Anonymous Referee #2

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Zhang et al. describe an updated WRF-Chem model with a new chemical mechanism (CBMZ_ReNOM) developed to improve predictions of photochemical O3 production in Eastern China, incorporating revised source chemistry of HONO and photolyzable chlorine species.

The paper is written well and is publishable. Ultimately, I wasn't sure how much an improvement this work actually represents. One might hope that a more explicit representation of chemistry within a model does improve its accuracy. Perhaps this part of the manuscript could be strengthened, for instance, through a more reasonable comparison of predicted with observed concentrations: instead of comparing averages (Tables 4 and 5), why not compare selected time series of measurements and model predictions, in particular for transient species such as HONO and ClNO2 whose concentrations are highly variable.

Response: We think that we have made a contribution to the development of this widely-used regional chemical transport model, WRF-Chem, which allows the model to be able to simultaneously consider the HONO and Chlorine chemistry. Besides, we evaluate the combined effects of HONO and chlorine chemistry on the lower tropospheric ozone in China at a regional scale which has been rarely reported before.

In addition to comparing the averages of simulations and observations, we did make a detailed comparison of modeled results and measurements during the CareBeijing 2014 campaign at Wangdu in the northern China. But we did not include this part into the manuscript to make this manuscript more concise and readable and also because that we had made detailed comparisons between modeled and measured HONO and $ClNO_2$ separately in our previous studies. We think the suggestion from Review 2 makes a good point. Therefore, we put these detailed comparisons during the CareBeijing 2014 campaign into the Supplement Information (details of the campaign can be found in Tham et al., 2016; Tan et al., 2017, and references therein). Please see the Table S2 listing the statistics of model performances for major pollutants and Figure S3 (in the revised supplementary materials) showing the time series of modeled and measured results.

Table S2. Observed and simulated major pollutants obtained from the CareBeijing 2014 campaign at Wangdu during the simulated period.

Species	OBS	BASE	ReNOM_Cl	ReNOM_HONO	ReNOM
CO (ppb)	541.0	577.4	578.4	572.3	574.2
SO_2 (ppb)	7.7	8.1	8.0	7.9	7.9
NO_2 (ppb)	12.8	13.5	12.4	11.4	10.7
O_3 (ppb)	55.6	51.5	54.6	55.5	56.5
$PM_{2.5}$ ($\mu g/m^3$)	84.9	90.5	101.6	96.8	106.6
HONO (ppt)	941.2	38.5	37.2	769.4	805.3
N_2O_5 (ppt)	28.0	/	28.0	/	23.9

$ClNO_2$ (ppt)	159.5	/	279.3	/	265.6

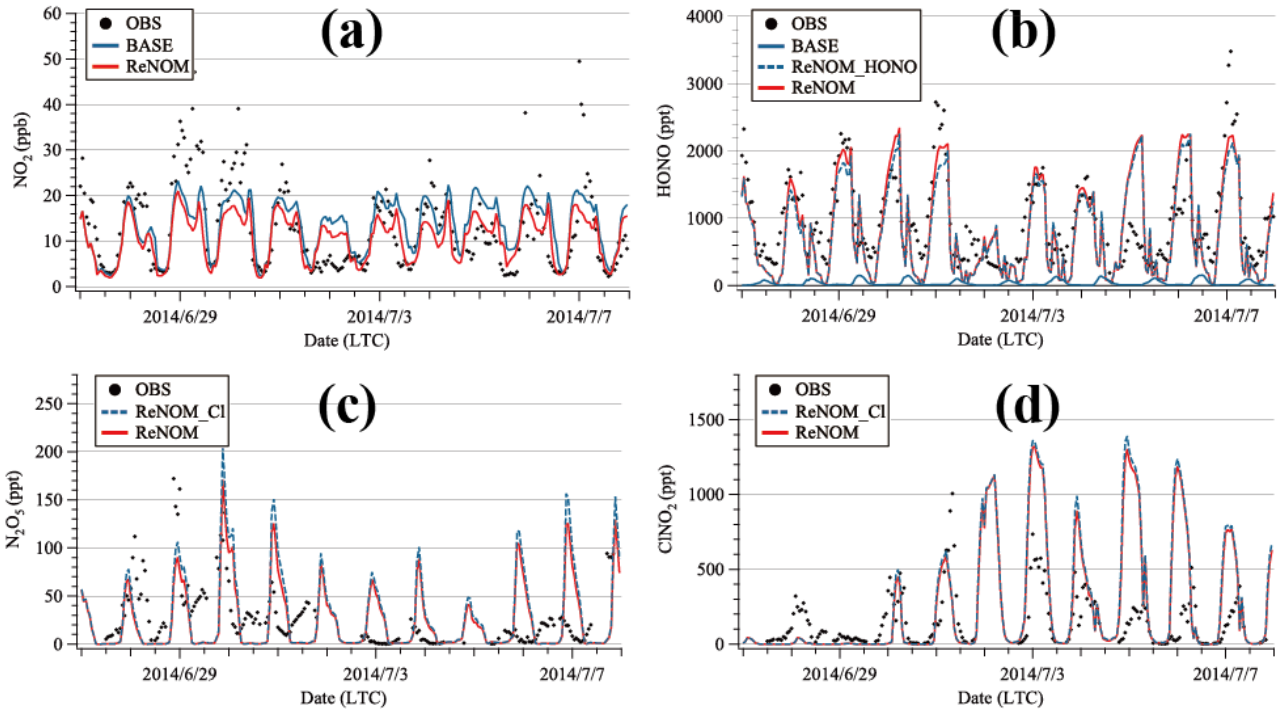

Figure S3. Observed and simulated (a) NO_2, (b) HONO, (c) N_2O_5 and (b) $ClNO_2$ at the Wangdu site during the simulation period (27 Jun - 7 Jul 2014). (Time series of NO_2 and HONO measurements were adapted from Tan et al, 2016)

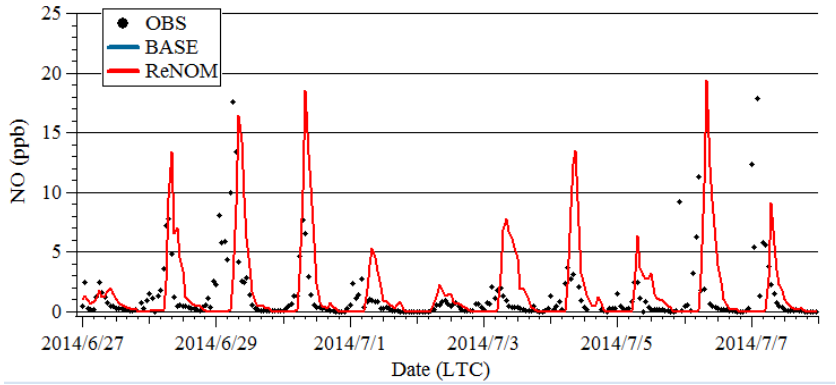

Figure R1. Observed and simulated NO levels at the Wangdu site during the simulation period (27 Jun - 7 Jul 2014).

As illustrated, the original model underestimated the HONO by an order of magnitude during the campaign and was not able to predict $ClNO_2$ (was treated as an inert gas). With our new development, WRF-Chem with CBMZ_ReNOM significantly improved the performance in HONO, $ClNO_2$, as well as O_3 at the Wangdu site during the CareBeijing 2014 campaign. The CBMZ_ReNOM module well reproduced the level and the variation of N_2O_5 during the period of Jun 27-Jul 1, but overestimated the N_2O_5 concentration from Jul 2 to Jul 7. The overestimation of N_2O_5 is partly due to the underestimation in NO (Figure 2), which leads to

the underestimation of the NO_3 loss. The CBMZ_ReNOM module in general overestimated the concentration of the $ClNO_2$ during nighttime which is because of the overestimates in N_2O_5 during nighttime (Figure S3) and the possibly high uptake coefficient of N_2O_5. Compared with previous studies, our simulations in N_2O_5 and $ClNO_2$ were, overall, satisfactory.

We have revised our manuscript according to each specific comment from the reviewer and given point-by-point responses as bellow: (Our replies to the comments are highlighted in blue here, and all changes in the revised manuscript are highlighted in red)

Specific comments

1. pg 3 line 17 "To the best of our knowledge, no global or regional models, however, have simultaneously considered the sources/processes of HONO and ClNO2 and evaluated their regional impacts on the formation of O3 pollution in the boundary layer of the atmosphere." I am not sure the statement as written is true. Many studies have simultaneously considered HONO and ClNO2 as radical sources and showed how these species affect O3. For instance, Sarwar et al 2004 [GRL, 2014] studied O3 formation using CMAQV5.02 which contains the RACM2 mechanism [Goliff et al., AE 2013] and HONO chemistry. Also, Ahmadov et al. [ACP, 2015] and Edwards et al. [Nature, 2014] used models and HONO/ClNO2 data to investigate high wintertime ozone pollution events in an oil- and natural gas-producing region of the western US. There have also been numerous papers using 0D box models examining this chemistry.

Response: Although there have been some studies considering HONO ***or*** Cl chemistry in chemical transport models, they tend to investigate HONO or Cl chemistry (and their effects) separately (e.g. Sarwar 2004 and Goliff 2013 as the reviewer mentioned) and none of them has introduced the combined effects of these two reactive nitrogen species on ozone pollution at a regional scale. Besides, we developed the chemical module in a 3D regional chemical transport model and evaluated the impacts of these chemistry on ozone formations over China at a regional scale, which is different from 0-D box modelling studies.

2. pg 4 line 9 "reproduced the observed HONO by 85% on average" Not sure what this means.

Response: The sentence has been revised into ‘We showed that including these additional sources of HONO very well simulated the observed HONO at a suburban site in southern China’.

3. pg 5 line 17. What is FMCl? A fluorine-metal compound?

Response: All definitions of the chemical species have been added in Table 1 in the revised manuscript. 'FMCl' means formyl chloride.

4. pg 7 line 7. "has been proved" A model cannot be proven, at least not in a mathematical sense. Why not simply say that this model has made reasonable predictions of PM2.5 and O3?

Response: Here we meant that the emission inventory was able to offer reasonable simulations. The sentence has been revised into "and this inventory has been suggested to offer reasonable model predictions of $PM_{2.5}$ and O_3 in multiple cities over China".

5. pg 7, section "2.2.3 O3 and NO2 measurement data" Please state how accurate these measurements are.

Response: These measurements in the China Ministry of Environmental Protection (MEP) air quality network have been conducted by each local environmental protection bureaus following the same standards for instrument operation and quality control set by the China MEP. The China MEP has set detailed technical specifications for installation, operation, and QA/QC for these stations which can found at http://english.sepa.gov.cn/Resources/standards/Air_Environment/(*in Chinese*). According to the standards, the accuracy for O_3 and NO2 measurement is ±5%.

6. pg 7, last line. The Mo converter also "detects" NO3, 2N2O5, HONO, ClNO2, PAN, and HNO3 to some degree as if it were NO2. The model should give some indication as what fraction of NOy is in the form of NOz (as a function of time of day); consider a sensitivity run in which the NO2 reported by the routine measurements is scaled down by this factor.

Response: As suggested, we used model simulated NOz to try to scale down the measured NO2* 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) at each hour. Since uncertainties exist in the emission inventories, chemical models, and, thus, the final model results, this calculated scaling factor is certainly subject to a large uncertainty. Table S1 in the revised SI lists the statistics of the comparisons between the simulated and measured (both original and adjusted) NO_2. The simulations agreed well with the NO_2 measurements after our adjustment. Both the original and scaled NO_2 measurements were shown in Figure S1 in the supplementary materials.

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%.

7. pg 8 " 3.1.2 Spatial and vertical distributions of N2O5 and ClNO2 ". These predicted concentrations are considerably lower than recent measurements in the HK area (see sections further down).

Response: This study did not predict the elevated N_2O_5 levels in the HK-PRD region which is different from the results in Li et al. (2016), probably due to the different season (summer in this study compared to winter in the HK measurement) and hence the meteorological condition (southeasterly winds in summer and northerly winds in winter) and emission intensity (higher industrial emissions in winter than in summer). Besides, the measurements in HK were carried out at a mountain top site (~1000 m) and observations at such a high altitude was difficult to be resolved by the model with a resolution of 27 km. But our previous WRF-Chem simulations considering similar chlorine chemistry as this study and using a fine model resolution of 1 km gave satisfactory simulations of N_2O_5 and $ClNO_2$ at this mountain-top site in winter season (Li et al., 2016).

Besides, the uncertainties in emissions of NOx and chlorine, incomplete model parameterizations of formation and loss processes of $ClNO_2$ (e.g. Roberts et al., 2009) would

also influence our models results. A brief discussion has been added in the revised manuscript.

8. pg 9, line 11 "The model very well captured the measured HONO at Wangdu in the NCP region during a matching simulation period, reproducing 86% of the observations (0.81 vs. 0.94 ppb)" I don't understand this sentence. How does a model reproduce 86% of observations? Consider instead a scatter plot of model concentrations vs observations.

Response: The sentence has been revised into "The model very well captured the measured HONO at Wangdu in the NCP region with an average simulation of 0.81 ppb comparing with a mean observed value of 0.94 ppb". Detailed comparisons between the observations and simulations at Wangdu have been added in the supplementary materials.

9. pg 9, line 25 onward. Brown, S. S., et al. (2016), Nighttime chemistry at a high altitude site above Hong Kong, J. Geophys. Res.-Atmos., 121(5), 2457-2475, doi: 10.1002/2015jd024566 observed much higher concentrations than the model predicts. Please discuss.

Response: Measurements reported in Brown et al. (2016) were observed during a joint field campaign with our group in Hong Kong, as we cited (Wang et al., 2016) in Table 4. Similar to our response to the comment 7, the differences between model predictions and observations were probably due to a low model resolution that we applied and the differences between observation and simulation season. We have added the discussion in section 3.2 in the revised manuscript.

10. pg 18, Table 1. Please state the units of the reaction rates.

Response: Thanks a lot for the suggestion. This information has been added in Table 1.

11. rxn 7. Water should have a subscript.

Response: The subscript has been added.

12. rxn 26. What are PAR and X? Also, define the other terms, such as OLI, ALD2 etc.

Response: Thanks a lot for the suggestion. All definitions of the chemical species in Table 1 have been added.

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