

## ***Interactive comment on “Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: Improvement and application of WRF-Chem model in southern China” by Qinyi Li et al.***

**Anonymous Referee #1**

Received and published: 27 June 2016

Li et al. present a set of regional photochemical modeling runs that simulate CINO<sub>2</sub> formation and impacts corresponding to recent field measurements in China. The field study reported the highest ever measured ambient concentration of CINO<sub>2</sub> 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 CINO<sub>2</sub> 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

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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<sub>2.5</sub> might lead to underestimates of the CINO<sub>2</sub> 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 CINO<sub>2</sub> 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. O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, CINO<sub>2</sub>) these averages are hard to interpret. For N<sub>2</sub>O<sub>5</sub> and CINO<sub>2</sub>, 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 . . . O<sub>3</sub> (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.

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Specific comments:

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.

Page 2, Line 16: hydrolysis of NO<sub>5</sub> is "A" major loss pathway of NO<sub>x</sub> but perhaps not "THE" major loss pathway. What about reactions of NO<sub>3</sub> with VOCs?

Page 2, Line 26: It would be good to clarify that gamma, the reactive uptake coefficient, represents the probability that a collision between N<sub>2</sub>O<sub>5</sub> and a particle will result in uptake and chemical reaction.

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.

Page 3, lines 6-20: You missed several important earlier studies in your summary of modeled impacts of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> chemistry on air pollution concentrations/chemistry: Dentener and Crutzen, 1993; Riemer et al., 2003; Evans and Jacob, 2005; Simon et al, 2009

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

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<sub>2.5</sub> mass, drives this chemistry that would be a useful comparison. Also, were there any speciated PM<sub>2.5</sub> measurements available to compare with the model (specifically aerosol nitrate and particulate chloride)? Were HCl and HNO<sub>3</sub> measured? These could all

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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 timeseries of model performance, r<sup>2</sup> 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<sub>2.5</sub> of 20-40 ppb and 10-30 ug/m<sup>3</sup> respectively.

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<sub>2.5</sub> 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<sub>2.5</sub> 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.

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.

Page 9, lines 4-5: I don't think Fig S2 supports the contention that temporal variations of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> 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.

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.

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Page 12, line 13-14: The difference between HET and HET+Cl also shows the impact of lower levels of N<sub>2</sub>O<sub>5</sub> conversion to HNO<sub>3</sub>.

Page 12, line 19: The decreases in O<sub>3</sub> appear to only occur over a very small area, not over rural and coastal regions generally.

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 ClNO<sub>2</sub> pathway which should mean that more N<sub>2</sub>O<sub>5</sub> is converted to HNO<sub>3</sub> and less is conserved in the ClNO<sub>2</sub> reservoir. Therefore, the HET+Cl simulation should increase NO<sub>x</sub> everywhere. What would cause broad decreases in NO and NO<sub>2</sub> across the domain with the addition of the ClNO<sub>2</sub> formation?

Page 12, line 23: Consider rephrasing, I don't consider a decrease of 2.35 ug/m<sup>3</sup> "slight".

Page 12, line 25: What fraction of N<sub>2</sub>O<sub>5</sub> produced ClNO<sub>2</sub>? 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.

Page 12, line 26-27: Simon et al. (2009) reported that half of the O<sub>3</sub> impact from ClNO<sub>2</sub> chemistry came from Cl activation while half came from the recycling of NO<sub>2</sub>.

Table 3: The authors should consider including O<sub>3</sub> 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?

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

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.

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Figure 6: The choice of the log scale makes variations in the O<sub>3</sub> concentrations harder to see. Consider using a linear scale.

### References:

Brown et al., 2006. "Variability in nocturnal nitrogen oxide processing and its role in regional air quality." *Science*, 411, 67-70.

Brown et al, 2009. "Reactive uptake coefficients for N<sub>2</sub>O<sub>5</sub> determined from aircraft measurements during the Second Texas Air Quality Study: comparison to current model parameterizations." *Journal of Geophysical Research – Atmospheres*, 114, Article No. D00F10

Chang et al., 2002. "Sensitivity of urban ozone formation to chlorine emission estimates." *Atmospheric Environment*, 36, p. 4991-5003.

Dentener and Crutzen, 1993. "Reaction of N<sub>2</sub>O<sub>5</sub> on tropospheric aerosols – impact on the global distributions of NO<sub>x</sub>, O<sub>3</sub>, and OH." *Journal of Geophysical Research – Atmospheres*, 98, D4, p. 7149-7163. Evans and Jacob, 2005. "Impact of new laboratory studies of N<sub>2</sub>O<sub>5</sub> hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH." *Geophysical Research Letters*, 23, 9, Article No L09813.

Osthoff et al, 2008. "High levels of nitryl chloride in the polluted subtropical marine boundary layer." *Nature Geoscience*, 1 (5), 323-328.

Reff et al., 2009. "Emissions inventory of PM<sub>2.5</sub> trace elements across the United States." *Environmental Science & Technology*, 43, 5790-5796.

Riemer et al, 2003. "Impact of the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> on chemistry and nitrate aerosol formation in the lower troposphere under photochemical conditions." *Journal of Geophysical Research – Atmospheres*, 108, D4, Article No 4144

Riemer et al., 2009. "Relative importance of organic coatings for the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> during summer in Europe." *Journal of Geophysical Research –*

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Atmospheres, 114, Article No D17307

Sarwar and Bhave, 2007. "Modeling the effect of chlorine emissions on ozone levels over the eastern United States." *Journal of applied meteorology and climatology*, 46, 1009-1019.

Simon et al., 2009. "Modeling the impact of ClNO<sub>2</sub> on ozone formation in the Houston area." *Journal of Geophysical Research – Atmospheres*, 114, Article No. D00F03.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-412, 2016.