

Response to anonymous referee #3

(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.)

The manuscript by Zhang et al describes a 3D chemistry and transport modeling study of the Pearl River Delta region with a focus on testing new nitrous acid formation mechanisms and their impact on HONO and ozone chemistry. The study is based on the CMAQ model, adapted and tested for the Pearl River Delta region. The authors carefully review the various proposed HONO formation mechanisms and discuss how these mechanisms are parameterized in the model. The main conclusion from the model study is that implementing additional HONO sources improve the comparison with direct measurements of HONO, in particular during the day. The authors conclude that heterogeneous chemistry is responsible for 60% of HONO, followed by surface photolysis, and direct emissions. Inclusion of HONO chemistry leads to an increase of maximum O₃ of ~ 8% and an increase of PM_{2.5} ~12% compared to the base case. The authors also show that inclusion of more accurate HONO chemistry impacts the design of ozone control strategies.

In general, this is a very interesting and well thought through manuscript. The authors spent considerable effort in considering all currently proposed HONO sources and including them in the model. The results confirm some earlier, much simpler, studies that predict that inclusion of HONO chemistry will have a 5-10% effect on ozone. The discussion of the impact on ozone control strategies has implications that go beyond pure science.

I recommend this manuscript for publication in ACP after some revisions and copyediting. Below are some specific comments.

Page 15083, line 7: Please clarify what you mean with “O₃-to-NO production rate”.

Response:

In here, the peer’s observation based model results (Zhang et al., 2008) is cited to support the importance of HONO chemistry, especially the heterogeneous part, to the PRD region radical recycling and photochemical O₃ production.

The “O₃-to-NO production rate” or P_{O₃-NO} is the net ozone formation and NO consumed, which was used as a common measure of the ozone formation potential. For instance, the Relative Incremental Reactivity (RIR, Carter and Atkinson, 1989) is the index to present the percent change in ozone production (P_{O₃-NO}) per percent change in precursor emission.

Hence, the original description “O₃-to-NO production rate” will be changed to “ozone production rate” in the revised manuscript in order to avoid misleading.

Page 15086, lines 10 – 25: Treating aerosol surfaces and the ground by the same physical mechanism seems inaccurate, because of transport limitations towards the ground surface that do not exist in the same way for the aerosol. Please explain why you can treat ground surface and aerosol heterogeneous chemistry by the same parameterization. Also, how do you reconcile treating heterogeneous conversion on the ground surface and the use of deposition velocities for surface loss separately?

Response:

For selected HONO heterogeneous reactions (R8 and R10) in this paper, they are treated as first order reactions in CMAQ with the reaction rate K_{HONO} proportional to the available surface-to-volume ratio (S/V) in the model, which include the aerosol surface and ground surfaces (vegetation, building and soil). It is an empirical parameterization method based on previous lab experiments and previous simulation works (e.g. Kleffman et al., 1998; Aumout et al., 2003; Sarwar et al., 2008). Although the “physical mechanism” for aerosol suspended on the atmosphere and the objects on the ground is quite different, we only considered the possible 3D HONO formation potential after each integration time step in chemical transport model (CTM) at this stage. In other words, after each the CTM time step, the CMAQ gaseous phase module will provide the 3D NO/NO₂/HNO₃ mixing ratio field and the CMAQ aerosol module will provide the 3D aerosol S/V value. In together with assigned the ground vegetation, building and soil S/V value (which is based on LAI value, land-cover database and empirical literature value), a 3D available S/V fields for the HONO heterogeneous reaction yield estimation can be created. The heterogeneous reactions are regarded as complete within each CTM time step, hence, the new HONO mixing ratio will be updated continuously in line with the evolution of CTM. No additional “physical mechanism” for aerosol and ground heterogeneous reaction is considered at this moment.

In terms of reconciling the independent treatment of heterogeneous conversion on the ground surface and the use of deposition velocity for surface loss, it is indeed one of the limitations of current application. The ideal process should weight the relative importance of HONO deposition velocity and the upward ground heterogeneous emission strength and combine the two factors with directional flux. Actually, in current CMAQ version 4.7, there is already a similar treatment by considering the bi-directional surface exchange of ammonia (NH₃) and mercury (Hg) (Cooter et al., 2010; Bash, 2010). In this method, emission of NH₃ and Hg is not independently treated by outside processor by as integral process in air-surface exchange module. Bi-directional exchange for NH₃ and Hg were developed based on canopy compensation, which consider the impact of land cover type, ambient temperature, and partitioning of NH₃ and Hg between atmospheric, apoplastic and vegetation surface compartment (Foley et al., 2010). In the future, the authors may

follow this flux concept to combine the surface emission and deposition in a more consistent way. Thanks for the value comment.

Page 15088, equation 5: Define z_s in the text.

Response:

In this paper, the parameterization of HONO formation through photolysis of absorbed HNO₃ on surface was following the methods by Zhou et al. (2003) to. In here “ z_s ” is the first layer model height in CMAQ simulation domain configuration. In Page 15083, line 22, it refers as “twenty vertical layers were constructed in CAMQ with the first layer around 17m above the ground”.

Page 15089, line 17: Please define “index of agreement”.

Response:

Index of Agreement (IOA) is a statistical metrics with value between 0 and 1 to compare the departure of predictions (P) from the mean value of observations (O) with the departure of individual observations from the mean (Ulrickson and Mass, 1990). It defines as (Willmott, 1981):

$$I = 1 - \frac{\sum_{i=1}^N (P_i - O_i)}{\sum_{i=1}^N (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$

IOA value “1” means prefect agreement while value “0” means no agreement.

Section 3: The most serious omission in the manuscript is the missing comparison of the observed diurnal variation of HONO at Xinken and Guangzhou with the results from the various model runs. This must be added to convince the reader that HONO is better described in the expanded model. Figure 4 is not sufficient for this purpose.

Response:

The reason to 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. The 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. Figure A1 is added 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 A2 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_SV*' 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.

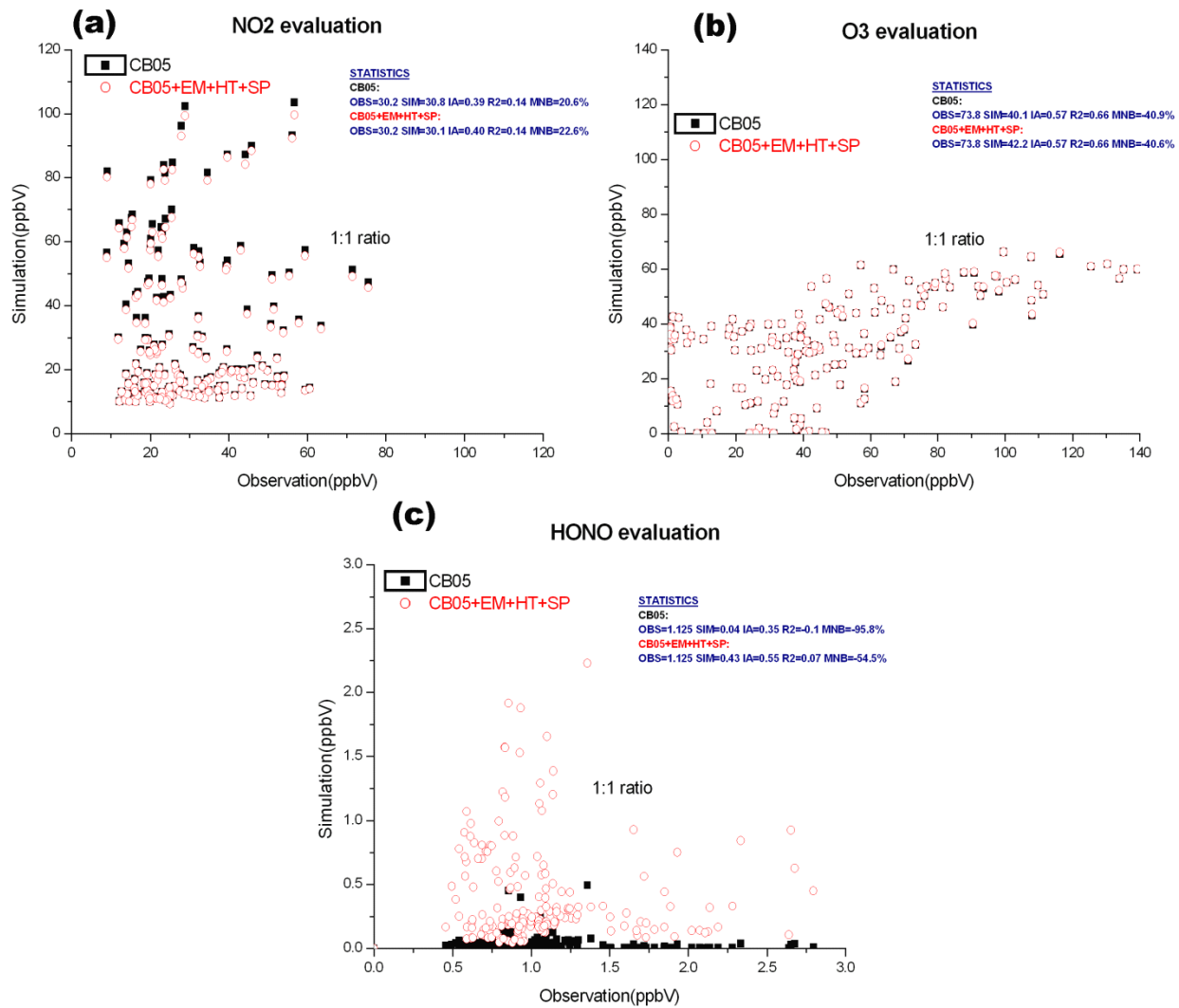


Figure A1. Model validation after incorporation of HONO chemistry at Xinken (XK) station for (a) NO₂, (b) O₃ and (c) HONO simulation

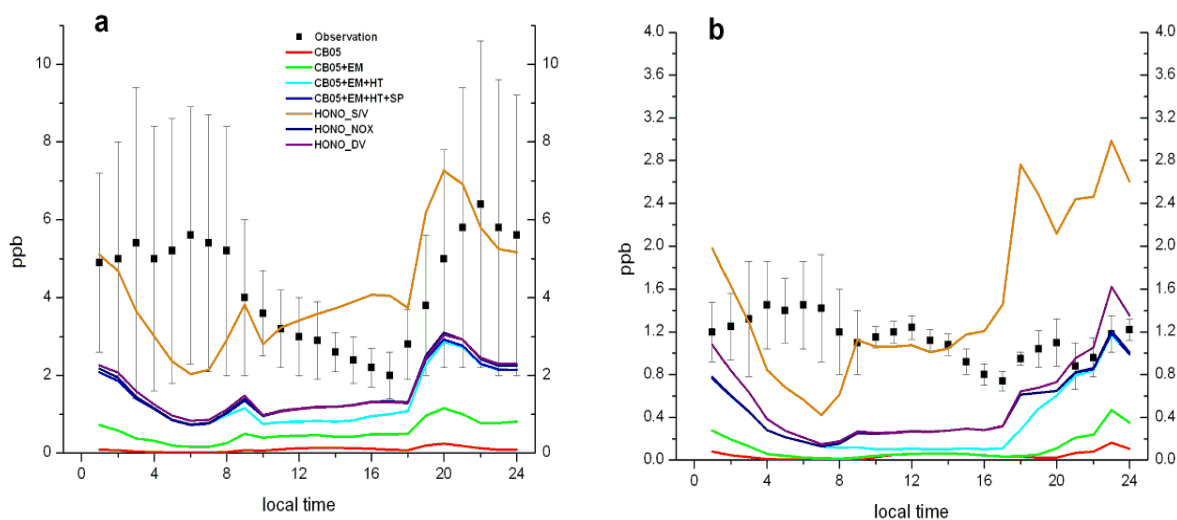


Figure A2. Diurnal pattern of simulated HONO at (a) Guangzhou and (b) Xinken with difference simulation cases

Figure 6: It is not completely clear what is shown in Figure 6. Is this the 24h average in the lowest grid cell of the model? In this case the plot is skewed towards the high nocturnal HONO cases. Figure 6 also does not seem to show any information that is not also shown in Figure 7.

Response:

The average contribution of homogenous reaction (black), direct emission (red), heterogeneous reaction (green) and surface photolysis reaction (purple) to total simulated ground HONO at XK and GZ site during the entire simulation period (10 days, in total 240 hourly data) is given in Figure 6. It is the average of 10 day simulation at the lowest grid cell since we focus on discussing the contribution budget of ground HONO mixing ratio only. In terms of daily average value, due the weighting of HONO mixing ratio at night is higher that of at daytime, the plot is indeed skewed towards the high nocturnal HONO case. In contract, Figure 7 breaks down the simulated ground HONO concentration at rural and urban site into average diurnal relative contribution. The purpose of this figure is to show the detail contribution by the four formation pathways at different time at the day. For instance, the surface photolysis pathway is the dominate contributor for simulated HONO mixing ratio during daytime, with the maximum contribution 64% in XK and 31% in GZ at the late afternoon. However, the high nocturnal HONO concentration is mainly controlled by the heterogeneous reaction.

Section 3.4, Figure 6 & 7: The results in Figures 6 and 7 are surprising in that the heterogeneous conversion plays such a major role. Current literature suggests a much higher relative

contribution of the photolytic source. The authors should comment on why they think that the heterogeneous pathway is so important in their case.

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. It 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 to 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 cased 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).

Figure 8: Please show separate plots for daytime and nighttime, following the arguments outlined above for Figure 6.

Response:

Please see the following updated Figure A3 in correspondent with Figure 8 to breaking down the HONO simulation comparison with daytime (0700-1800 LST) and nighttime (1900-0600 LST).

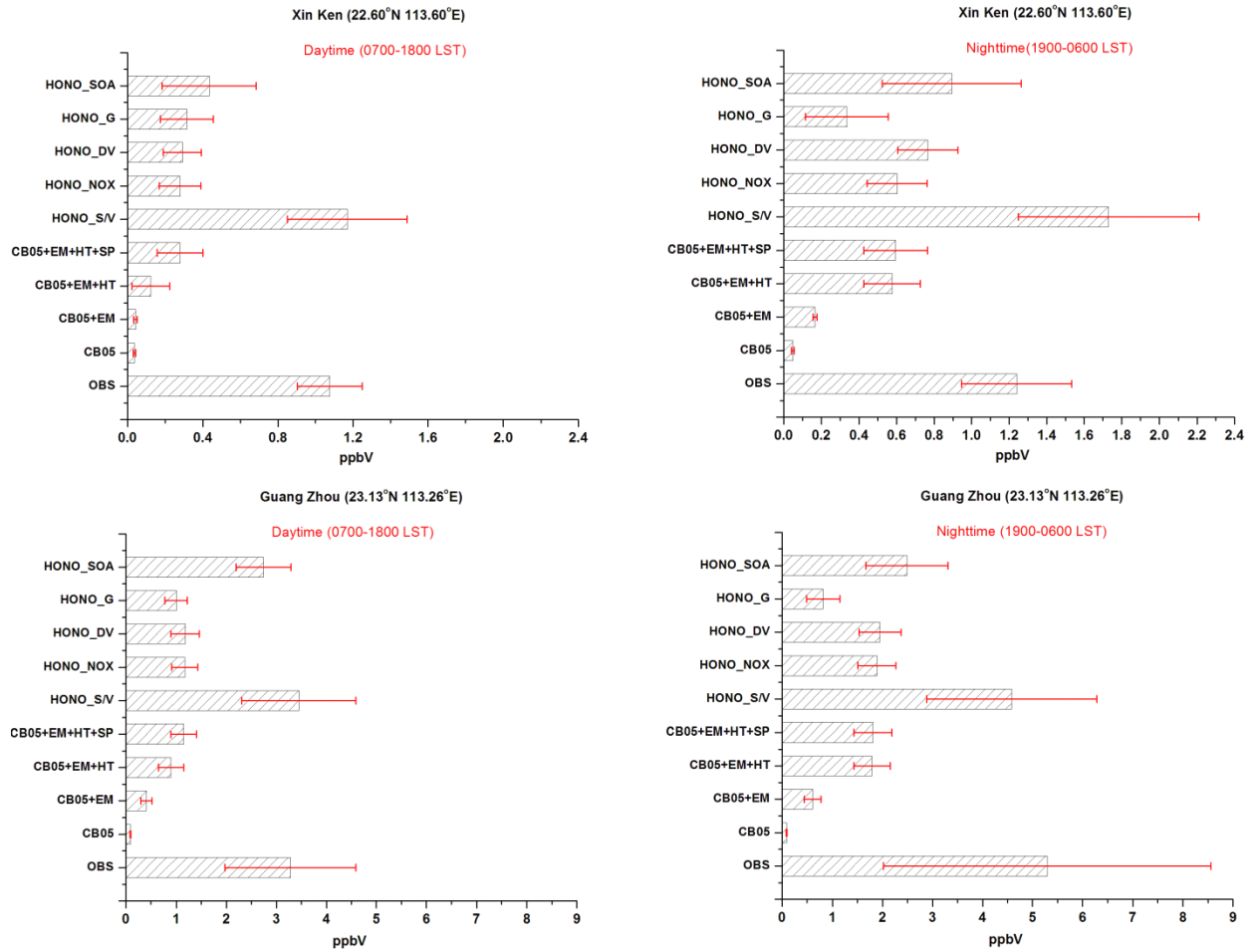


Figure A3. Simulated mean daytime and nighttime HONO concentration in Xinken and Guangzhou for different simulation case.