Response to Referee #3 (acp-2018-1158)

We Thank Reviewer for his/her constructive comments

Responses to the Specific comments

General comments: This work evaluated 14 model simulations of NO2, CO and NH3 over China under the framework of MICS-Asia III with the aim to assess the capability and uncertainty of current CTMs in East Asia. Model results were provided by a larger number of independent groups and covered a full year (2010). The results show that most models well captured the monthly and spatial patterns of NO2 in NCP though NO2 levels are slightly underestimated, but relatively poor model performance was observed in the PRD region. All models significantly underpredict CO concentrations both in the NCP and PRD regions and failed to reproduce the observed monthly variation of NH3 in NCP. This work quantifies the impacts of model uncertainties on simulations of the three primary gases, which shows the large uncertainty (spread) in simulating more reactive and/or short-lived primary pollutants (e.g. NH3). This work is important and valuable to the scientific and regulatory community as it provides information on the capability and limitations of some widely used models. The manuscript is well organized and well written, and model results (tables and figures) are clearly presented. I recommend its publication after the authors have addressed my comments listed below.

Reply: The authors appreciate the reviewer for his/her valuable suggestions. In the revised manuscript we have considered each comment for improvement, revision, and correction. Please refer to our responses for more details given below.

Comment 1: For comparison with the NO2 measured from the regular monitoring networks, please note that these networks employ a thermal conversion method which converts NO2 to NO, followed by detection of NO. This method is known to overestimate NO2 as it also converts other NOy species such as HONO and PAN etc (e.g., Xu et al., 2013). It is important to correct this measurement problem before making the comparison, using, for example, the approach by Zhang et a. (2017). After corrections of the measurement data, a closer agreement would be seen between the modelled results and the observations in the present work. If the author cannot make such corrections in view of a large number of groups involved, at least some discussions should be provided on this point.

Reply: Thanks for this important point. According to Xu et al., 2013, the thermal conversion method has

a problem of overestimating the NO_2 concentrations due to the positive interference of other oxidized nitrogen compounds. Zhang et al., 2017 has proposed a method to correct this measurement error based on the model simulations 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 corrected NO_2 observations; $NO^{*}_{2\,obs}$ is original measurement of NO2; $NO_{2\,mod}$ is the simulated NO_2 concentration; $NO_{z\,mod}$ 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; and $Nitrate_{mod}$ is the simulated nitrate.

However, as the reviewer mentioned, it is hard to make such corrections using a large number of models due to the model uncertainties in predicting the concentrations of NO_2, NO_Z and Nitrate. Thus, following the suggestions of reviewer, we have added the discussions of the positive biases in the measurement NO_2 concentrations in the revised manuscript (*see lines 190–192 in the revised manuscript*), which as follows:

"It should be noted that these networks measured the NO_2 concentrations using a thermal conversion method, which would overestimate the NO_2 concentrations due to the positive interference of other oxidized nitrogen compounds (Xu et al., 2013)."

According to this, the underestimated NO_2 predictions by the models may also be related to the positive biases in the NO_2 observations, which has been clarified in the revised manuscript (*please see lines 234–236 and lines 416–417 in the revised manuscript*).

Comment 2: Section 2.2. The comparison of NO2 and CO concentrations are only for NCP and PRD. Any reasons why not to include other regions?

Reply: Thanks for this comment. This manuscript focuses on the evaluation and uncertainty investigation of NO_2, CO and NH_3 modeling over China under the framework of MICS-Asia III. The CTMs were run at the base year of 2010 when the observations were very limited in China, thus observation data for NO_2 and CO concentrations only included that from Chinese Ecosystem Research Network (NCP), Pearl River Delta Regional Air Quality Monitoring Network (PRD RAQMN) and the Acid Deposition Monitoring Network in East Asia (EANET). Since the observation data from EANET was very limited in China, we only evaluated the CO and NO_2 modeling results in the NCP and PRD regions, the two typical industrialized regions in China. In next phase of MICS-Asia (MICS-Asia IV), more observations will be available in China, which would allow us a more thorough evaluation of the model performance over

China.

Comment 3: For simulations of NO2 (and NH3), accurate representation of nitrogen chemistry is critical. Recent studies have shown that the HONO sources may be under-represented in some models which would give rise to larger simulated NO2 values (as it underestimates the oxidation of NO2 by OH) (e.g., Zhang et al., 2017; Fu et al., 2019); N2O5 uptake on aerosol may be treated differently in models which could also affect the NO2 simulations. Therefore, in discussing the discrepancy in modelled NO2, information on how models treat these nitrogen processes would be helpful.

Reply: Thanks for this comment. We agree with the reviewer that the HONO chemistry has an important role in the nitrogen chemistry in the atmosphere, which influences the simulations of NO_2 and NH_3(Fu et al., 2019;Zhang et al., 2016;Zhang et al., 2017). Previous studies also indicated that the HONO sources were commonly underestimated in models (Zhang et al., 2016). The heterogenous reactions of NO_2 on the surfaces ($2NO_{2(g)} + H_2O_{(l)} \rightarrow HONO_{(l)} + HNO_{3(l)}$) was one of the dominant sources of HONO in the atmosphere, which has been considered in most models of MICS-Asia III, including CMAQ since version 4.7, NAQPMS, NHM-Chem and GEOS-Chem. However, some other important sources of HONO may still be underestimated by models in MICS-Asia III. For example, Fu et al., 2019 suggested that the high relative humidity and strong light could enhance the heterogeneous reaction of NO_2 , and the photolysis of total nitrate were also important sources of HONO. These sources has not been included in the models of MICS-Asia III, which would lead to the deviations from observations. As the reviewer suggested, different treatment of hydrolysis of N_2O_5 would help explain the differences in the modeled NH_3 concentrations. The hydrolysis of N_2O_5 has not been considered in M7, which would leads to a lower tendency in the prediction of NO_3^- (Chen et al., 2019) and may partly explain the higher NH_3 predictions in M7.

Based on these results, we have added the discussions of HONO chemistry in the revised manuscript (*please see lines 441–449 in the revised manuscript*).

Comment 4: The photo-chemical mechanisms used in this study are CBMZ, CB05, and SAPRC 99, and some of them have an updated version such as CB06 and SPARC 07. These updated mechanisms could give different results on model performance. The author is advised to discuss this point to alert the reader that their conclusion may not be applicable to the newer version of the respective mechanism.

Reply: Thanks for this important point. We have clarified this point in the revised manuscript (*please see lines 472–474 in the revised manuscript*), which as follows:

"The gas chemistry mechanisms used in this study are SAPRC 99, CB05, CBMZ, RACM and RADM2, and some of them have an updated version such as CB06 and SPARC 07. Our conclusions may not be applicable to these newer versions of mechanisms and thus more comparisons studies can be performed to understand the differences in these new mechanisms."

Comment 5: The present comparisons focused on yearly and monthly model performance. It would be interesting to show how different models compare during severe pollution episodes. An important application of CTMs in China is to forecast severe episodes based on which emergency source control measures are activated.

Reply: We agree. Comparisons of different model performance in severe pollution episodes would be very important for the understanding of the capability of current CTMs and their applications in air quality forecast and emission controls. However, in current phase of MICS-Asia, only monthly modeling results has been provided by different CTMs, which limited the comparisons at the yearly and monthly scale. The model performances in pollution episodes will be investigated in MICS-Asia IV with more observation data and hourly simulation results at severe pollution episodes.

Comment 6: The model comparisons were conducted for NO2, CO, and NH3. How about SO2, which is another important primary pollutant? I think the reader would be interested in seeing the model performance for SO2 as well.

Reply: Thanks for this suggestion. Our study mainly focused on the model performance of NO_2, CO and NH_3. The model comparisons of SO_2 has been covered in a companion paper (Tan et al., 2019), where both the performance of SO_2 and sulfate has been investigated.

Comment 7: Conclusion (1) recommends to improve the CO emission inventory which is for year 2010. Does the recent CO emission have similar problem?

Reply: Thanks for this important point. Since we only evaluated the CO simulations for year 2010, the direct evaluations of CO emissions for recent years were not available in this study. However, we have added some discussions on the recent CO emissions in the revised manuscript (*please see lines 427–433*

in the revised manuscript), which as follows:

The underestimations of CO emissions may be alleviated in recent years due to the decreasing trends of the Chinese CO emissions in recent years(Jiang et al., 2017;Zhong et al., 2017;Sun et al., 2018;Muller et al., 2018;Zheng et al., 2018;Zheng et al., 2019). The inversion results of Zheng et al., 2018 also agree well with the regional MEIC (Multi-resolution Emission Inventory for China) inventory for CO emissions in China from 2013 to 2015. However uncertainties still exist in the CO emissions in recent years, according to previous studies, the estimated CO emissions for the whole China for year 2013 ranges from 134–202 Tg/yr (Jiang et al., 2017;Zhong et al., 2017;Sun et al., 2018;Muller et al., 2018;Zheng et al., 2018;Zheng et al., 2019). Zhao et al., 2017 also suggested a -29%–40% undertainty of CO emissions from industrial sector in year 2012.

Comment 8: This study reveals a large spread of model simulations for reactive gases. As the exact causes for the difference have not been identified for the individual model, I think it is important to emphasize the need to validate the individual model before using its results to make important policy recommendation.

Reply: Thanks for this important point. We have clarified this point in the revised manuscript (*please see lines 462–466 in the revised manuscript*), which as follows:

"For some highly active and/or short-lived primary pollutants, like NH_3, model uncertainty can also take a great part in the forecast uncertainty. Emission uncertainty alone may not be sufficient to explain the forecast uncertainty and may cause underdispersive, and overconfident forecasts. Future studies are needed in how to better represent the model uncertainties in the model predictions to obtain a better forecast skill. ***Such model uncertainties also emphasize the need to validate the individual model before using its results to make important policy recommendation****."*

Minor Comments:

Line 40 page1, line 4 page 4, the "Peral" should be "Pearl".

Reply: We have revised it.

References

Chen, L., Gao, Y., Zhang, M., Fu, J. S., Zhu, J., Liao, H., Li, J., Huang, K., Ge, B., Wang, X., Lam, Y. F., Lin, C. Y., Itahashi, S., Nagashima, T., Kajino, M., Yamaji, K., Wang, Z., and Kurokawa, J. I.: MICS-Asia III: Multi-model comparison and evaluation of aerosol over East Asia, Atmos. Chem. Phys. Discuss., 2019, 1-54, 10.5194/acp-2018-1346, 2019.

Fu, X., Wang, T., Zhang, L., Li, Q. Y., Wang, Z., Xia, M., Yun, H., Wang, W. H., Yu, C., Yue, D. L., Zhou, Y., Zheng, J. Y., and Han, R.: The significant contribution of HONO to secondary pollutants during a severe winter pollution event in southern China, Atmos. Chem. Phys., 19, 1-14, 10.5194/acp-19-1-2019, 2019.

Jiang, Z., Worden, J. R., Worden, H., Deeter, M., Jones, D. B. A., Arellano, A. F., and Henze, D. K.: A 15-year record of CO emissions constrained by MOPITT CO observations, Atmos. Chem. Phys., 17, 4565-4583, 10.5194/acp-17-4565-2017, 2017.

Muller, J. F., Stavrakou, T., Bauwens, M., George, M., Hurtmans, D., Coheur, P. F., Clerbaux, C., and Sweeney, C.: Top-Down CO Emissions Based On IASI Observations and Hemispheric Constraints on OH Levels, Geophys. Res. Lett., 45, 1621-1629, 10.1002/2017gl076697, 2018.

Sun, W., Shao, M., Granier, C., Liu, Y., Ye, C. S., and Zheng, J. Y.: Long-Term Trends of Anthropogenic SO2, NOx, CO, and NMVOCs Emissions in China, Earth Future, 6, 1112-1133, 10.1029/2018ef000822, 2018.

Tan, J., Fu, J. S., Carmichael, G. R., Itahashi, S., Tao, Z., Huang, K., Dong, X., Yamaji, K., Nagashima, T., Wang, X., Liu, Y., Lee, H. J., Lin, C. Y., Ge, B., Kajino, M., Zhu, J., Zhang, M., Hong, L., and Wang, Z.: Why models perform differently on particulate matter over East Asia? – A multi-model intercomparison study for MICS-Asia III, Atmos. Chem. Phys. Discuss., 2019, 1-36, 10.5194/acp-2019-392, 2019.

Xu, Z., Wang, T., Xue, L. K., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S. L., Chai, F. H., and Wang, W. X.: Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China, Atmos. Environ., 76, 221-226, 10.1016/j.atmosenv.2012.09.043, 2013.

Zhang, L., Wang, T., Zhang, Q., Zheng, J. Y., Xu, Z., and Lv, M. Y.: Potential sources of nitrous acid (HONO) and their impacts on ozone: A WRF-Chem study in a polluted subtropical region, J. Geophys. Res.-Atmos., 121, 3645-3662, 10.1002/2015jd024468, 2016.

Zhang, L., Li, Q. Y., Wang, T., Ahmadov, R., Zhang, Q., Li, M., and Lv, M. Y.: Combined impacts of nitrous acid and nitryl chloride on lower-tropospheric ozone: new module development in WRF-Chem and application to China, Atmos. Chem. Phys., 17, 9733-9750, 10.5194/acp-17-9733-2017, 2017.

Zhao, Y., Zhou, Y. D., Qiu, L. P., and Zhang, J.: Quantifying the uncertainties of China's emission inventory for industrial sources: From national to provincial and city scales, Atmos. Environ., 165, 207-221, 10.1016/j.atmosenv.2017.06.045, 2017.

Zheng, B., Chevallier, F., Ciais, P., Yin, Y., Deeter, M. N., Worden, H. M., Wang, Y. L., Zhang, Q., and He, K. B.: Rapid decline in carbon monoxide emissions and export from East Asia between years 2005 and 2016, Environ. Res. Lett., 13, 9, 10.1088/1748-9326/aab2b3, 2018.

Zheng, B., Chevallier, F., Yin, Y., Ciais, P., Fortems-Cheiney, A., Deeter, M. N., Parker, R. J., Wang, Y. L., Worden, H. M., and Zhao, Y. H.: Global atmospheric carbon monoxide budget 2000-2017 inferred from multi-species atmospheric inversions, Earth Syst. Sci. Data, 11, 1411-1436, 10.5194/essd-11-1411-2019, 2019.

Zhong, Q. R., Huang, Y., Shen, H. Z., Chen, Y. L., Chen, H., Huang, T. B., Zeng, E. Y., and Tao, S.: Global estimates of carbon monoxide emissions from 1960 to 2013, Environ. Sci. Pollut. Res., 24, 864-873, 10.1007/s11356-016-7896-2, 2017.