Comments

The authors applied the CMAQ model to simulate HONO over PRD region in China for a winter episode. The standard CMAQ model underestimates observed HONO data. They incorporated several additional HONO pathways in the model which substantially increased HONO production. HONO produces OH via photolysis; thus, it increases OH, HO2, and enhances secondary pollutants. Model performance improves with additional HONO sources. The article is well written and merits publication. Several issues need to be addressed before publication.

Specific comments:

1. Line 49-51: The sentence appears to indicate that NOx, SO2, and VOC is oxidized by OH, O3, and H2O2. The sentence needs revision since VOC or NOx is not oxidized by H2O2.

Response: The sentence has been revised to "The oxidation of oxides of nitrogen (NO_X=NO+NO_2), sulfur dioxide (SO_2) and VOC by OH and O_3 also produce secondary aerosols, which are the key components of haze."

2. Line 107-132 and results: The spin-up period was only 3 days. If the model simulation is performed for a longer time, then deposited HNO3/nitrate amount will increase with time which in turn will enhance HONO production from the photolysis of deposited material. For a long-term simulation, HONO over-estimation is likely to be worse than those shown in the article. Some discussions are needed.

Response: Thanks for your comment. We would like to point out that "3" was a typo in the original submission, but should be "6". We have compared the simulation result for 6 and 12-day spin up. As shown in Fig. R1, not much difference can be seen for simulated HONO concentrations. So we believe that the current spin-up setting (6 days) is acceptable for our simulation.

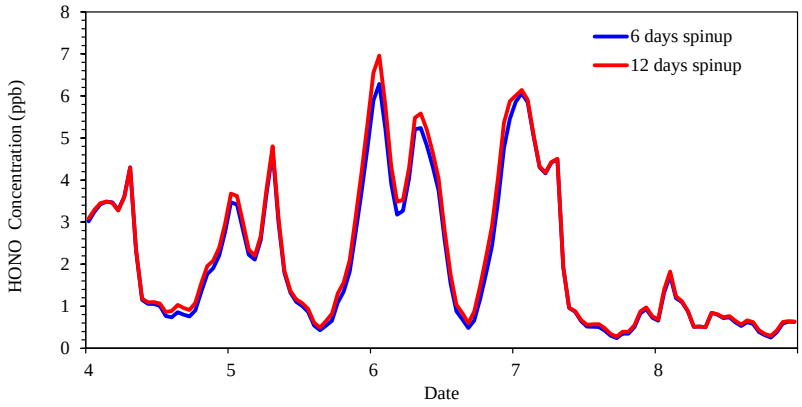

Fig. R1. Temporal comparison of simulated HONO concentrations with the spin-up of 12 and 6 days

We agree with the reviewer that HONO production from the photolysis of deposited nitrate may be overestimated if simulation period is long and the study region is arid. Apart from precipitation, the amount of nitrate deposited on surfaces can be also affected by other factors, e.g.

wind. Additionally, photolysis rate of deposited nitrate may decrease with the increase of deposited nitrate (Ye et al., 2016). But these factors are not included in the current parameterization. We have added the limitation in the last paragraph of the revised manuscript, as below:

Line 424-425:

"Additional efforts are needed to improve current representation of HONO sources such as evaporation of dew and more accurate simulation of deposited nitrate."

3. Line 124-128: The simulations were done for 2017. However, 2010 and 2013 emissions were used for PRD and other region of China. Were any adjustments made to account for simulation for 2017? Some discussions are needed.

Response: No adjustments were made for the current simulations due to the lack of publicly available high-resolution emission information in 2017 for PRD region at the time of this modeling study. We have conducted a sensitivity test by linearly adjusting the emissions based on the ratio of 2017 emission to 2010 emission for China reported in a very recent paper (Zheng et al., 2018). As shown in Fig. R2, the model performance with the updated 2017 emissions did not get better for the Heshan site. The present study aims to highlight the key role of HONO chemistry in this winter pollution episode, by comparing the difference of two simulations with and without HONO sources. The simulations with the current and adjusted emission inventory gave similar results. The increases due to the HONO chemistry were 24 vs. 23 ppb for daytime average O_3 concentrations, and 13 vs. 10 ug/m^3 for average $PM_{2.5}$ concentrations at Heshan site. Therefore, we think that the current emission setting is acceptable for our simulation.

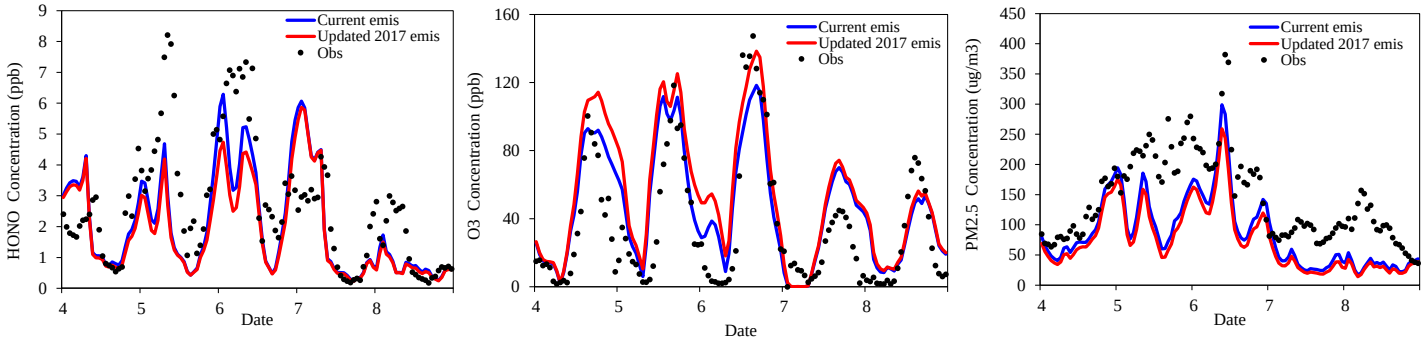

Fig. R2. Temporal variation of observed and simulated HONO, O_3, and $PM_{2.5}$ concentrations with the current emissions and updated 2017 emissions.

Nonetheless, we agree that there is need to adopt an update-to-date high-resolution emission inventory to revisit the topic when it is available.

The following paragraph has been added in the revised text.

Line 297-302:

"We have conducted a sensitivity test to compare the simulations with those considering more recent emission by linearly adjusting the emissions based on the ratio of 2017 emission to 2010 emission for China reported in a very recent paper (Zheng et al., 2018), but no improvements were

indicated for HONO, O_3, and $PM_{2.5}$ at the Heshan site (Fig. S4). Despite the uncertainty, we think that the current emission setting is acceptable for simulations of the present case."

4. Line 129-132: Zhang et al. (2016) is not the proper reference for HONO/NOx emissions ratios. Need to cite the proper reference.

Response: The reference has been changed to the following ones:

Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lorzer, J. C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, Atmospheric Environment, 35, 3385-3394, 10.1016/s1352-2310(01)00138-8, 2001.

Gutzwiller, L., Arens, F., Baltensperger, U., Gaggeler, H. W., and Ammann, M.: Significance of semivolatile diesel exhaust organics for secondary HONO formation, Environmental Science & Technology, 36, 677-682, 10.1021/es015673b, 2002.

5. Line 202-212: Need measurement accuracy for HONO, HNO3, sulfate, nitrate, ammonium, and PM25.

Response: Instrumental section has been revised including adding more description on HONO and giving references which have already described HONO and other chemicals. This section now reads:

"Field observations of HONO and other major air pollutants were conducted at Heshan site (112°55′17″E, 22°42′50″N) in the PRD region (Fig. 1). Hourly HONO concentration was measured using a Long Path Absorption Photometer (LOPAP) (QUMA, Model LOPAP-03) (Heland et al., 2001).The same instrument was employed by our group in several previous field campaigns (Zha et al., 2014; Xu et al., 2015; Liang et al., 2017; Yun et al., 2018). The reader referred to these sources (e.g., Yun et al., 2018) for description of measurement principle. Following our previous practice, the instrument background was determined with synthetic air 4 times a day, and calibrations with a nitrite solution standard were conducted every 3 days. The time resolution of this instrument was 10 min. The detection limit was 7 ppt with an accuracy of ±20%. The sample inlets were placed at the roof of a 4-floor building, at a height of about 15 m above the ground.

Other instruments whose data are used in the present paper have been summarized in Yun et al. (2018) with references provided for each instrument. Briefly, $PM_{2.5}$ concentrations were determined by a Multi Angle Absorption Photometer (Thermo Scientific, Model 5012). Sulfate, nitrate and ammonium in $PM_{2.5}$ were measured by a gas and aerosol collector coupled with an ion chromatography (GAC-IC) system. Gas HNO_3 concentrations were also measured by this GAC-IC system. O_3 concentrations were measured by a UV photometric analyzer (Thermo Scientific, Model 49i). NO_2 concentrations were measured using a chemiluminescence instrument (Thermo Scientific, Model 42i) coupled with a photolytic converter (Droplet Measurement Technologies, model BLC). The sample inlets for these instruments were placed at the same height as LOPAP."

6. Line 247-249: Overestimation of nighttime HONO may not be related to uncertainties of emission inventory and meteorological simulation. Emissions inventory appears to be reasonable since Figure S1 suggests that model NO2 is similar to observed data. Meteorological performance shown in Table S1 is reasonable. Thus, meteorology is not the problem either.

Response: We agree and have revised the description for possible reasons, as below.
Line 265-269:

"Overestimation was seen at the nighttime of 4 and 7 January, which was possibly related to some missing HONO sinks, e.g. the uptake of HONO on the ground surface (VandenBoer et al., 2014). Additionally, the overestimation of NO_2 could also explain partially the overestimation of HONO at the nighttime of 7 January."

7. Line 308-309 Do the authors mean that fast conversion occurs between OH and HO2?

Response: Yes, we have revised the sentence to "fast conversion exists between OH and HO2 radical"

8. Line 306-382: The HONO chemistry increased daytime average HO2 by 336% which means it also likely increased H2O2 substantially. Some discussion is needed.

Response: The simulation results showed that the surface daytime average H_2O_2 concentration didn't change much, with an increase from 320ppt to 323ppt at Heshan site. The possible reasons are: (1) the increased HO_2 and OH can increase the production of H_2O_2 (P1-P3), but also increase the loss of H_2O_2 (L1-L3); (2) compared with HO_2 and OH, H_2O_2 has longer lifetime and thus undergoes more vertical mixings and depositions. In this case, we don't have surface and vertical observation data to evaluate the H_2O_2 predication, and further studies are needed in the future.

$$HO_2 + HO_2 \rightarrow H_2O_2 \text{ (P1)}$$

$$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 \text{ (P2)}$$

$$OH + OH \rightarrow H_2O_2 \text{ (P3)}$$

$$H_2O_2 + h\nu \rightarrow 2OH \text{ (L1)}$$

$$OH + H_2O_2 \rightarrow HO_2 \text{ (L2)}$$

$$H_2O_2 + O \rightarrow OH + HO_2 \text{ (L3)}$$

9. Figure 8 Difficult to read the figure. A better plot is needed.

Response: Thank you. The plot has been improved.

References cited in this response:

Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, Environmental Science & Technology, 35, 3207-3212,

10.1021/es000303t, 2001.
Liang, Y. T., Zha, Q. Z., Wang, W. H., Cui, L., Lui, K. H., Ho, K. F., Wang, Z., Lee, S. C., and Wang, T.: Revisiting nitrous acid (HONO) emission from on-road vehicles: A tunnel study with a mixed fleet, J. Air Waste Manage. Assoc., 67, 797-805, 10.1080/10962247.2017.1293573, 2017.
Tham, Y. J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Groess, J., Shao, M., Wiedensohler, A., Zhang, Y., and Wang, T.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmospheric Chemistry and Physics, 16, 14959-14977, 10.5194/acp-16-14959-2016, 2016.
VandenBoer, T. C.; Markovic, M. Z.; Sanders, J. E.; Ren, X.; Pusede, S. E.; Browne, E. C.; Cohen, R. C.; Zhang, L.; Thomas, J.; Brune, W. H.; Murphy, J. G.: Evidence for a nitrous acid (HONO) reservoir at the ground surface in Bakersfield, CA, during CalNex 2010, J. Geophys. Res. Atmos., 119, 9093–9106, doi:10.1002/2013JD020971, 2014
Xu, Z., Wang, T., Wu, J. Q., Xue, L. K., Chan, J., Zha, Q. Z., Zhou, S. Z., Louie, P. K. K., and Luk, C. W. Y.: Nitrous acid (HONO) in a polluted subtropical atmosphere: Seasonal variability, direct vehicle emissions and heterogeneous production at ground surface, Atmospheric Environment, 106, 100-109, 10.1016/j.atmosenv.2015.01.061, 2015.
Ye, C., Gao, H., Zhang, N., and Zhou, X.: Photolysis of Nitric Acid and Nitrate on Natural and Artificial Surfaces, Environmental Science & Technology, 50, 3530-3536, 10.1021/acs.est.5b05032, 2016.
Yun, H., Wang, W., Wang, T., Xia, M., Yu, C., Wang, Z., Poon, S. C. N., Yue, D., and Zhou, Y.: Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-698, in review, 2018.
Zha, Q., Xue, L., Wang, T., Xu, Z., Yeung, C., Louie, P. K. K., and Luk, C. W. Y.: Large conversion rates of NO2 to HNO2 observed in air masses from the South China Sea: Evidence of strong production at sea surface?, Geophysical Research Letters, 41, 7710-7715, 10.1002/2014gl061429, 2014.
Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions, Atmos. Chem. Phys., 18, 14095-14111, https://doi.org/10.5194/acp-18-14095-2018, 2018