Comments

The authors present results from a modeling study on sources of nitrous acid during a large pollution event in the Pearl River Delta, China. The CMAQ model was updated with 4 new HONO sources, based on previous lab and field studies. The modeled HONO was compared to observations and was shown to agree well when the additional sources were included. The authors also discuss the impact of the high HONO observed on the oxidation capacity of the atmosphere. The manuscript is well written and the work is important for future modeling studies of HONO sources. I recommend this manuscript for publication once the following comments have been addressed.

1. L202-212: In agreement with Referee 1, further information on the accuracy of the measurements used in this study is required. Additionally, information on the location of the instruments, i.e. how far above ground level were they located, would be useful.

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."

2. L218: It is not clear from the reference provided how the NO_2 were adjusted to correct for interference. Suggest including a brief sentence or two describing the adjustments made, either in the main text or supplementary material.

Response: An annotation has been added under Table 1, as below:

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"*The NO_2 observation data were adjusted based on the method of Zhang et al. (2017):

$$NO_{2\,obs}=NO_{2\,obs}^{*}\times\frac{NO_{2\,sim}}{NO_{2\,sim}+NO_{z\,sim}-Nitrate_{sim}},$$ where $NO_{2\,obs}^{*}$ is the measured concentration of NO_2 by the

catalytic conversion technique. $NO_{2\,sim}$, $NO_{z\,sim}$ and $Nitrate_{sim}$ is the simulated concentration of NO_2, NO_Z and nitrate, respectively"

3. L245-247: I am unsure as to whether the re-release of HONO from the evaporation of dew water could account for the large differences between modeled and measured HONO in the early morning. Could you estimate the HONO released from dew using the method discussed in He et al, (2006), to determine the potential contribution from this source. For example, on 5 January the model underestimates the HONO morning peak by approximately 3 ppb (based on Fig 2). Could re-release from dew be such a large contributing source? If so, this is an important observation.

Response: Thank you for your comments. We have estimated HONO released from dew during the morning on 5 January using the method discussed in He et al, (2006). As shown in Fig. R1, dew existed during 0:00-8:00 on 5 January, and the total HONO dry deposition was 1.28×10^{-6} moles/m^2. At 9:00, if 80% of accumulated HONO was emitted to the surface model layer (about 0-30m), the total released HONO amount would be 0.76 ppb. This suggests that evaporation of dew may be a considerable source, but other sources may also exist.
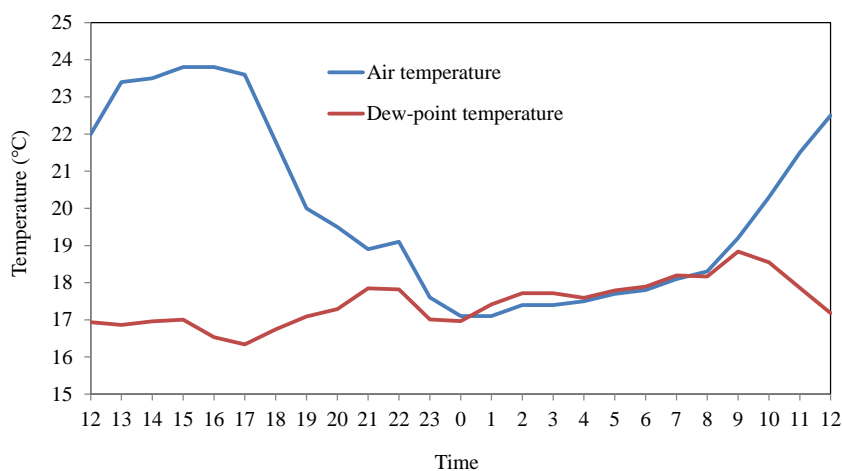
Fig. R1. Hourly variation of observed air temperature and calculated dew-point temperature based on the method of Hyland et al. (1983), from 12:00 on 4 January to 12:00 on 5 January.

We have added the following paragraph in the revised version:

Line 260-265:

"Here we have simply estimated HONO released from dew during the morning on 5 January when dew existed during 0:00-8:00 using the method described in He et al, (2006). The total HONO dry deposition was 1.28×10^{-6} moles/m^2. At 9:00, if 80% of accumulated HONO was emitted to the surface model layer (about 0-30m), the total released HONO amount would be 0.76 ppb. This suggests that dew evaporation may be a considerable source, but other sources may also exist."

4. Suggest making the legends in Figures 3 and 5 larger as they are difficult to read.

Response: We have enlarged the legends.

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.

Hyland, R. W., Wexter, A.: Formulation for the thermodynamic properties of the saturated phases of H_2O from 173.15K to 473.15 K, Ashrae Transactions, 89, 500-519, 1983.

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.

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.

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.

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, Atmospheric Chemistry and Physics, 17, 9733-9750, 10.5194/acp-17-9733-2017, 2017.