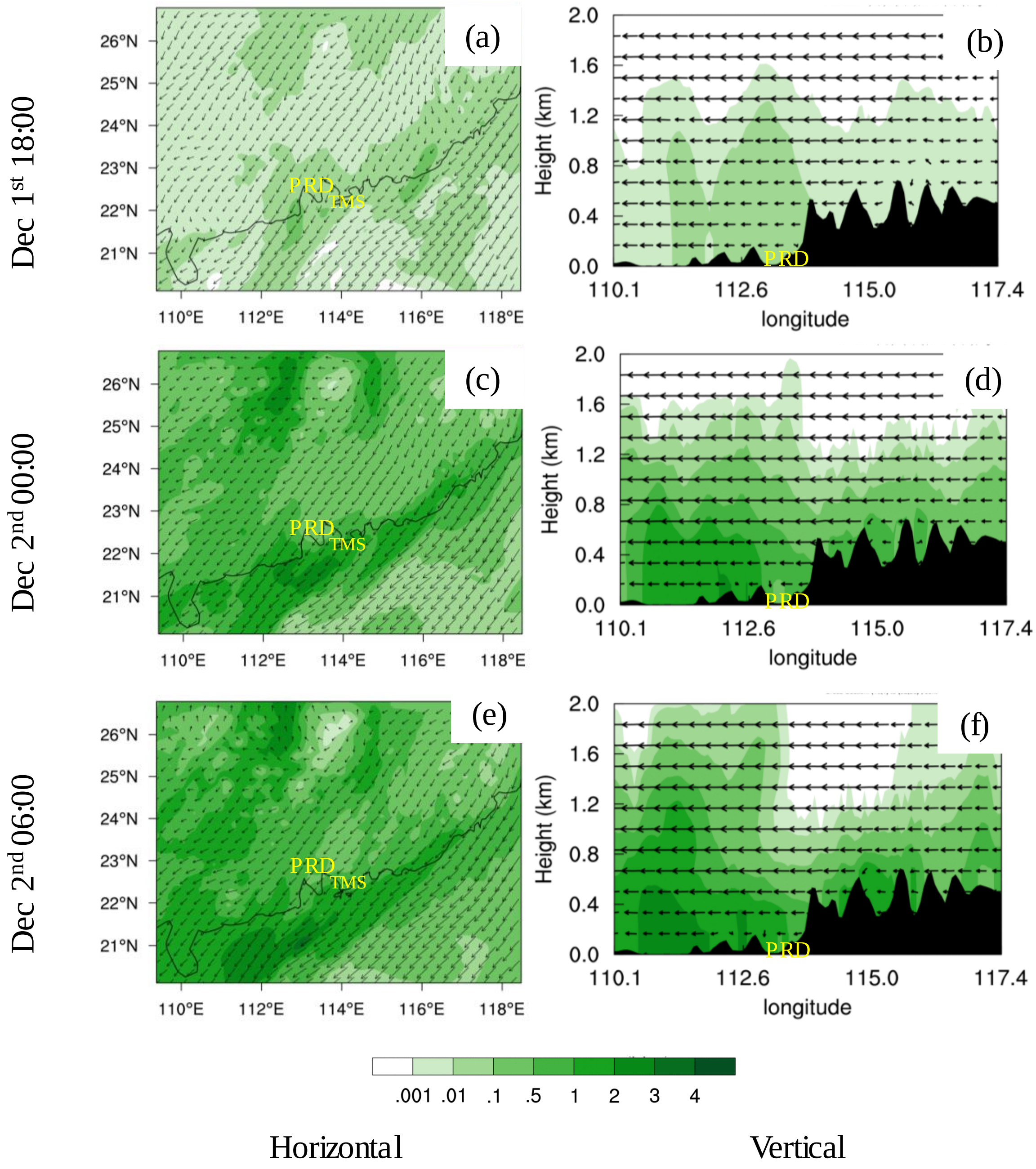

Figure 4. Horizontal distributions of ClNO$_2$ concentrations (ppb) at (a) 18:00 Dec 1, (c) 00:00 Dec 2, and (e) 06:00 Dec 2, LT within the PBL from HET+Cl case; vertical distributions of ClNO$_2$ concentrations (ppb) at (b) 18:00 Dec 1, (d) 00:00 Dec 2, and (f) 06:00 Dec 2, LT in the domain intercepting PRD and along the prevailing wind direction from HET+Cl case.

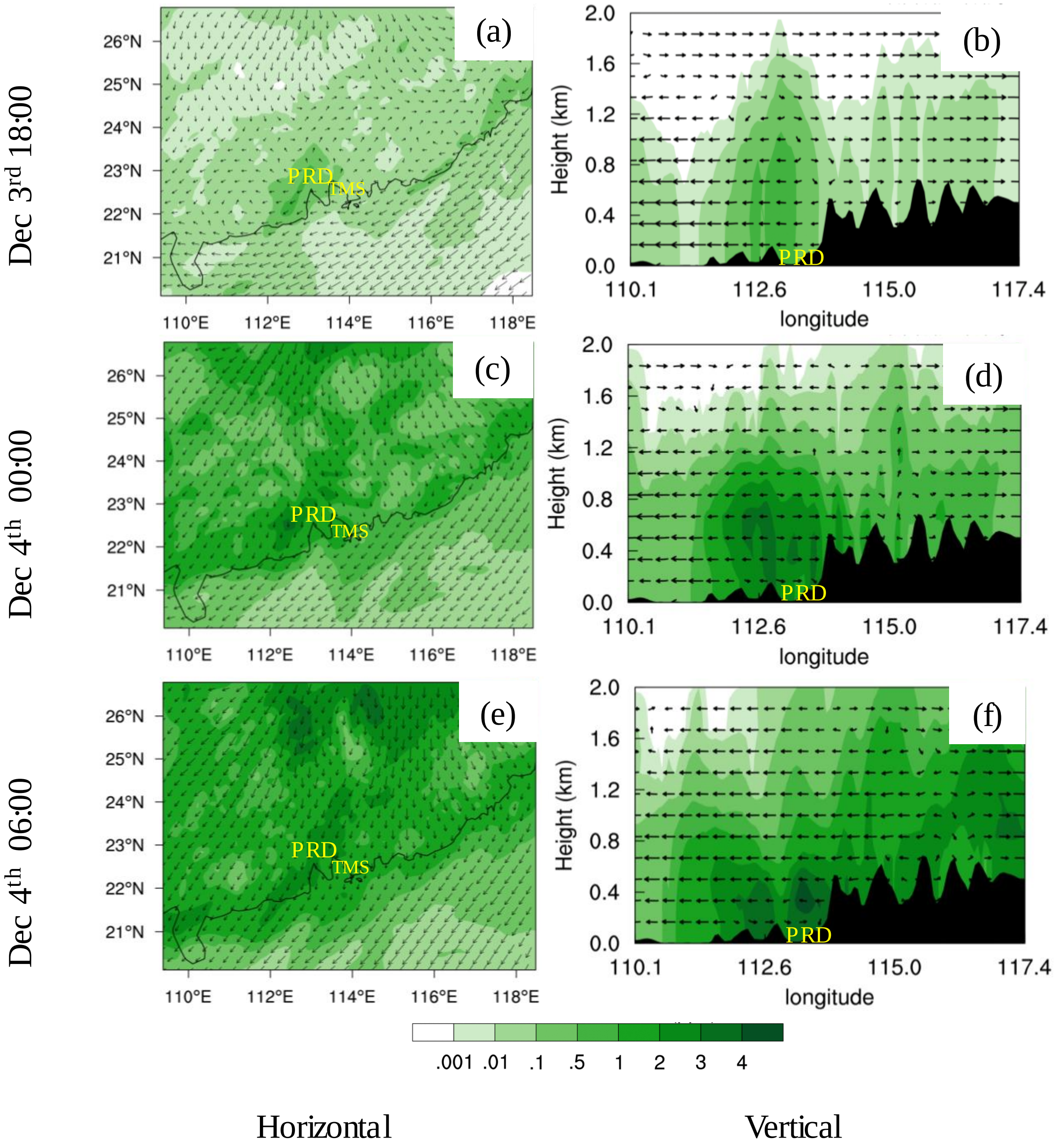

Figure 5. The same as in Figure 4, except at the night of December 3/4.

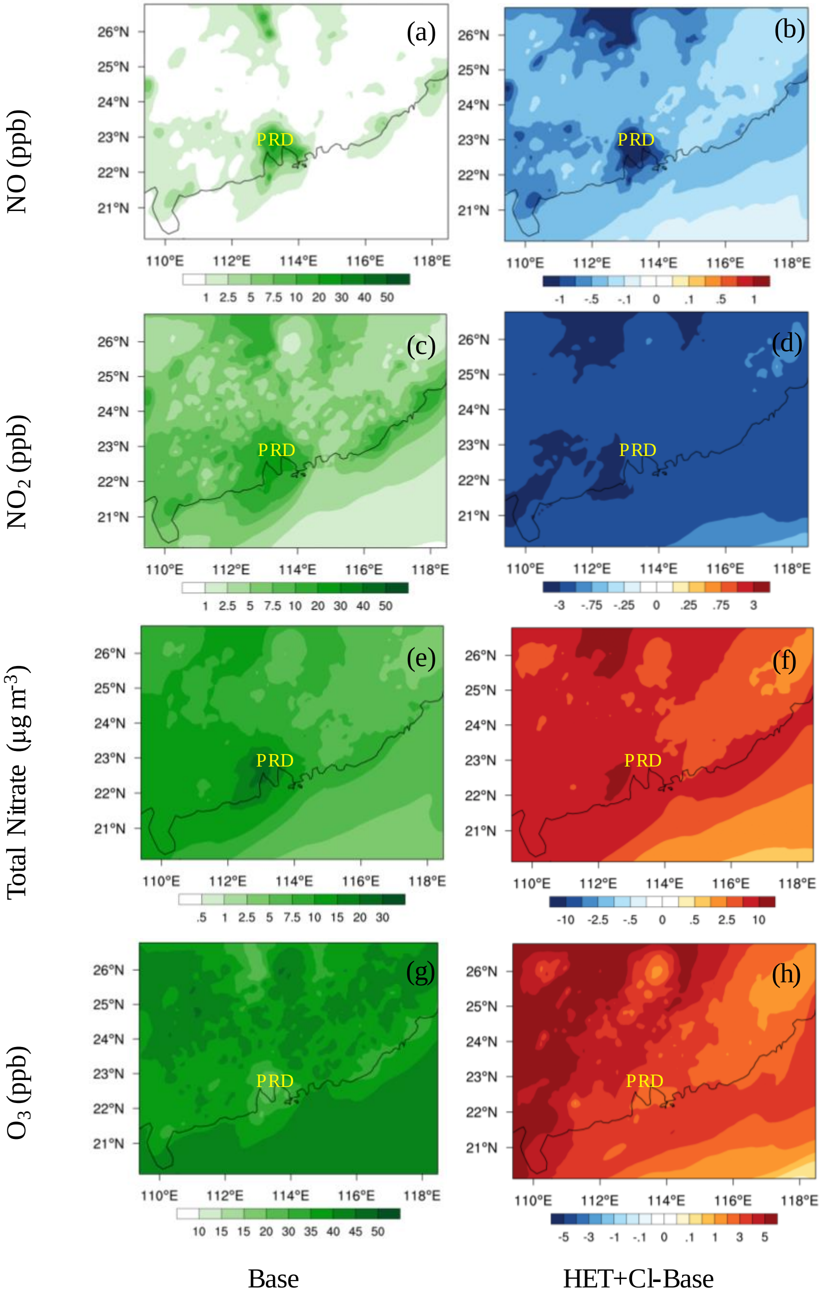

Figure 6. Horizontal distributions of (a) NO (ppb), (c) NO$_2$ (ppb), (e) total nitrate (µg m^{-3}) and (g) O$_3$ (ppb) average concentrations during the study period within the PBL from Base case; the average impacts of N$_2$O$_5$ uptake and Cl activation on (b) NO (ppb), (d) NO$_2$ (ppb), (f) total nitrate (µg m^{-3}) and (h) O$_3$ (ppb) average concentrations during the simulation period in the horizontal domain within the PBL.

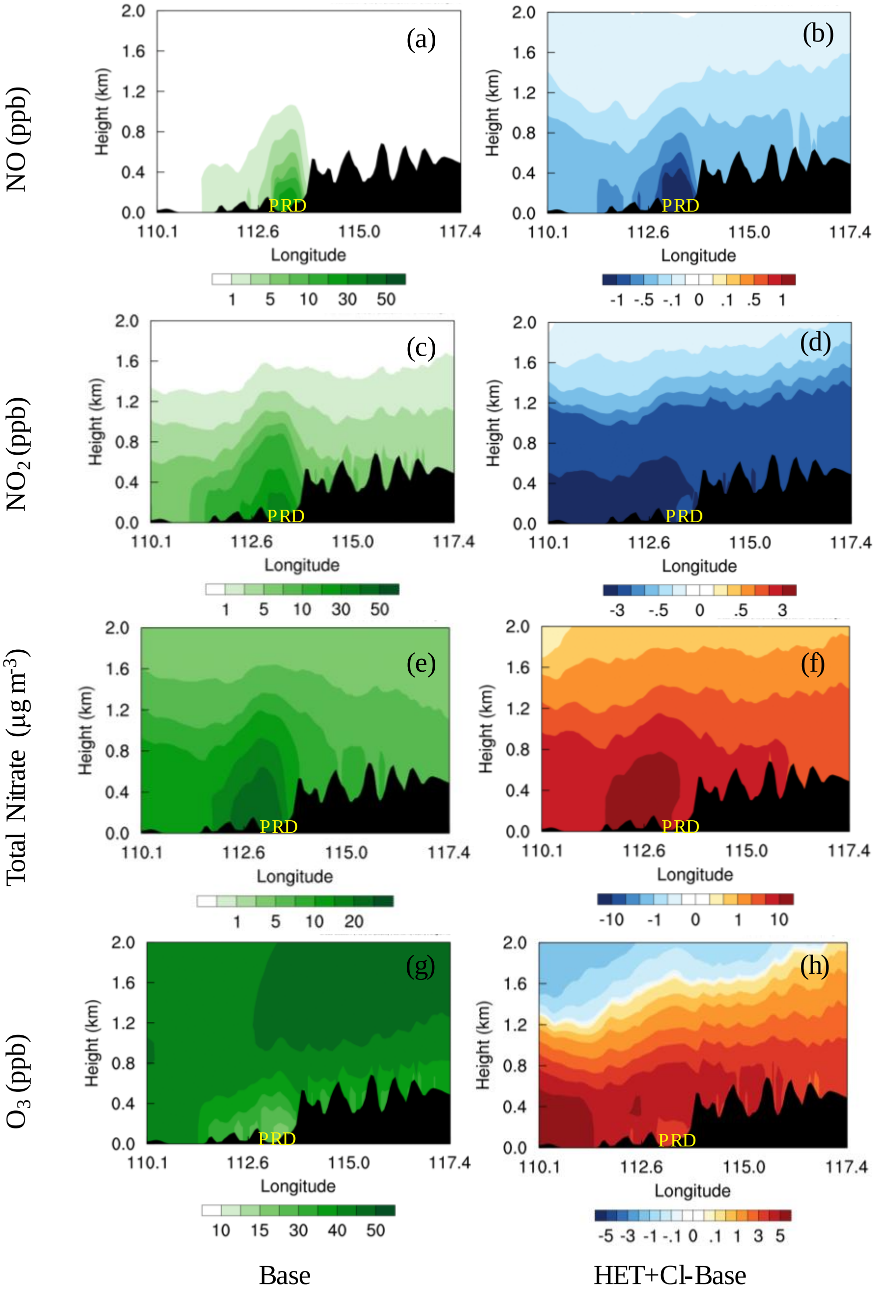

Figure 7. Vertical distributions of (a) NO (ppb), (c) NO_2 (ppb), (e) total nitrate (μg m^{-3}) and (g) O_3 (ppb) average concentrations during the study period in the domain intercepting PRD and along the prevailing wind from Base case; the average impacts of N_2O_5 uptake and Cl activation on (b) NO (ppb), (d) NO_2 (ppb), (f) total nitrate (μg m^{-3}) and (h) O_3 (ppb) average concentrations during the simulation period in the vertical domain.

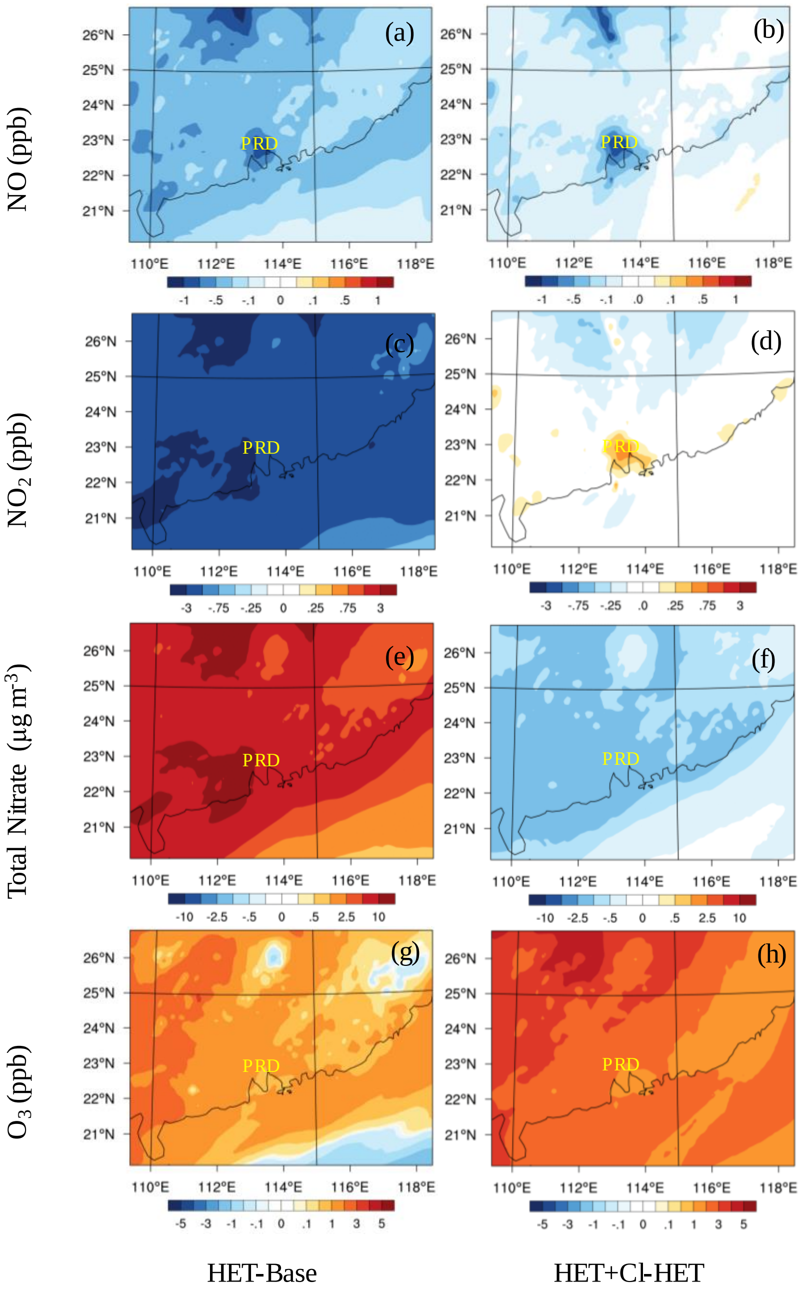

Figure 8. Average impacts of N_2O_5 heterogeneous uptake on (a) NO (ppb), (c) NO_2 (ppb), (e) total nitrate (µg m^{-3}) and (g) O_3 (ppb) average concentrations during the simulation period in the horizontal domain within the PBL; average impacts of Cl activation on (b) NO (ppb), (d) NO_2 (ppb), (f) total nitrate (µg m^{-3}) and (h) O_3 (ppb) average concentrations during the simulation period in the horizontal domain within the PBL.

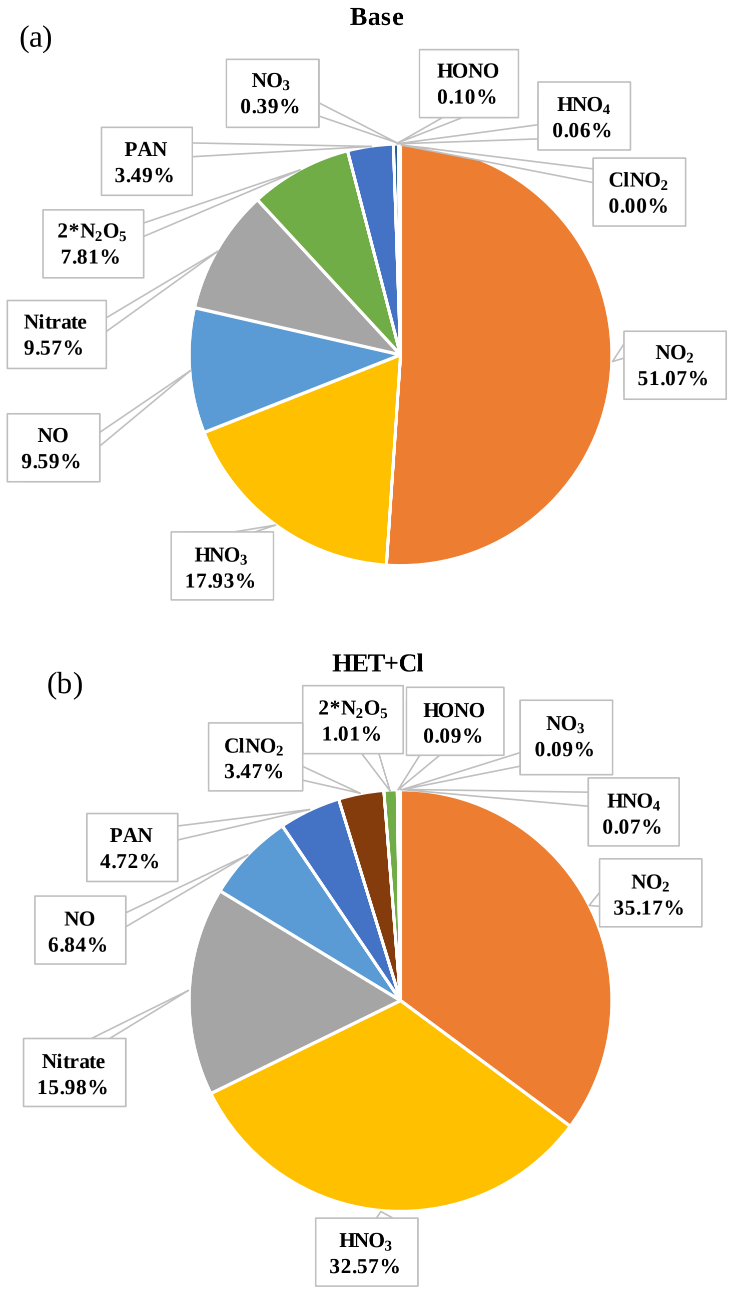

Figure 9. Average NO$_y$ partitioning during the study period in southern China within the PBL as simulated in (a) Base and (b) HET+Cl case

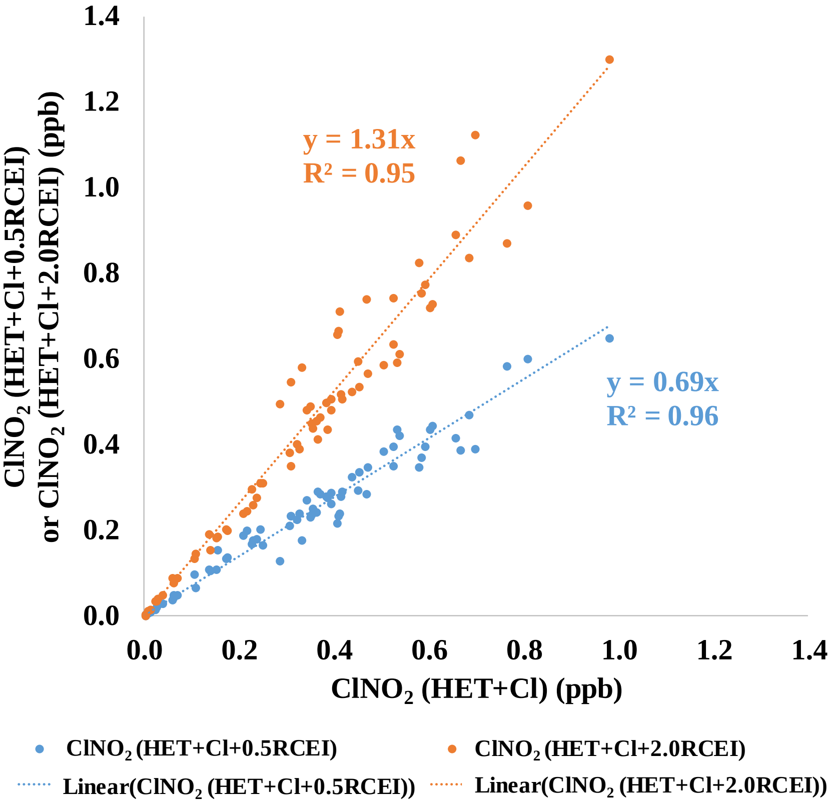

Figure 10. Scatter plots of $ClNO_2$ (ppb) from simulations with half (HET+Cl+0.5RCEI) and twice (HET+Cl+2.0RCEI) RCEI emissions against $ClNO_2$ (ppb) from simulations with original RCEI emissions (HET+Cl).

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