

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 PM_{2.5} 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 N₂O₅ and ClNO₂ observed at a mountain-top site in Hong Kong, but overestimates N₂O₅ uptake and ClNO₂ 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 $\text{PM}_{2.5}$, 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 NO_5 is “A” major loss pathway of NO_x but perhaps not “THE” major loss pathway. What about reactions of NO_3 with VOCs?

Response: Indeed, the loss of NO_x 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 γ , the reactive uptake coefficient, represents the probability that a collision between N_2O_5 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 γ , you should also mention that γ 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 PM_{2.5} mass, drives this chemistry that would be a useful comparison. Also, were there any speciated PM_{2.5} 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 PM_{2.5} 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 HNO₃ were measured.

Time series of the comparison of measured and simulated PM_{2.5}, NO₂, and O₃ 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 PM_{2.5} 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 PM_{2.5} 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 N₂O₅ and ClNO₂ 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 ClNO₂ 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 ClNO₂ production, showed that less N₂O₅ were transformed into HNO₃ (and nitrate aerosol). And in the manuscript, we used total nitrate (HNO₃+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 NO_x 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 ClNO₂ yield was set to be zero, and all N₂O₅ loss was transformed into total nitrate.

The possible causes for the changes of NO and NO₂ from HET to HET+Cl case are discussed below. The produced ClNO₂ (1) releases NO₂ and Cl radical after sunrise, and both of them increase the formation of O₃. The increased O₃ enhances the reaction of NO with O₃, which leads to the (2) loss of NO, and the (3) formation of NO₂. The increased O₃ also increases the level of OH radicals, which enhances the reaction of NO₂ with OH and then results in the (4) loss of NO₂. The combination of the effects (1), (2), (3) and (4) mentioned above are the net effects of the ClNO₂ production on NO and NO₂. Our study showed that the NO was reduced across the domain. And for the NO₂, the enhanced production outweighed the loss in urban areas, while in other regions, the NO₂ 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 ClNO₂ 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 O₃ 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 calculate 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 O₃ concentration figure.

Reference:

Dentener, F.J. and Crutzen, P.J.: Reaction of N₂O₅ on tropospheric aerosols: Impact on the global distributions of NO_x, O₃, and OH, *J. Geophys. Res. Atmos.*, 98, 7149-7163, 1993.

Evans, M.J. and Jacob, D.J.: Impact of new laboratory studies of N₂O₅ 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 N₂O₅ 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., Bhawe, P. and Yarwood, G.: Examining the impact of heterogeneous nitril 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 ClNO₂ on ozone formation in the Houston area, *J. Geophys. Res.*, 114, doi:10.1029/2008JD010732, 2009.