

# ***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 #2**

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This paper presents WRF/Chem model simulations to assess the impacts of the heterogeneous hydrolysis of  $\text{N}_2\text{O}_5$  on atmospheric chemistry for southern China, a region where high concentrations of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  were recently observed. A chlorine chemistry module was added to WRF/Chem to not only include  $\text{HNO}_3$  as a product of  $\text{N}_2\text{O}_5$  hydrolysis, but also  $\text{ClNO}_2$ , which is 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,  $\text{N}_2\text{O}_5$  heterogeneous hydrolysis

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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 N<sub>2</sub>O<sub>5</sub> hydrolysis has been available. Obtaining good agreement between simulation and observation of N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> 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.

1. page 2, line 25:  $S_{aer}$  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.
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?
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.
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?
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

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water uptake is handled in CTMs. It would be interesting to see how this study compares in this regard.

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

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 N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> 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.)

8. Table 3: Explain “Fac2”

9. Table 3 and Figure S1: It sounds like the observations of PM<sub>2.5</sub>, NO<sub>2</sub>, and O<sub>3</sub> are available for the entire period, not only for the nights when N<sub>2</sub>O<sub>5</sub> and ClNO<sub>2</sub> 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.

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?

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

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

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

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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 CINO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> and a model simulation, but I'd rather suggest not making such statements in a case like this.

14. To enhance the process-level analysis of this paper I suggest to comment on the spatial distribution of the yield  $\phi$ . Where in the model domain is it that CINO<sub>2</sub> is produced?

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”.

16. page 9, line 7: the overprediction of CINO<sub>2</sub> can also be due to an underestimation of the sinks.

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

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.

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 N<sub>2</sub>O<sub>5</sub> and overprediction of CINO<sub>2</sub>? Please add some discussion.

19. page 10, line 5: change “suppression” to “reaction”. NO<sub>3</sub> also reacts with VOC. Does this also contribute to low NO<sub>3</sub> concentrations near the ground?

20. page 10, line 9: reference to Sarwar et al (2012): Many studies have shown

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evidence for pronounced vertical gradients in the profiles of N<sub>2</sub>O<sub>5</sub> before that study, see my comment 7 above.

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

References Brown, S. S., W. P. Dube, H. D. Osthoff, D. E. Wolfe, W. M. Angevine, and A. R. Ravishankara (2007a), High resolution vertical distributions of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> through the nocturnal boundary layer, *Atmos. Chem. Phys.*, 7, 139–149.

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tical profiles of NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, O<sub>3</sub>, and NO<sub>x</sub> in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000, J. Geophys. Res., 109, D12306, doi:10.1029/2003JD004209.

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