

Response to anonymous referee #2

(for the interactive comment on “Impact of nitrous acid chemistry on air quality modeling results over the Pearl River Delta region” by R. Zhang et al.)

In this manuscript, the authors incorporated various HONO formation mechanisms into the CMAQ model for the Pearl River Delta in China. Significant improvement in HONO prediction compared to the observed was achieved. The addition of HONO formation mechanisms showed only relatively small effects on the predicted air quality in the region, i.e., O₃ and PM_{2.5}. While this manuscript is a good attempt to model atmospheric HONO behavior and its potential impact on urban air chemistry, I have several major concerns and comments as listed below.

1. When calculating relative contributions from different HONO sources (e.g., Section 3.4, Figures 6, 7 and 8), the term of HONO production rate (i.e., source strength) would be more appropriate than HONO concentration, and should be used. Although the nighttime HONO concentration is higher than that during the day, the HONO production rate is actually much higher during the day. The plots in Figures 6, 7 and 8 will look quite different, and conclusions may also be quite different, if the production rate term is used. For example, the surface photolysis mechanism would become much more important than heterogeneous mechanism and direct emission (figure 6). It is also suggested that HONO formation rate is used in Figure 7 so that the actual source strength from each mechanism can be easily seen as a function of time of the day.

Response:

When calculating the relative contributions from different HONO pathways, the term of simulated HONO mixing ratio was used in Section 3.4 and Figure 6 & 7. From this prospective, we have the conclusion that heterogeneous conversion plays the major role for simulated HONO concentration either in XK and GZ, which is ‘opposite’ to current knowledge. We should state that the importance of surface photolysis to HONO production is important in terms of source strength: although the nighttime HONO concentration is higher than that during the day, the HONO production rate is actually much higher during

the day. We may mislead readers by only compare the contribution of different pathways to the concentration of HONO in the model (the balance of yield and loss term) but not mention the source strength (the yield term). Thus the high night-time concentrations caused by slow sources and missing HONO sinks ($\text{HONO} + h\nu \rightarrow \text{OH} + \text{NO}$) is directly compared with the low day-time concentration caused by very fast photolysis. A very strong daytime HONO formation pathways (e.g. surface photolysis) is needed to maintain the high daytime HONO levels observed in PRD region (e.g. ~ 1 ppb in rural area and ~ 4 ppb in urban area, Zhang et al., 2008). It would be a quite different picture if we use the 'source strength' to discuss the contribution budget. Hence, we will emphasize the current discussion on the relative contribution from different pathways is only valid in terms of final simulated HONO mixing ratio (for the health effects studies). In terms of atmospheric chemistry discussion, the HONO formation rate comparison is more proper to use.

The most proper way to conduct HONO formation rate calculation is through the integrate rate reaction (IRR) analysis. However, IRR is normally conducted to analyze the gaseous phase close loop system. For the case like HONO formation with heterogeneous reaction, a intense modification work for CMAQ is needed before the analysis. Instead, the HONO yield/loss budget is given by manually calculating the formation rate with the parameter information extracted from CMAQ and the kinetic of reaction R1, R2, R4 or parameterization scheme for reaction R8, R10-R12. Fig. A2 provide the daily average HONO formation budget at GZ site. It can be seen that HONO photolysis is the dominate sink, without considering the heterogeneous reaction R8 and R10 and surface photolysis reaction R11 and R12, the net HONO formation rate would be few pptV per hour, which is only sufficient to maintain a very low ambient concentration during the daytime. However, with the consideration of heterogeneous reaction and surface photolysis, the average hourly net HONO formation rate will be thousands pptV. Notice that the direct HONO emission contribution to HONO formation is accounted here. Based on Fig 2. The weighting of homogeneous reaction, heterogeneous reaction and photolysis reaction to HONO formation is roughly 38%, 33% and 29% respectively.

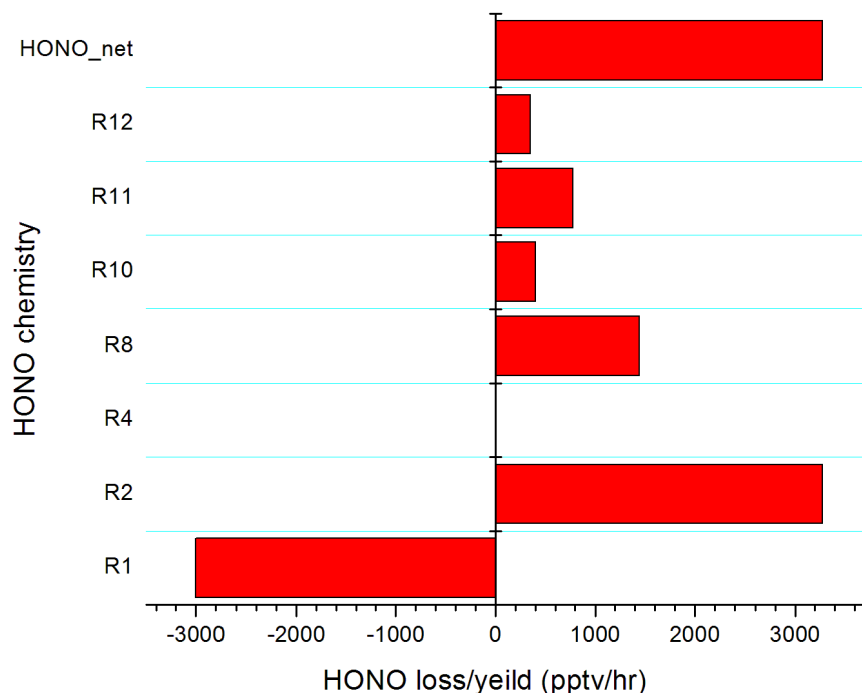


Fig A1. Daily mean HONO contribution budget for different reaction at Guangzhou site

2. The mean daytime HONO concentration of 4 ppb in this manuscript was probably the highest value reported in literature. The photolysis HONO, in the order of 15-20 ppb/hr, probably contributed a major fraction of new daytime HOx production. So it is quite surprising to see no significant effects on the modeling O₃ and PM_{2.5} productions from the HONO formation mechanism additions.

Response:

From the Fig 9 and Table 3, it is clearly demonstrate that additional HONO/OH source do have impact on the atmosphere oxidization capacity and the secondary pollutant yields. For 8hr average maximum ozone, up to 6 ppb V (8%) increase is expected at the downwind of Guangzhou during the synoptic steady weather condition. Morning ozone enhancement is slightly significant with the largest value 9 ppb V. For PM_{2.5} daily mean mass concentration can increase by up to 17 ug/m³.

In terms of the significance of secondary pollutants enhancement it is indeed not as large as expected. The peer's study on the same topic but using the box model (e.g. Lu et al., 2010 using observation based box model, Elshobany et al., using a simple quasi-photostationary-state model) tends to report the promising results. However, the similar work by using 3D regional air quality model reported the similar O₃ and PM_{2.5} enhancement level. For instance, Lei et al. (2004) consider reaction R8 in 3-D chemical transport model in Huston, they reported daytime increase O₃ by 4-12 ppbV. Sarwar et al. (2008) used CMAQ and added R8 and R12, they reported the additional HONO source at daytime increase average OH and O₃ by 10% and 1.4 ppbV. Li et al. (2010) used WRF-Chem and consider reaction R9, they reported the enhancement of midday average O₃ by 6 ppb V. Gonçalves et al. (2010) applied the WRF-ARW/HERMES/CMAQ modeling system to quantify the effect of HONO direct emission as well as heterogeneous formation on the predictability of HONO profiles and their impact on O₃ and PM_{2.5} simulation. They reported O₃ peak concentrations are slightly affected by 0.7-4 ppb V (1-4.5%) while PM_{2.5} simulation is significant change by 16% (2.6 ug m⁻³).

The nature of more diffusivity and transportation of 3D air quality model compared with simple box model may be the reason for the "not significant enhancement" of the secondary pollutant yield. In box model, all the initial conditions are react with in single point without exchange, while the 3D box have more freedom to transport the pollutant by average wind or turbulence, the impact of HONO chemistry may not constrained on the ground level.

Another important reason for this "not significant enhancement" for secondary pollutant may due to the model limit to generate sufficient OH radical for oxidation. In Section 3.2 of Page 15092, the simulated daytime average OH at GZ and XK are compared with the different simulation cases. The OH level is significant lower than the measurement OH level over GZ area (around 5×10^{-6} cm⁻³, Hofzumahaus et al., 2009). As an emission based model, the accuracy of emission data in crucial for the quality of air pollutant prediction. The uncertainty of VOC species emission estimation may be one of the factor. For instance, if comparing the VOC species emission strength with corresponding observed ones,

toluene is underestimated 14 times. Additional runs by adjusting the original VOC emission rate are conducted for case 'CB05' and 'HONO_S/V', Fig A2 gives the spatial distribution of maximum 8hr average O₃ enhancement for due to the HONO chemistry, compare the value with Fig. 9 (a-2), the maximum value increase from 6.4 ppbV to 11 ppbV, with the relative increase about 9%. More importantly, the predicted daytime average OH concentration for simulation case 'HONO_S/V' after adjusting the VOC species emission, increase from 2.5×10^{-6} molec cm⁻³ to 2.9×10^{-6} molec cm⁻³ at XK site while from 1.9×10^{-6} molec cm⁻³ to 2.6×10^{-6} molec cm⁻³ at urban GZ site.

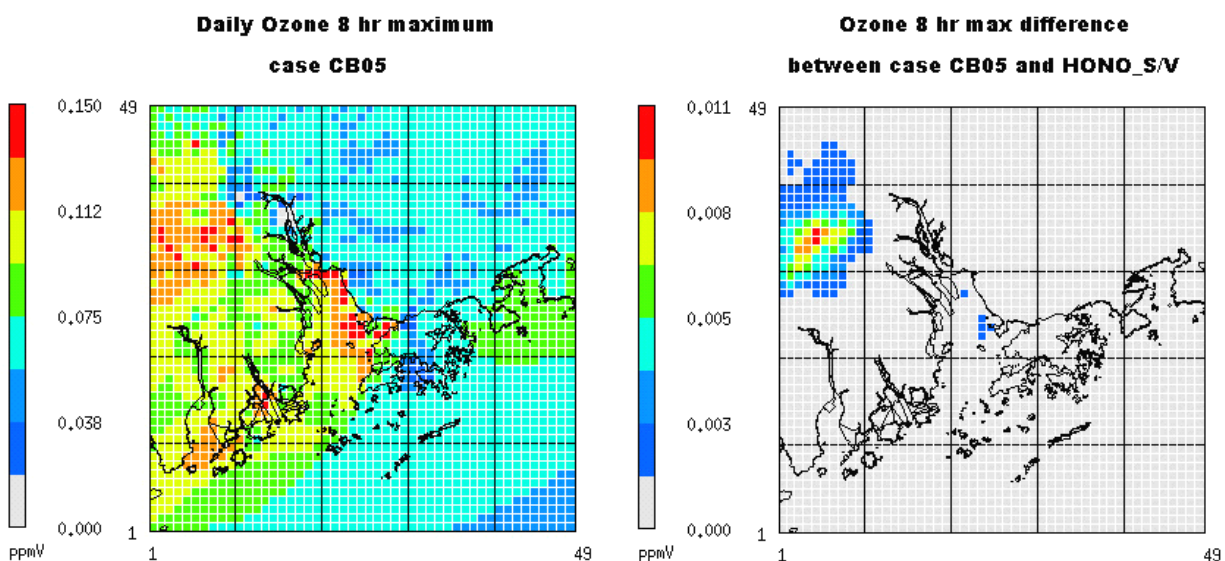


Fig A2. Spatial distribution of the 8 hr maximum ozone enhancement due to HONO chemistry during the entire simulation period.

3. It is not quite sufficient to validate the model through the comparison between the predicted and the observed using just daytime and nighttime averages in Figure 4. A time-series plot of the observed and the predicted (incorporating different mechanisms) would be more desirable. The detailed time profiles will help the authors and the readers to evaluate relative importance of different mechanisms as well as the overall performance of the model.

Response:

The reason that we show the comparison of HONO simulation for various model runs with observations in terms of mean value instead of hourly or diurnal variation is due to the limit of observation database. Our observation data for HONO and related NO_x, Ozone are mainly coming from the papers in PRD campaign (Zhang et al., 2008; Su et al., 2010). Only little detail raw hourly data is available at Xinken (XK) site (the rural site) during the simulation window. We add the Figure A3 here to demonstrate the model performance at XK for simulation case '*CB05*' and '*CB05+EM+HT+SP*'. The model has a fair capability to simulate NO₂ and O₃ with mean normalized bias (MNB) value around ±20%~±40%. After incorporating the additional HONO formation pathways, the mean O₃ simulation increased 2.1 ppbV or 5%, and slight portion of NO₂ was consumed for HONO formation. For NO₂ and O₃, no obvious improvement is found for the evaluation metrics. However, for HONO simulation in XK, the improvement is remarkable. The standard CMAQ heavily underestimate the observed mean HONO level (1.125 ppbV) by 28 times with the IOA=0.35, nearly no correlation, and MNB=-95.8%. The case '*CB05+EM+HT+SP*' can reproduce 38% of ambient HONO level with the significant improved statistic metrics IOA=0.55 and MNB=-54.5%.

In order to show the comparison of HONO diurnal variation in XK and Guangzhou (GZ), namely, the contrast at rural site and urban site, we add other Figure A4 here for demonstration. Notice that the mean observation diurnal variation with error bars over PRIDE-PRD2004 campaign are directly extracted from the Figure 3 of Zhang et al. (2008). The diurnal variation of different simulation cases are the mean of each local hour HONO mixing ratio over the simulation window. The characteristic of HONO diurnal profile over PRD region with high peak at night and relatively low during morning is consistent with the observation worldwide (Kleffmann et al., 2005; Ren et al., 2006; Elshorbany et al., 2009; Mao et al., 2010). The adding of direct emission (case '*CB05+EM*') contributed the HONO morning peak at the rush hour 0700~0800 local standard time (LST). The adding of heterogeneous reaction (case '*CB05+EM+HT*') mainly contributed the late afternoon (1700-2200 LST) build-up of HONO concentration. The simulation case '*HONO_S/V*' nearly followed the observed HONO diurnal variation pattern at GZ, but in XK, it shows the large overestimation occurred after sunset. However, the current implementation

cannot repeat observed elevated HONO level late at night (0200~0600 LST), the model tends to have the steep jump after the peak near the midnight.

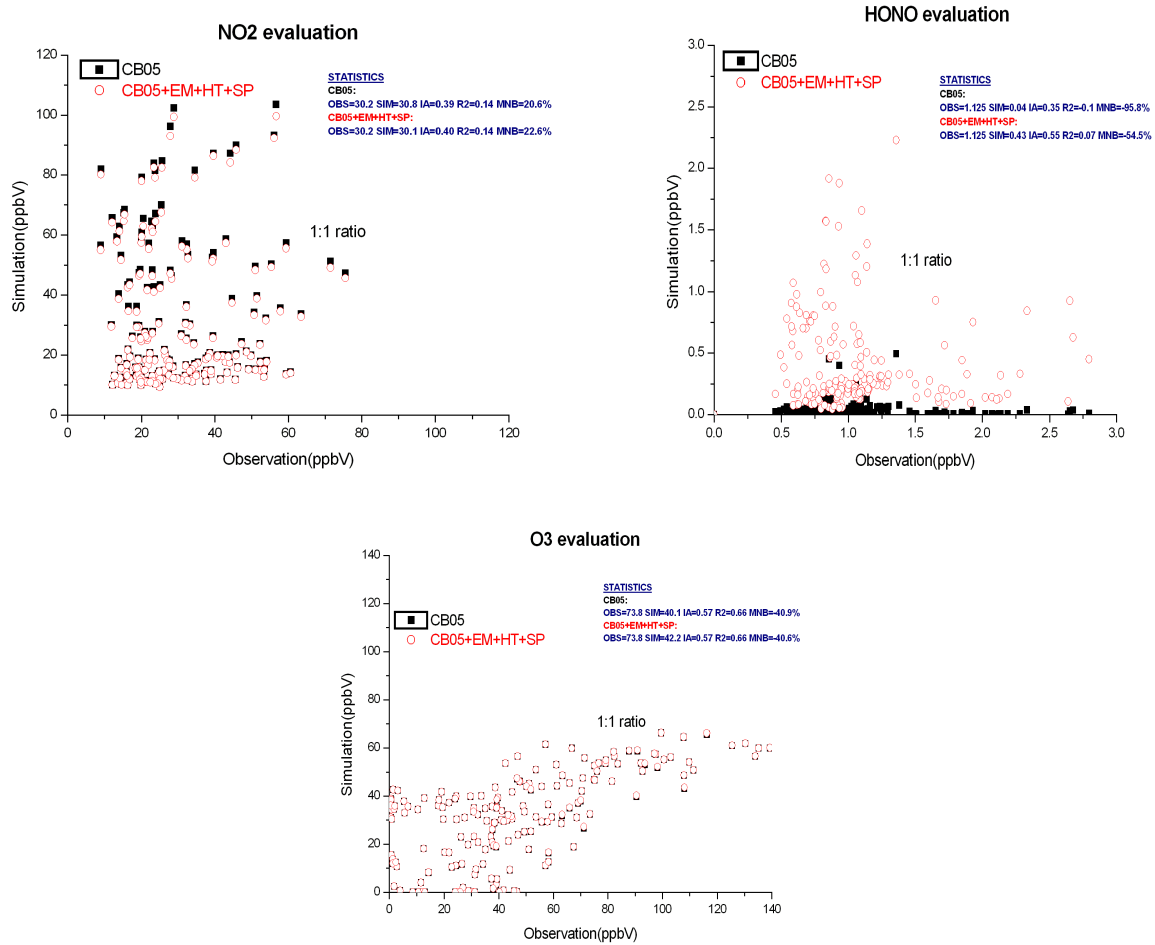


Figure A3. Model validation after incorporation of HONO chemistry at Xinken (XK) station for NO₂, HONO and O₃ simulation

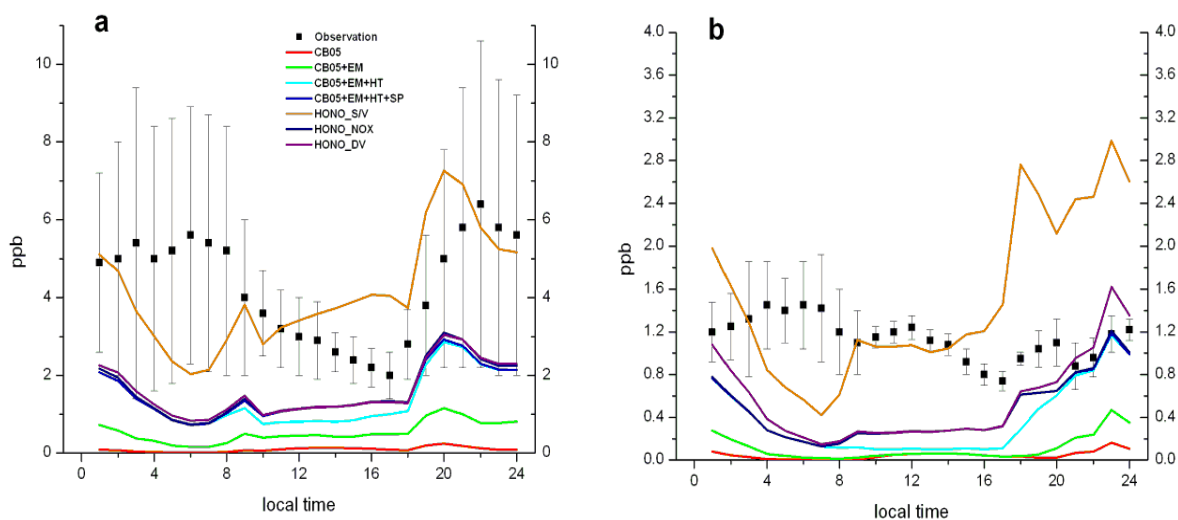


Figure A4. Diurnal pattern of simulated HONO at (a) Guangzhou and (b) Xinken with difference simulation cases

4. Even with all the mechanisms incorporated into the model, there are still large discrepancies (by a factor of 2-3, Figure 4) in the observed and the best predicted concentrations of HONO. While models may be “re-tuned” to get better agreement, it is important to make sure that the measured HONO values are correct and accurate, especially when such a high daytime mean HONO concentration (4 ppb) is reported.

Response:

The high HONO observed value in PRD region has been reported by some studies. For instance, early-morning HONO mixing ratio of up to 12 ppbV was measured at Guangzhou (GZ) in June 2000 (Hu et al., 2002). Mean noon value of about 4 ppbV at GZ was measured during the first Program of Regional Integrated Experiments on air quality over the PRD in October 2004 (PRIDE-PRD2004, Zhang et al., 2008a). A nocturnal peak HONO mixing ratio of over 8 ppbV was reported in PRIDE-PRD2006 campaign (Qin et al., 2009). High nighttime HONO levels of up to 4 ppbV (Su et al., 2008) occurred even at the rural site Xinken (XK). The high HONO concentration recently is proposed to connect with the source of soil nitrite (Su et al., 2011). They acclaim that fertilized soils with low PH appear to be particularly strong sources of HONO and OH. The agricultural land use in PRD region is abundant of fertilizer containing nitrate, hence have a large potential to release

HONO and OH radicals. In terms of the observed high OH concentration over PRD region, an amplified trace gas removal mechanism is proposed, in which the regeneration of OH is independent of NO and amplifies the degradation of pollutants without producing ozone (Hofzumahaus et al., 2009).