Anonymous Referee #1

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General comments:

The authors previously expanded the gas-phase CBMZ mechanism in WRF-Chem model to include comprehensive sources of HONO. Here, they update the CMBZ mechanism by incorporating HONO and chlorine chemistry including the heterogeneous ClNO2 formation. They perform four different model simulations over China for a 12-day period using a 27-km horizontal grid resolution, describe impact of the chemistry, compare model results with observed data and suggest that the additional chemistry increases HONO, ClNO2, and ozone and improves model performance. Overall, the article is written clearly and merits publication. However, several issues need to be addressed before publication.

Response: Thanks for the encouragement. We have revised our manuscript according to the helpful comments.

(Our replies to the comments are highlighted in blue here, and all changes in the revised manuscript are highlighted in red)

Specific comments

1. Introduction, line 12-13 While chlorine atoms react with hydrocarbons, the reactions of NO2 with hydrocarbons are generally negligible. Clarifications are needed.

Response: The sentence has been revised into '$ClNO_2$ is photolyzed to recycle NO_2 and release reactive chlorine atoms (R4), the latter of which further react with hydrocarbons to produce additional peroxy radicals'

2. Heterogeneous formations, line 16-18 Foley et al. (2010) article does not provide any reaction rates for R5–R7. Correct reference is needed. It will be convenient to readers to include the reaction rates for R5–R7 in this article.

Response: As suggested, we have made corrections on the reference and added the reactions rates.

3. Direction emissions, line 20-23 HONO emissions prescribed as 1.6% of NO2 emissions appear to be too high. Generally, HONO emissions are prescribed as a function of NOx emissions. A reference is needed.

Response: We checked that we applied an emission ratio of 0.8% (HONO to NOx). Corrections have been made and a reference has been added.

4. Model configurations, line 17-19 The Model for Ozone and Related Chemical Tracers likely did not contain any ClNO2 and/or additional HONO sources. The authors may include a sentence to clarify the issue.

Response: As suggested, a sentence has been added to clarify this: 'Note that the MOZART model does not treat chlorine chemistry nor consider any HONO sources.'

5. Model configurations, line 24-25 The spin-up time of 24 h appears to be too small.

Response: Since we used global model simulations as initial and boundary conditions and the lifetimes of those reactive nitrogen compounds are relatively short, we think that a spin-up time of 24 h is acceptable.

6. Emission data, line 3-6 SO2, NOx, CO, CO2, NH3, PM2.5, PM10, BC, OC are not defined anywhere.

Response: Definitions of these species have been added as suggested.

7. Spatial and vertical distributions of N2O5 and ClNO2, line 30-31 A plot of chloride distribution will be helpful to readers.

Response: Very good suggestion. Plots of spatial and vertical distributions of chloride have been added in the supplementary materials (Figure S2).

8. Model performance of HONO and N2O5/ClNO2 NOx emissions affect HONO, ClNO2, as well as O3 production. Thus, NOx emissions are critical for this study. Authors present a qualitative comparison of observed and measured NO2 in Figure S1. Is it possible to calculate model performance for NO2 and present a table similar to Table 5?

Response: Here we only presented a qualitative for NO_2 because what the MEP monitoring network measured were NO_2* instead of real NO_2. The NO_2 measurements in the MEP's network, as in regulatory networks of other countries, were made with the catalytic conversion of NO_2 to NO. In addition to NO_2, the MoO converter would also PAN, HNO_3, HO_2NO_2, HONO, $ClNO_2$, etc. into NO, and these interferences would let the instrument "detect" higher NO_2. So the catalytic method was suggested to overestimate NO_2 by 6%-280%, especially during the photochemically active daytime and in locations away from the sources of emissions.

In order to give a more reliable quantitative comparison, we used the model simulated NOz to try to scale down the measured NO2* at each hour by using a factor: $NO_{2\ obs} = NO^{*}_{2\ obs} \times$

$\frac{NO_{2\ mod}}{NO_{2\ mod}+NO_{z\ mod}-Nitrate_{mod}}$. (gas-phase HNO_3 is assumed to be converted into NO by 80% due to its loss on inlet (Xu et al., 2013); other gas-phase NOz species are assumed to be converted by 100% in the Mo converter). **Table S1** in the revised supplementary materials lists the comparisons between the simulated and measured (both original and adjusted) NO_2. The simulations agreed well with the adjusted NO_2 measurements over China, except for the Yangtze River Delta region. The revised **Figure S1** in the supplementary materials also shows the original and scaled measurements of NO_2.

Table S1. Statistics of model performance in the base and ReNOM cases for hourly NO_2 measurements (ppb) at the MEP air quality monitoring stations during the simulation period (27 Jun-7 Jul 2014).

Region	Case	No. OBS	OBS[a]	MOD	COR	MB	RMSE	NMB	NME
NCP	BASE	48362	19.4	18.4	0.35	-1.0	16.3	-5.0%	58.6%
	ReNOM			14.4	0.35	-5.0	15.8	-25.8%	56.3%
YRD	BASE	35421	17.7	27.0	0.21	9.3	23.5	52.3%	96.9%
	ReNOM			19.2	0.17	1.4	17.9	8.1%	75.8%
PRD	BASE	15651	12.1	8.3	0.38	-3.9	11.9	-31.8%	71.5%
	ReNOM			7.2	0.35	-5.0	11.5	-40.8%	69.7%
China	BASE	213308	15.6	14.2	0.32	-1.4	16.3	-9.2%	73.1%
	ReNOM			10.9	0.32	-4.8	14.6	-30.5%	67.4%

Region	Case	No. OBS	OBS_scaled[a]	MOD	COR	MB	RMSE	NMB	NME
NCP	BASE	48362	15.6	18.4	0.48	2.8	14.4	17.9%	62.2%
	ReNOM		13.5	14.4	0.51	0.9	11.7	6.9%	57.6%
YRD	BASE	35421	14.4	27.0	0.37	12.6	23.3	87.3%	113.9%
	ReNOM		11.7	19.2	0.38	7.5	16.6	64.4%	92.7%
PRD	BASE	15651	10.0	8.3	0.37	-1.7	11.0	-17.1%	77.0%
	ReNOM		8.1	7.2	0.42	-0.9	9.1	-11.5%	75.3%
China	BASE	213308	12.3	14.2	0.43	1.9	14.7	15.2%	77.6%
	ReNOM		10.5	10.9	0.45	0.4	11.3	3.7%	70.7%

[a] OBS: original observations of NO_2; OBS_scaled: scaled observations of NO_2 based on model simulated reactive nitrogen species by using the equation of $NO_{2\ obs} = NO_{2\ obs}^{*} \times \frac{NO_{2\ mod}}{NO_{2\ mod}+NO_{z\ mod}-Nitrate_{mod}}$, where $NO_2{}^*{}_{obs}$ is the original measurement of NO_2, $NO_{2\ mod}$ is the model simulation of NO_2, $NO_{Z\ mod}$ is the sum of simulations of HONO, $2\times N_2O_5$, $ClNO_2$, $ClONO_2$, NO_3, HNO_3, HNO_4, PAN, and Nitrate, $Nitrate_{mod}$ is the simulated nitrate; gas-phase HNO_3 is assumed to be converted into NO by 80% in the Mo converter due to its possible loss on inlet; other gas-phase NO_Z species are assumed to be converted by 100%.

9. Enhancements in regional ROX and O3 levels over polluted regions, line 11-12 ROx is defined in line 12 but used in line 10 prior to defining. It is good to define it at the time of first introduction.

Response: Thanks. The definition of ROx has been added in section 3.3.1 when it was introduced for the first time.

10. Summary and conclusions, line 1-15 HONO production is related to the prescribed NOx emissions while ClNO2 production is related to the prescribed NOx and chloride emissions. A very brief discussion on the uncertainty of NOx and chloride emissions is needed.

Response: We have added the following brief discussion on the uncertainties of NOx and chlorine emissions as suggested in section 3.2: "Since the emissions of NOx, the main precursor of HONO and N_2O_5, are subject to uncertainties in terms of intensity and spatial distribution (e.g. the possible overestimates over the YRD as we discussed) and the chlorine emission provided by the RCEI that we applied in the present study is with large uncertainties due to its relatively low resolution and its temporal coverage being 1990, our model results of HONO and $ClNO_2$ (and their impacts) are certainly with uncertainties."

11. Summary and conclusions, line 1-8 Simulations were conducted for a 12-day period, not for the entire summer. Thus, it is I suggest adding the first sentence as follows (or something similar it): In this study, we incorporated comprehensive processes of HONO and chlorine chemistry into a new chemical mechanism option, CBMZ_ReNOM, in the WRF-Chem model and applied the new model to simulating the spatial distribution of HONO, ClNO2, and N2O5 and their impact on O3 in China during the 12-day simulation period in summer.

Response: Thank you very much for this suggestion. The sentence has been modified as suggested.

12. NCP, YRD, PRD have already been defined earlier; no need to redefine them.

Response: The definitions were deleted here.

13. Summary and conclusions, line 12-13 Model performance improved at NCP, PRD, and China but deteriorated at YRD (Table 5). Thus, some caveat is needed. Perhaps, the authors may revise the sentence as follows (or something similar): With current emissions estimates, the revised WRF-Chem generally improved O3 prediction across China.

Response: Very good suggestion. We have revised this conclusion sentence as suggested.

14. Table 1 It appears that some of the references are not correct. For example, reaction 18 (Cl + NO2 = ClNO2 is not included in IUPAC). Please check all references and update as appropriate.

Response: Thanks a lot for pointing this out. We have carefully checked all the references we used and made the corrections accordingly. Please refer to the revised Table 1 in the manuscript. The reaction rate for R18 was taken from Tanaka, et al. 2003 (Development of a chlorine mechanism for use in the carbon bond IV chemistry model, J. Geophys. Res.-Atmos., 108, 4145, 10.1029/2002JD002432, 2003).

15. It appears that rate constant for reaction 12 (ClO + NO2 = ClONO2) is not taken from IUPAC. IUPAC recommends a pressure dependent rate constant.

Response: It is true that the rate constant for this reaction in IUPAC database is pressure dependent. But we considered that those low-pressure rate coefficients (applicable for pressure ranging from 1.3 to 7 mbar) are not suitable for calculating this reaction in PBL, and thus we applied the preferred high-pressure rate value recommended in IUPAC, which is 7×10^{-11} and is independent of temperature over the range 250-350 K (http://iupac.pole-ether.fr/htdocs/datasheets/pdf/iClOx32_ClO_NO2_M.pdf). This constant rate has been applied in our previous MCM model development study for chlorine chemistry (Xue, L. K. et al., Development of a chlorine chemistry module for the Master Chemical Mechanism, Geosci. Model Dev., 8, 3151-3162, 10.5194/gmd-8-3151-2015, 2015).

16. All symbols need to be defined.

Response: We have added the definitions of all symbols.

17. Figure S2. It will be helpful to readers to define eastern China. Perhaps, the authors can mark "eastern China" in Figure S1 or other figures.

Response: Thanks a lot for the suggestion. We now define the eastern China area in Figure S1.