

Response to anonymous referee #1

(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.)

General Comments:

In the manuscript, different HONO sources were implemented into the 3D CMAQ model for the Pearl River Delta (PRD) region and compared to direct measurements. In addition, the impact of these sources on secondary species, like e.g. O₃ or PM, was also investigated. Since HONO plays an important role as radical initiation source in the atmosphere, and since HONO chemistry and emissions are typically not properly considered in 3D models, any further improvements are of high interest. However, I have several general concerns about this manuscript:

1) Used HONO chemistry:

While the HONO emissions are correctly used (0.8 % HONO/NO_x and realistic sensitivity run with 1.2 % for modern vehicles), some considered reactions are completely unimportant and could be omitted, while others are either not correctly used or are missing. For example, R4 has such a low third order rate coefficient that this reaction will not play any role in the atmosphere, which is also true for the heterogeneous reaction R7. This can be easily demonstrated by many field campaigns, in which HONO is formed without NO being present. In addition, also several laboratory studies excluded HONO source reactions involving NO. The old correlation studies from which the NO contribution were derived (see Calvert et al.), were confuted in several more recent studies (artificially caused by the diurnal variation of the vertical mixing) and are not state of the art. Thus, R4 and R7 could be ignored.

Response:

For homogeneous reaction R4, it include into the CB05 mechanism (Yarwood et al., 2005), which is chosen as the gaseous phase mechanism in CMAQ modeling. In CB05, the rate constant value is very low ($K_{\text{HONO}} = 5 \times 10^{-40}$), hence the impact on HONO formation is trival. However, as a standard setting in CB05, this reaction is kept in CMAQ modeling.

For heterogeneous reaction R7, this reaction is not used in later new HONO formation pathway in CMAQ (see Table 1) due to the high uncertainty in rate constant and the trivial contribution to HONO formation (see line 2-4 of Page 15079).

R5 is also an extremely slow second order reaction ($<10^{-21} \text{ cm}^3 \text{ s}^{-1}$), which needs not to be taken into consideration, besides deposition and photolytic losses.

Response:

Similarly, Reaction R5 the standard component in CB05 mechanism with the rate constant $K_{\text{HONO}} = 1 \times 10^{-20}$, it is a very small sink of HONO compared with photolysis.

While some unimportant gas phase sources are used in the model, the authors at least missed to mention the photolysis of nitroaromatic species (Bejan et al.), which may be also not one of the most important sources, but which will be much more important compared to R4/R7 used here.

Response:

Add the sentence “Bejan et al. (2006) proposed the photolysis of aromatic compounds containing the *ortho*-nitrophenol as the new gas phase source of HONO, which would partially help to explain the high contribution of HONO to oxidation capacity in urban atmosphere environment.”

The corresponding citation is:

Bejan I., Abd El Aal, Y., Barnes, I., Benter, T., Bohn, B., Wiesen, P., and Kleffmann, J.: The photolysis of *ortho*-nitrophenols: a new gas phase source of HONO, *Phys. Chem. Chem. Phys.*, **8, 2028-2035, doi:10.1039/b516590c, 2006.**

R8 and R9 are also not properly used here. Whereas gamma values between 10^{-7} - 10^{-8} can be derived for R8 based on smog chamber results summarized in the review of Finlayson-Pitts et al. (2003), typical gamma values for the dark reaction of NO₂ with adsorbed hydrocarbons (R9) are

around 10^{-6} (see studies by Gutzwiller et al., Arens et al., Ammann et al, ...). However, later the higher value of 10^{-6} is used incorrectly for reaction R8. In addition, R9 is used here for two different reactions a) NO_2 +soot and b) NO_2 +semivolatile organics. Both reactions should be separated. Thus, also some conclusions to R9 (e.g. on page 15079, line 15) may be true for the soot reaction, but not necessarily for the reaction of NO_2 with semivolatile VOCs. I suggest here to use humidity dependent gamma values (10^{-7} - 10^{-8}) for R8 (see Finlayson-Pitts) and a gamma value of 10^{-6} for R9. This would directly include the HONO_SOA run which was later incorrectly used (see below). For the soot reaction (add a new reaction) very fast deactivation is published, thus for a model a simple emission factor could be used. In laboratory studies, integrated HONO formation on soot of 10^{14} HONO cm^{-2} of soot surfaces was measured (see e.g. Arens et al., Kleffmann et al.), which can be easily converted into a soot mass related number to be used here (the model contains PM ...).

Response:

For heterogenous reaction to form HONO, only reactions R8 and R10 are considered in this paper. For R8, the reported rate constant value is uncertainty. The rate constant value suggested by Aumont et al., 2003 is used in this study. A sensitivity run by assigning the gamma values as $10^{-7} \sim 10^{-8}$ linearly depending on the ambient humidity as Finlayson-Pitts et al., (2003) proposed is conducted and the results are given below.

For reaction R9, it is not incorporated into standard CMAQ in this study due to the complicated parameterization for fast deactivation process in 3D model. The "emission factor" method as the referee suggested should be a simple approach to simulate heterogeneous HONO formation. Li et al. (2010) used the similar method to study the reaction on semivolatile surface to HONO formation.

Change lines 12-14 of Page 15079 as "Reaction (R9) can produce HONO either on soot or on semiorganic surface (Ammann et al., 1998 and Gutzwiller (2002). However, the surface deactivation occurs within a few minutes and the heterogeneous reaction on soot may not be

an important pathway for HONO (Kleffman et al., 1999, Arens et al, 2001). In regards to the reaction on organic surface, the parameterization method is still open. "

Add the corresponding citation in the reference list:

Finlayson-Pitts, B.,J., Wingen, L.M., Summer, A.L., Syomin, D., and Ramazan K. A.: The Heterogeneous Hydrolysis of NO₂ in Laboratory Systems and in Outdoor and Indoor Atmospheres: An Integrated Mechanism, Phys. Chem. Chem. Phys., 5, 223, 2003.

In addition, the heterogeneous reaction of NO+HNO₃ (R10) was used in the model. However, also this reaction was demonstrated to be insignificant at conditions closer to the atmosphere compared to the study of Rivera-Figueroa et al. and gamma values for heterogeneous HONO formation of <10⁻¹⁰ were published (Kleffmann et al., 2004).

Response:

There exists large uncertainty for the gamma value used in R10. In this paper, the value proposed by Rivera-Figueroa et al (2003) is taken. Knipping and Dabdub (2002) demonstrated the improvement of modeling ozone concentration (especially for the peak) by inclusion this renoxification reaction into the airshed model for South Coast Air Basin in southern California. This renoxification process needs to be considered as the potentially important in pollutant urban atmosphere such as intense city cluster over Pearl River Delta, China. Still, a sensitivity runby ignoring taking small rate constant value is conducted, please see the simulation results below.

For the surface photolysis reactions two mechanisms were used here. However, also recently a photo-enhancement of the NO₂+soot reaction was observed in the laboratory (Monge et al., 2010). This reaction should be at least also mentioned here.

Response:

At the end of reaction (R12), add one short paragraph as:

"Recently, Monge et al. (2010) demonstrated the enhancement of NO₂ to HONO conversion on soot particles with the presence of artificial solar radiation, which would be a potential pathway for HONO formation through surface photolysis".

Update the reference list with the corresponding citation:

Monge, M.E., D'Anna, B., Mazri, L., Giroir-Fendler, A., Ammann, M., Donaldson, D.J., and George, C.: Lights changes the atmospheric reactivity of soot: Proc. Natl. Acad. Sci., 15, 6605-6609, doi:10.1073/pnas.0908341107, 2010.

For R11 a parameterization (4) derived in the study of Stemmler et al. (2007) in aerosol experiments was used for a ground surface in the model. However, for their bulk experiments (2006) ca. a factor of two higher gammas were obtained, which may be one reason for the relative small contribution of this source (see also below ...).

Response:

A sensitive case run by increasing the gamma value is conducted and simulation results is given below.

In addition, the HONO yield for R12 is typically much lower than the 50 % used here. The quantum yield for nitrate photolysis from laboratory studies is typically 10 %, while the major product channels goes to NO₂+O (see reviews on this reaction). In addition, in the parameterization (5) used here the HNO₃ surface concentration is overestimated. Caused by the very high J-value (24x gas phase value, still controversial under discussion) the lifetime of nitrate on the surface will be <1 day, in contrast to gas phase HNO₃ used in equation (5). Thus, if the "accumulated time" to the next precipitation event is longer than 1 day, R12 is overestimated.

Response:

The parameterization method as well as photolysis value (J) for R12 is rooted in the empirical relationship developed by Zhou et al. (20003) from lab measurement. In CMAQ,

the absorbed HNO₃ on ground surfaces is assumed to equal the amount of HNO₃ accumulated over time by dry deposition since the last precipitation event. R12 indeed have the potential to overestimate HONO formation rate by using high J value and the too long accumulation time. The fine tune of this part of parameterization needs more field and lab experiment support. A sensitivity run by decreasing the HONO yield is conducted for comparison. See below for detail.

And finally, in the sensitivity runs the conversion of NO₂ on semivolatile hydrocarbons studied for diesel engine emissions by Gutzwiller et al. is used. For this run an additional fraction of 2.3% HONO/NO_x is used in the model. Although the average modelled HONO gets closer to the measurements the authors excluded this source since during rush hour peaks up to 40 ppb HONO were modelled (see page 15095, lines 20-24), which would be indeed out of the range ever measured in the atmosphere. However, the reason for these unrealistic results is not the unimportance of this source, but the incorrect way how the authors used this source in the model. The reaction studied in Gutzwiller et al. is NO₂ + organics. In contrast, for any rush hour peaks with NO_x levels near 2 ppm (40 ppb HONO / 0.023 emission ratio), the main NO_x component will be NO (something around 90 %). But NO is not reacting, see Gutzwiller's study. Thus, only the NO₂ should be used for this reaction, see above (gamma ca. 10⁻⁶ derived in several lab studies).

Response:

Indeed, the parameterization of HONO conversion rate from NO₂ on semivolatile organics has a problem. Empirical emission factor is used but it should be based on the active compound NO₂ instead of non-active compound NO.

Based on all the recommendations on the usage of HONO chemistry, an additional case is introduced here by setting the parameter as referee request. For reaction R8, the gamma value is set as 5.0×10^{-8} ; for reaction R10, the gamma value is set as 1.0×10^{-10} ; for reaction R11, the gamma value is set as 3×10^{-6} ; for reaction R12, the HONO production is reduced by half. Meanwhile, the emission factor 0.023 as diesel vehicle active NO₂ emission is used

to construct the contribution of heterogeneous reaction on semi-volatile organics surface is also considered.

In Fig. A1, The predicted mean HONO diurnal variation (case 'referee recommendation', blue line) is compared with simulation case 'CB05' (red line) and 'CB05+EM+HT+SP' (green line), as well as the mean observed HONO diurnal profile with error (black line) at Guangzhou (GZ) and Xinken (XK) site. Generally, the diurnal pattern for different simulated cases is similar, with the maximum at evening and the morning peak during rush hour (only at GZ). The model still have problem to repeat the high concentration plateau after midnight. The recommended case decrease the weighting of R8 and R10 for HONO yield contribution, and increase the photolysis weighting. The reason that recommended case have the same concentration level as 'CB05+EM+HT+SP' case during night time is the contribution of heterogenous reaction happened in the surface of semivolatile organic surface. During daytime (i.e. 8:00am - 17:00 pm), the recommended case increase the predicted HONO concentration by 10% due to the increase contribution form R11.

Predicted daytime average OH for recommendation case is 1.7×10^6 molec cm^{-3} at GZ and 2.4×10^6 molec cm^{-3} at XK, which is slightly lower than that for simulation case CB05+EM+HT+SP.

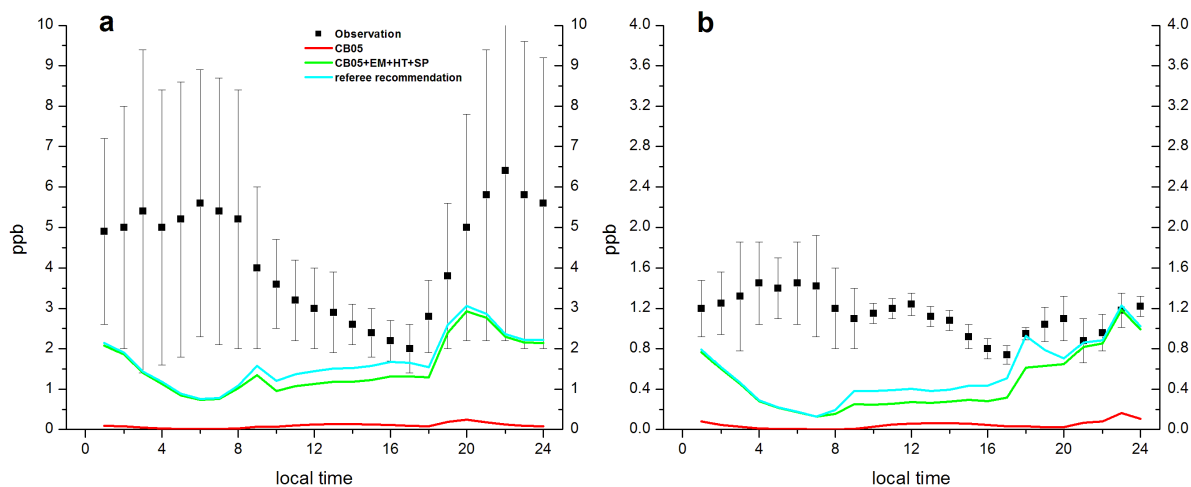


Fig A1. Diurnal pattern of simulated HONO at (a) Guangzhou and (b) Xinken with difference simulation cases

2) Presentation of the results:

From the results presented, the reader will get the impression that the heterogeneous sources are much more important compared to the surface photolysis sources, see for example Figure 6, 7, 8 and see also "Summary" lines 11-12: "Heterogeneous reaction is the dominant HONO source contributing nearly 60 % of HONO formation, followed by: : :)" (by the way check grammar..). Especially this sentence is definitely wrong, since the authors considered concentrations, but not formation rates in their calculations ("HONO source" means a rate of formation, see also below). Even only for R11 the authors used a gamma value of ca. 3×10^{-6} during daytime (which should be ca. 6×10^{-6} , see above), but only of 1×10^{-6} during night-time (which should be 10^{-7} - 10^{-8} for R8, see above). Thus, surface photolysis sources (R11+R12) should have a much higher contribution than shown here. The reason for the incorrect conclusion is that the authors calculated the contribution of the sources to the concentration of HONO in the model (see Figure 6), but did not compare their source strengths. Thus, the high night-time concentrations caused by slow sources and missing HONO sinks (photolysis), are directly compared with the low daytime values, which still exist against the very fast photolysis. In contrast to the night-time, a very strong source is necessary during daytime to maintain HONO levels of higher than 1 ppb (see Fig. 4). For example, in the dark/light experiments in George et al. (2005) and Stemmler et al. (2006) 1-2 orders of magnitude faster NO₂ conversion was observed during irradiation, which is in agreement with recent field studies. Thus, if the authors would compare the average source strengths of the different sources used in the model, a completely different picture would appear (the heterogeneous source contribution would significantly decrease, compared to the photochemical sources). This would even more change if the correct gamma values are used (see above). May be for health effects studies, the concentration is the right argument, however when atmospheric chemistry (OH, O₃-formation etc.) is studied, the formation rates should be used (see conclusion sentence).

Response:

Indeed, the way to qualify the relative contribution from different HONO formation pathway in this paper is by controlling the formation pathway (open/close flag) and by

calculating the difference of predicted HONO concentration for different simulation cases. Since the HONO prediction in CMAQ is the process of conservation of mass, the final HONO concentration value should be the balance between yield and lost. The dominate HONO sink is through photolysis during daytime. Hence, by direct comparing the concentration difference to quantify the HONO formation contribution is not proper. Fig. 6 results is misleading given the caption named "average contribution of different source to HONO formation". The pie chart discard the offset role of HONO photolysis to predicted concentration. The HONO formation strength should be the proper parameter to discuss the relative contribution of different source to HONO formation.

The most proper way to conduct such 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.

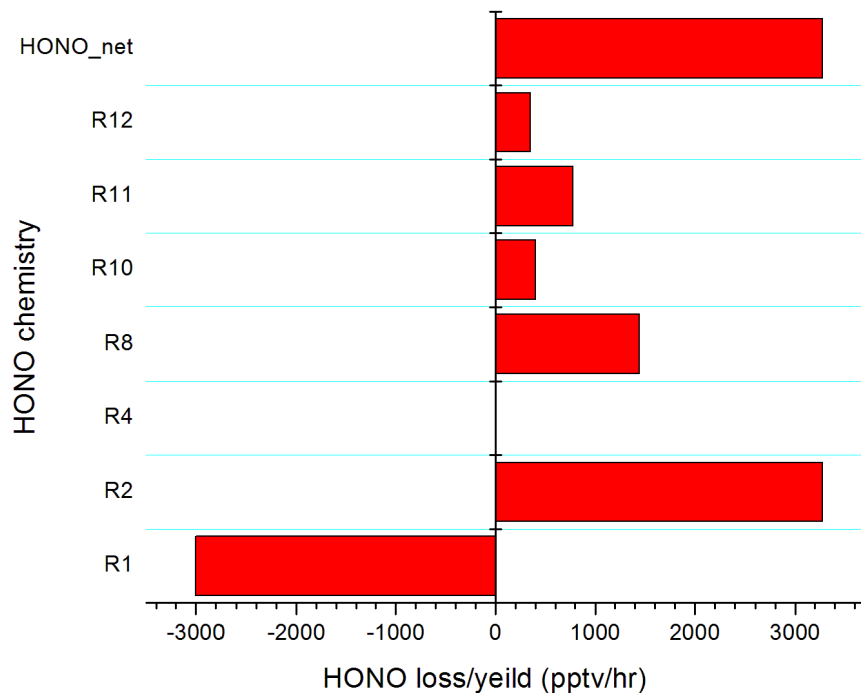


Fig A2. Daily mean HONO contribution budget for different reaction at Guangzhou site

3) Unrealistic model results:

While in Fig. 4 the author could clearly demonstrate a strong impact of the different sources compared to the base model for the HONO levels, there is absolutely no impact on the modelled O₃ levels. This is completely unclear. In their most realistic model (CB05+EM+HT+SP) the authors modelled for example for Guangzhou HONO daytime concentrations of ca. 1.5 ppb, which is ca. 1.4 ppb higher than using only gas phase reactions (CB05). Thus, a net OH source by HONO photolysis of $>5 \times 10^7 \text{ OH cm}^{-3} \text{ s}^{-1}$ is present in the atmosphere during daytime in the model calculations. This source will be one of the largest OH radical initiation sources and thus, certainly should have a strong impact on the modelled secondary products (ozone is a product of the OH initiated chemistry in the atmosphere ...). The daytime levels considered here are very similar to recent studies in Santiago de Chile (Elshorbany et al., Atmos. Environ., 2009, not the one cited here ...) and also during the CareBeijing - 2006 campaign (Lu et al., 2010). In these studies a strong HONO contribution to the ozone concentration (35 % in Elshorbany et al.)

and to PO₃ (ca. factor of two in Lu et al.) was observed. Thus, I expect any error in the author's calculations.

Response:

In Fig 4 at the single location Guangzhou and Xinken, the enhancement of ozone and PM_{2.5} is trivial during the observation window. However, 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. The 3D box provide more diffusivity and transportation of pollutant compared with simple box model, which may be the reason for the 'not significant enhancement of the secondary pollutant yield.

Moreover, as the referee pointed out, the model in this study seems to significantly underestimate OH level so that it can not provide sufficient oxidization to foster SO₂, NO₂ to sulfate and nitrate. One of the possible reason is the high uncertainty for emission files, especially for the reactive VOC species. 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 A3 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.

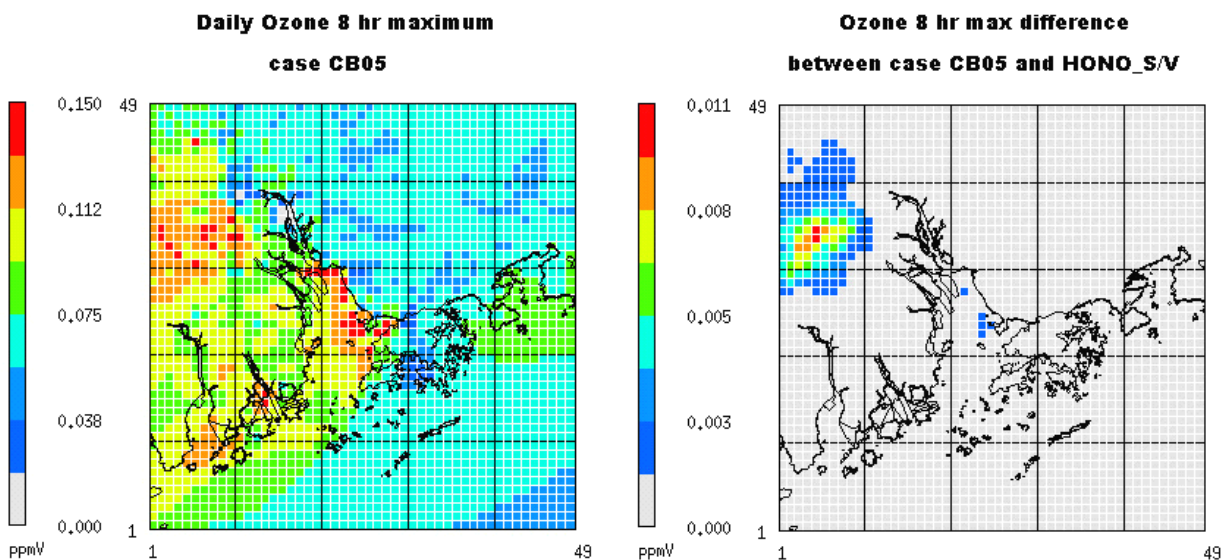


Fig A3. Spatial distribution of the 8 hr maximum ozone enhancement due to HONO chemistry during the entire simulation period.

In addition, one should highlight, that still when using all sources, the model results were significantly below the measurements, especially during daytime (see Fig. 4). Thus, using the more realistic higher gamma values for R11 on organic ground surfaces (see discussion in Stemmler et al., 2007 and comparison with the 2006 results), may lead to better model description of the measurements.

Response:

Please refer to the comparison between case 'referee recommendation' and case 'CB05', case 'CB05+EM+HT+SP'. The daytime predicted HONO value will increase 10% on the basis of case 'CB05+EM+HT+SP', however the model still underestimate HONO concentration by a factor of 2, which may suggest the room for parameter tuning and HONO formation mechanism study.

Specific Comments:

Page 15076, line 20: More recent results on the topic e.g. from the MILAGRO campaign, or from PRD, or from Santiago de Chile are missing here.

Response:

Add the citations in line 20 for MCMA-2006/MILAGRO campaign (Li et al., 2010), PRD-PRIED 2004 campaign (Zhang et al., 2008), Santiago de Chile study (Elshorbany et al., 2009), and Carebeijing-2006 Campaign (Lu et al., 2010). Update the corresponding citations in the reference list, add one reference:

Lu, K., Zhang, Y. , Su, H., Brauers, T., Chou, C.C., Hofzumahaus, A., Liu, S.C., Kita. K., Kondo, Y., Shao, M., Wahner, Wang, J., Wang, X., and Zhu, T.: Oxidant (O₃+NO₂) production processes and formation regimes in Beijing, J. Geophys. Res., 115(D07303), doi:10.1029/2009JD012714, 2010.

Page 15077, line 6: Mao et al., 2010 is missing in the reference list, and the 2006 paper does not fit here.

Response:

Add the missing reference for Mao et al. (2010):

Mao, J., Ren, X., Chen, S., Brune, W., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., Leuchner, M.: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmos. Environ., 44, 4107-4115, 2010.

Page 15077, line 16: There are at least three reviews on HONO (also Lammel and Cape, 1996).

Response:

Change the line 16-20 of Page 15077 change to :”There exist some review papers (e.g. Calvert et al. (1994), Lammel and Cape (1996), and Kleffmann (2007)) to summarize the current knowledge on HONO formation mechanisms. Normally, four groups of HONO formation pathways were indentified: direct emission, homogeneous reactions, heterogeneous reactions and surface photolysis reactions.”

Add one citation in the reference list:

Lammel, G. and Cape J.N.: Nitrous acid and nitrate in the atmosphere, Chem. Soc. Rev., 25, 361-369, doi:10.1039/CS9962500361, 1996.

Page 15078, line 4: Ackermann (a PhD thesis) and Kurtenbach (a paper, Atmos. Environ.) are about the same study. Thus, Kurtenbach et al. should be used here.

Response:

Delete the Ackermann 2000 citation here and replace with the AE paper by Kurtenbach et al., (2001). Update the corresponding reference list.

Page 15078, line 14: Whether the PSS daytime concentration of HONO is only several ppt (as mentioned) or several hundred ppt mainly depends on the daytime NO and OH levels. E.g. in Elshorbany et al., 2009, nearly a ppb was formed by R2 caused by the very high daytime NO levels. Thus it should be “in the range from a few ppt to several hundreds of ppt”.

Response:

Change the line 13-15 at Page 15078 to “...Reaction (R2) is only in the range from a few ppt to several hundreds of ppt over urban areas, which cannot explain the observed daytime high level.”

Page 15078, NO₂+H₂O: Another argument not to use R3 is that the rate coefficient of this reaction is most probably more than a factor of 15 lower than the number given in Li et al. (see Carr et al. and Crowley and Carl).

Response:

Add a sentence in line 19 of Page 15708 after “...in the current US atmosphere” as “Given the considerable controversy regarding the estimation of rate coefficient of this NO₂ chemistry (i.e. 15 times difference, Crowley and Carl, 1997, Carr et al., 2009 and Li et al. 2009), Reaction (R3) is not considered as a significant contribution to HONO formation in this study.”

Also add the corresponding citation in the reference list:

Carr, S., Dwayne, E., and Blitz, M.A.: Comment on “Atmospheric hydroxyl radical production from electronically excited NO₂ and H₂O”, Science, 324, 336, doi:10.1126/science.1166669, 2009.

Crowley, J.N. and Carl, S.: OH formation in the photoexcitation of NO₂ beyond the dissociation threshold in the presence of water vapor, J. Phys. Chem., 101, 4178-4184, 1997.

Li, S., Matthews, J., and Sinha, A.: Response to comment on “Atmospheric hydroxyl radical production from electronically excited NO₂ and H₂O”, Science, 324, 336c, doi:10.1126/science.1166877, 2009.

Page 15079, line 3, Cai, 2005: Better use original references and not a PhD thesis, which is not easily accessible.

Response:

Change the line 3 to “Reported rate constant of Reaction (R7) differ by two orders of magnitude and is quite uncertain (e.g. Graham and Tyler, 1972, Calvert et al., 1994).”

Delete the Cai, 2005 PhD thesis citation due to the not easily accessible suggestion as the referee. Add one citations in the reference list:

Graham, R.A. and Tyle, B.J.: Formation of nitrous acid in a gas phase stirred flow reactor, J. Chem. Soc. Farad. Trans., 1, 68, 683-688, 1972.

Page 15079, line 6: The reference of Aumont et al. (model ...) should not be used here but the review about lab studies on this reaction by Finlayson-Pitts et al., 2003.

Response:

Change the line 4-6 of Page 15079 to “the reaction rate k_{HONO} for Reaction (R8) is believed to be first order in NO₂ (Kleffmann et al., 1998; Svensson et al., 1987; Finlayson-Pitts et al., 2003).”

Page 15079, line 8: The field study by Stutz et al. cannot proof any humidity dependence (may give some hint) but only lab studies. Again the reference to Finlayson-Pitts et al. is recommended.

Response:

Follow the recommendation of referee cite the reference by Finlayson-Pitts et al. (2003) instead of Stutz et al. (2004). Delete the citation of Stutz et al. in the reference list.

Page 15079, line 9: Although this has been suggested also in other studies, vegetation surfaces were found to be a perfect sink of HONO (see Schimang et al., Atmos. Environ., 2006) and thus should be excluded as source here.

Response:

In this study, the total surface area available for HONO heterogeneous and surface photolysis formation pathway include aerosol and ground surface. The ground surface include vegetation surface, soil surface and building surface. All of them are consider as the contribution to HONO yelid instead of sink. This paramertization is follow the work of Cai (2005), Sarwar et al. (2008) and Gonçalves et al. (2010).

If treated vegetation surface as the HONO sink, the equation (2) in Page 15086 will become:

$$[S/V]_{\text{surface}} = [S/V]_{\text{aerosol}} + [S/V]_{\text{building}} + [S/V]_{\text{soil}}$$

The foresee heterogeneous HONO formation will decreased especially over the vegetation canopy.

Page 15081, lines 17-20: The statement is true for soot but not for R9 (see above).

Response:

Changed the format of reaction R9 into two parts: one is NO₂ + soot with the fast deactivation while the other one with NO₂+semivolatil VOC, which may has significant impact on the HONO heterogeneous reaction formation (Li et al., 2010).

Page 15082, lines 2-5 and see also equation (1) and page 15095, lines 10-14: While the approach of Aumont et al. (using deposition velocities of NO₂) is correct, the approach used here may be an overestimation of the reality. For high uptake coefficients equation (1) cannot be used since HONO formation will be limited by convective and diffusive transport (see resistance models to describe deposition). Equation (1) is valid for particles and even there only for gamma values $<10^{-3}$ but not to model uptake on ground surfaces. Only when gamma values are very small ($<10^{-6}$) and the turbulent mixing is high (e.g. for high wind speed during daytime conditions), the application of equation (1) for a lowest layer of 17 m height is warranted. The limit for using equation (1) depends on several parameters, which cannot be easily implemented into a 3D model and thus the use of deposition velocities calculated by the use of three resistances (turbulent, diffusive and reactive) is recommended (there are simple parameterizations with the wind speed available). The problem for most models is the simplified use of constant deposition velocities, which are typically too low for NO₂ in models (should be around 1 cm/s during daytime). This is the main reason why models using deposition velocities of NO₂ underestimate HONO formation in the atmosphere (see the given reference), but nevertheless this is recommended concept.

Response:

In stead of using simplified constant deposition velocities, the integral bi-directional flux surface exchange concept may be introduced to model HONO formation process near the ground.

Page 15082: A very recent study by Goncalves (ACPD) may be also added as reference for HONO model studies.

Response:

Add one paragraph after the discription of the work of Li et al. (2010) on the HONO simulation during MCMA-2006/MILAGO campaign (line 22) for the introduction on very recent study by Gonçaves et al. (2010):

"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 found in urban area HONO emission contribute 66-94% of HONO peak while NO₂ hydrolysis on building and vegetation surface contributes up to 30% of HONO peak. Noticeable change in PM_{2.5} and O₃ concentration are also predicted especially during the early morning when the higher OH release via HONO photolysis. However, their simulation period is too short (1 day) and the results is lack of evaluation by observations."

Also add the corresponding citation in reference list:

Gonçalves, M., Dabdub, D., Chang, W.L., Saiz, F., Jorba, O., and Baldasano, J. M.: The impact of different nitrous acid sources in the air quality levels of the Iberian Peninsula, *Atmos. Chem. Phys. Discuss.*, **10, 28183-28230, doi: 10.5194/acpd-10-28183-2010, 2010.**

Page 15083, top: The recent Science study by Hofzumahaus et al. about HONO measurements at a later PRD campaign (see also their supplementary material) is missing here and also later in the discussion.

Response:

Add the citation in Line 29 as "A nocturnal peak HONO mixing ration of over 8 ppb V was reported in PRIDE-PRD 2006 campaign (Qin et al., 2009, Hofzumahaus et al., 2009)." Since the topic sentence of this paragraph is "measurements in PRD region indicate the presence of elevated ambient HONO levels in urban as well as rural areas", the detail amplified tracer gas removal mechanism proposal is not described here. However, later in section 3.2 on the discussion of predicted daytime OH value, the OH measurement in this paper will be referred.

Also add the corresponding citation in reference list:

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T, Chang, C, Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner A., Zhang, Y.: Amplified trace gas removal in the troposphere, Science, 324, 1702-1704, 2009.

Page 15085, line 2, "known reactions": Also nitroaromatics photolysis is missing (see above).

Response:

Change line 1-4 of Page 15085 as "The CB05 gas-phase chemical mechanism in CMAQ model contains known homogeneous reactions involving HONO except the excited NO₂ chemistry and the photolysis of *ortho*-nitrophenols (Bejan et al. 2006). Reaction R3 is not included in this study since Sarwar et al. (2010) reported that it contributes only a small amount to daytime HONO." Also notice that the description of nitroaromatic photolysis is updated at the Section 1.3 HONO heterogeneous reactions review.

Page 15085, line 24 and also Figure 2: The unit is wrong. Should be mol s⁻¹ area⁻¹. Most probably this is the emission for each grid cell (4.5x4.5 km), but has to be defined. In addition, "molec." is the abbreviation for molecules, however should be moles with the unit [mol].

Response:

Change line 24 of Page 15085 as "Multiple hotspots with average daily emission rate greater than 0.5 mol s⁻¹ area⁻¹ (area in this study is 4.5x4.5km) are found at GZ city ...".

The updated Fig. 2 with correct unit is shown below:

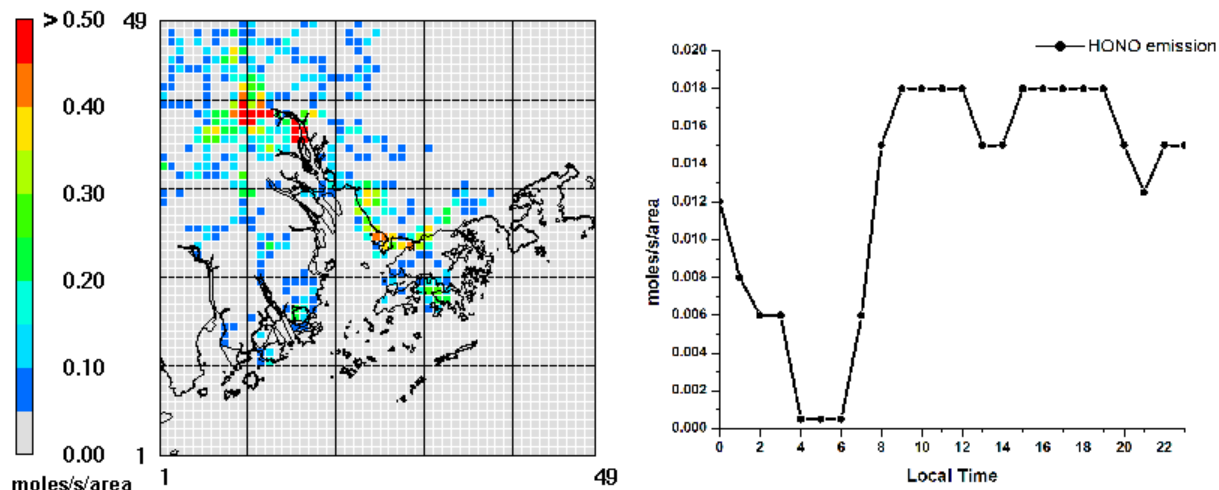


Fig 2. (a) Average daily HONO emission rate (moles s⁻¹ area⁻¹) distribution pattern and (b) diurnal profile of HONO emission in the PRD urban area.

Page 15087, line 7: Reaction R9 is not mentioned to be used in the model (see Tab. 1). Thus, should be R8 here? In addition, not only this reaction should take place on aerosols in all layers and on the ground only in the lowest layer, but all heterogeneous reactions, except the soot part of R9, for which deactivation will take place before soot deposition on the ground (for parameterization of this reaction, see above). Thus, also R8, R11, R12 should take place on particles in all layers and on the ground in the lowest layer. See e.g. R11 on page 15087, line 22 and compare to Stemmler et al.,2007 (were aerosol experiments ...).

Response:

In line 7 of Page 15087, it should be reaction R8. It is a typo, already corrected. About the available area (S/V value) for heterogeneous and photolysis HONO formation considered in CMAQ in this study, reaction R8 is taken aerosols surface area in all layer and the ground only in the lowest layer, however, reaction R10, R11 and R12 is only considered formation at the lowest model layer follow Sarwar et al. (2008). However, unless during heavily polluted days, the S/V ratio for aerosol is much smaller than corresponding S/V values for available surface on the ground. Hence, even if adding the surface area by aerosol in surface photolysis reaction R11 and R12, the impact to HONO yeild from

heterogeneous reaction is relatively small. Please also see the response to "General comment 1) used HONO chemistry".

Page 15089, line 19: The difference between model and measurements for sulphate looks more than +30 % in Fig. 3. Thus, not only PM but also sulphate and nitrate are underestimated ca. by a factor of two. It seems that the model generates not enough OH radicals for oxidation of NO₂ and SO₂, see also below (modelled OH radical levels).

Response:

Actually from the Table 2 of Page 15106, in terms of the mean value, the mean normalized bias (NMB) for PM_{2.5}, aerosol sulfate and aerosol nitrate simulation is around -40%, -20% and +45%, which means the PM_{2.5} and sulfate mass concentration is underestimated while the nitrate is underestimated. The authors agreed the statement by referee that the model generate insufficient OH radicals to oxidate. Besides the defect of complex secondary pollutant formation mechanism parameterization in CMAQ, as a emission-based model, the uncertainty in emission inventory, especially uncertainty the local VOC speciation profile may influence the accuracy of emission, hence the simulated aerosol product. Also see the sensitive simulation reasons by increasing the active VOC species emission in the response for "General comment 3) unrealistic model results".

Page 15089, line 23 and Fig. 1: Is PM_{2.5} or PM₁₀ measured? In the text and Fig. it is PM_{2.5}, in the figure caption PM₁₀?

Response:

It is PM_{2.5} measurement. The hourly PM_{2.5} mass concentration, aerosol sulfate, aerosol nitrate, as well as SO₂, NO_x, and O₃ mixing ratio are provided by Hong Kong Environmental Protection Department (HKEPD) and are used for the routine model verification in this paper. The PM₁₀ in Fig. 1 caption is a typo, it already corrected.

Page 15090, lines 10-11 and line 22: The argument is wrong here. The model under(...)estimates sulphate and nitrate. Thus, the model needs a higher(...) uptake of N_2O_5 to get more closer to the measurements and is not overestimating but underestimating.

Response:

From the Table 2 of Page 15106 for the model performance of gaseous pollutant and particulate matter simulation over October 2004, aerosol sulfate (ANO_3) in terms of mean is overestimated but not underestimated. The mean normlized bias (MNB) at CW site is 87.5% while the MNB at YL site is 19.1% (the detail time serise plot for ANO_3 is shown in Fig. 3 (f), the general impression is underestimation, but notice the high predicted peaks during Oct 9 ~ Oct. 15 and Oct. 26 ~ Oct. 29, the simulation mean is slightly higher than observation mean). Hence, for the base case CB05, the model UNDERESTIMATE sulfate but OVERESTIMATE nitrate. "The poor nitrate perfomance" conclusion is mainly derived from the poor correlation between simulation and observation (i.e. Low index of agreement value). In line 10-25 of Page 15090, the authors suggested this nitrate overestimation and poor performance may due to "the high uptake coefficient for heterogeneous hydrolysis of N_2O_5 , rate constant for homogeneous hydrolysis of N_2O_5 as well as the uncertainty in ammonia emission".

Page 15091, first paragraph: It would be nice to see the agreement between models and measurements not only for the average data (Fig. 4) but also concentration-time profiles, e.g. like in Fig. 3 or one campaign averaged day. Such a plot helps more to identify problems/agreements of the model, see also Vogel et al. (2003), for which the daily averaged values would have agreed well, but not the decay of HONO in the morning, from which a daytime source was identified.

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 A4 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 $\pm 20\% \sim \pm 40\%$. 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 A5 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.

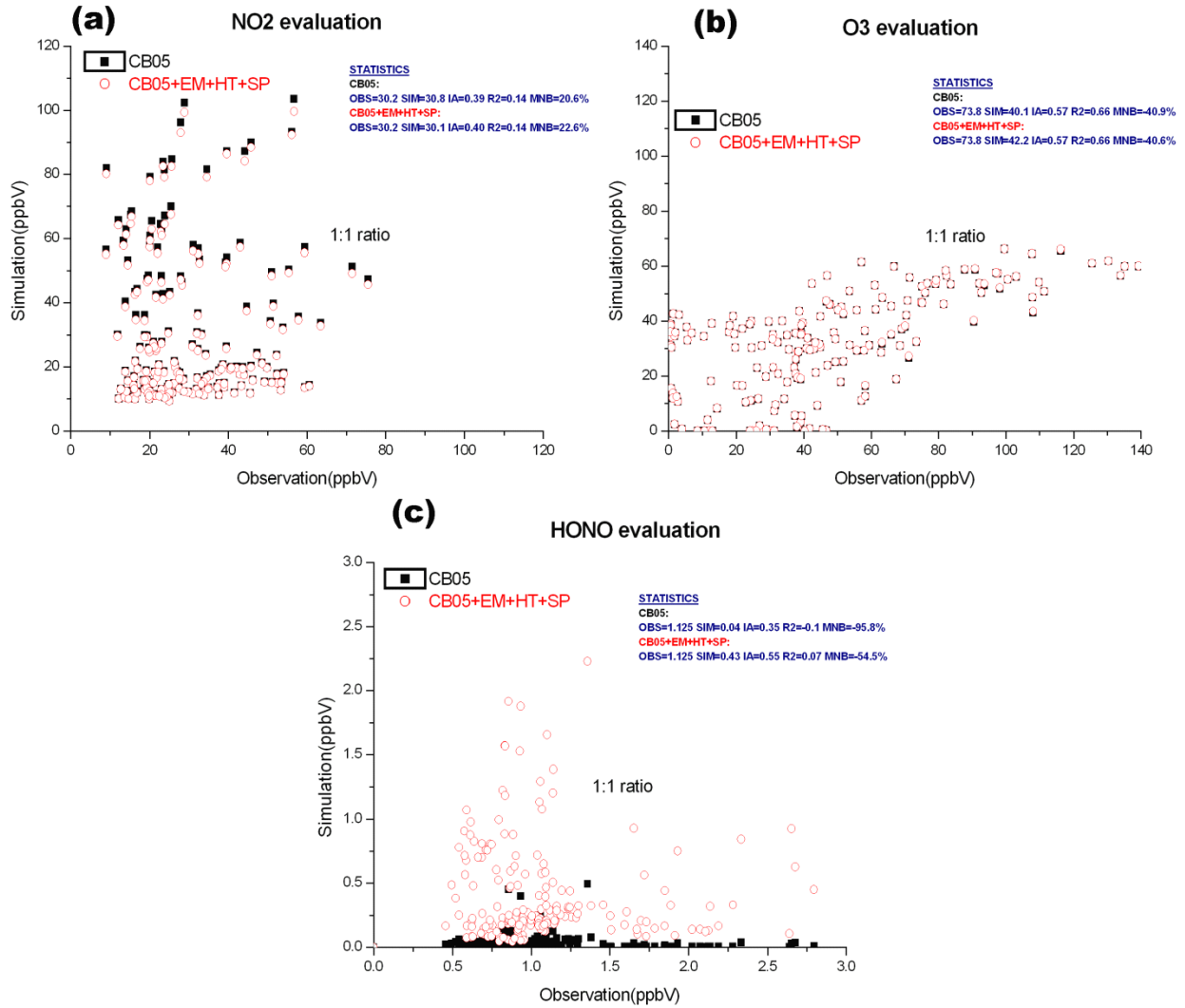


Figure A4. Model validation after incorporation of HONO chemistry at Xinken (XK) station for (a) NO₂, (b) O₃ and (c) HONO simulation

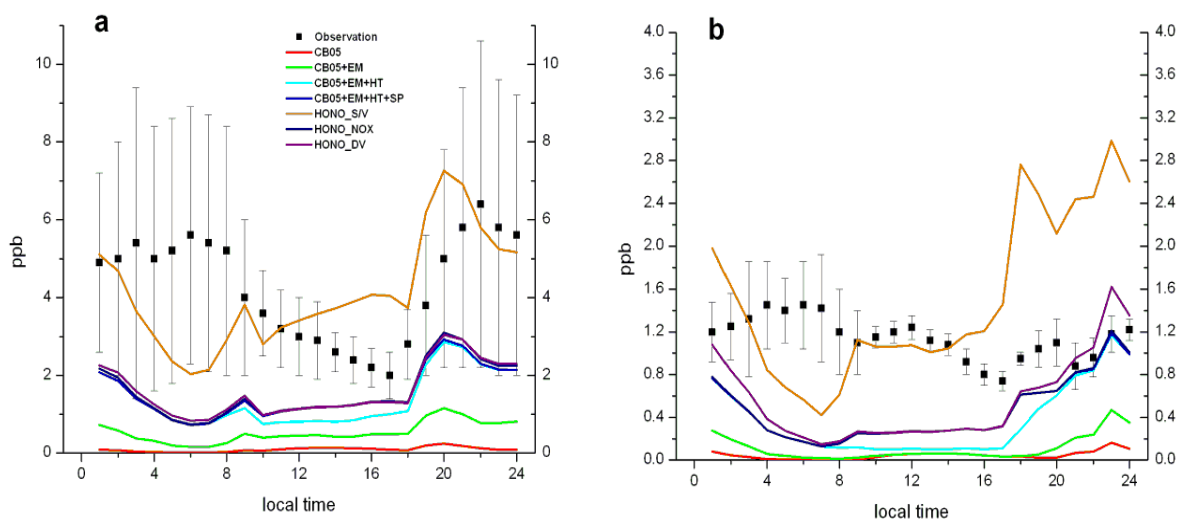


Figure A5. Diurnal pattern of simulated HONO at (a) Guangzhou and (b) Xinken with difference simulation cases

Page 15092, first paragraph: The modelled OH concentrations ($1.5\text{-}2.5 \times 10^6 \text{ cm}^{-3}$) are at least a factor of two lower than those directly measured at PRD in Hofzumahaus et al. (ca. $5 \times 10^6 \text{ cm}^{-3}$). This may be one reason for the too low secondary products (sulphate, nitrate, PM) and may be at least in part caused by the still underestimated HONO (compare Fig. 4). However, since the implementation of the HONO source in the model caused an increase of OH by ca. 20 %, it is again not clear why ozone did not change in Fig 4.

Response:

Base on the suggestion of referee, the following sentence is added at the end of paragraph.

"OH concentration were measured during PRD-PRIDE 2006 campaign at the upper wind of Guangzhou city, the average daytime OH concentration is above $5 \times 10^6 \text{ molec cm}^{-3}$, which is a factor of two higher than the simulated OH value in GZ."

In Fig. 4, the increase HONO/OH source do boost the formation ozone around 2-9 ppb V (see Table 3, Fig. 9 (a-2)). However, the increase at Guangzhou and Xinken site is negligible as shown in Fig. 4. Please also see the response below on "Contradiction of results for Fig. 4 and Fig. 9 (a-2)" and the response on "General comment 3) unrealistic model results".

Page 15092, second and third paragraph: The numbers of the modelled HONO concentrations (2 ppb, <50 ppt and 800 ppt) are significantly different compared to those shown in Fig. 4 (ca. 1.3 ppb, <50 ppt, <100 ppt). Any reason?

Response:

The numbers of the modelled HONO concentrations are the estimated value directly read from the Fig. 5 of Page 15112. Moreover, the Fig 5. is not the average spatial distribution of simulated HONO concentration filed over the 10 days simulation window, it is just the one day average on October 28, 2004 with the maximum ozone enhancement (see Fig. 9 (a-2) of Page 15116). Notice that the numbers shown in Fig. 4 at Guangzhou and Xinken site is the 10 day average value for daytime and nighttime, the "significantly different numbers" can be explain. It can be seen that, at that day, the daytime average HONO concentration over Guangzhou area for simulation case CB05+EM+HT+SP is around 3 ppb V while the predicted nighttime value is about 5 ppb V., which is singficant larger the 10 days average daytime HONO concentration at Guangzhou (around 1.3 ppb V).

In case of confusion, one sentence is added in line 11 after "... are presented in Fig. 5 separately":

The HONO feilds for different cases in Fig. 5 are the daily average of October 28 with the maximum ozone enhancement during the simulation period.

Page 15094, lines 17-19: While the surface reactivity (uptake coefficient) of NO₂ may be lower than that of HONO the overall deposition velocity (convective, molecular and surface residence) to be used in a model will not differ very much in the 17 m layer and should be mainly limited by the transport to the surface (both have gamma values higher than 10⁻⁶ on the ground. Thus, the deposition velocity of NO₂ is most probably too low in the model (see above, difference in the two model approaches).

Response:

The low deposition velocity of NO₂ may cause the surface HONO underestimation. The difference with simulation case 'CB05+EM+HT+SP' and 'HONO_DV' by replacing the deposition velocity of HONO to NO₂ still can not solve the HONO underestimation problem (see Fig. 8). Indeed as the referees pointed out, the small layer height for the first layer may will smooth the difference for the uptake coefficient between NO₂ and HONO.

Page 15096, line 2: Caused by the VOC limited conditions, additional HONO/OH sources should lead to increasing O₃ levels, which are observed here (up to 6 ppb). However, the results of Fig. 9a2 are in contradiction with those shown in Fig. 4? In addition, caused by the significant OH initiation by the additional HONO sources ($5 \times 10^7 \text{ cm}^{-3} \text{ s}^{-1}$, see above), I would expect much stronger increase.

Response:

Fig. 4 (b) and Fig. 9 (a-2) both display the ozone enhancement by considering the HONO formation source by direct emission, heterogeneous reaction and surface photolysis, but from different angle. In Fig. 4 (b), predicted ozone concentration time-series at Guangzhou site and Xinken Site are pin-pointed and averaged during the whole simulation window (10 days) with daytime and nighttime separately. It is a point-by-point comparison with mean value. Differently, in Fig. 9 (a-2), the spatial distribution of maximum ozone enhancement at single day (i.e. On 28 October 2004 associate with the northeasterly moderate synoptic wind and relatively steady atmosphere) is presented. It is a snapshot plot. The purpose of Fig. 4 (b) is to compared the AVERAGE impact of HONO chemistry on ozone enhancement ONLY at Guangzhou and Xinken sites, where the observation data available for comparison. While the purpose of Fig. 9 (a-2) is to give more 'big picture' on MAXIMUM ozone enhancement by considering HONO chemistry. Hence, there is no contradiction for the results shown in Fig. 4 (b) and Fig. 9 (a-2). Indeed, caused by the VOC limited conditions (Zhang et al., 2008), additional HONO/OH sources will lead to the

increasing of O₃ levels. However, the maximum impact location is neither at the Guangzhou nor Xinken sites shown in Fig. 4 (b), but normally on the downwind of Guangzhou site. Even for the single point location Guangzhou and Xinken, the average simulated ozone by considering HONO chemistry do increase, but in a very insignificant portion. That is why in line 15-19 of Page 15091, the authors summarized the model performance by "... The HONO chemistry does not have obvious improvement on the NO₂ and O₃ model performance at XK and GZ sites during the campaign. In other places over PRD region, the HONO chemistry does have potential to enhance the simulated O₃ peak value ...". In addition, in Table 3 of Page 15107, the authors also highlighted the importance of morning O₃ enhancement by additional HONO/OH sources compared with daily mean 8 hr maximum O₃: the former enhancement value is between 3-9 ppbV while the latter value is 3-7 ppbV, which again confirmed the important of HONO source to providing OH radical for ozone production especially in the morning.

In terms of expecting "stronger ozone increase", please refer to the response for the "General comment 3) Unrealistic model results".

Page 15108, figure 1: The sites mentioned in Fig. 1 and in the caption have a different spelling compared to the text: Guang Zhou vs. Guangzhou; Xin Ken vs. Xinken; etc.

Response:

All the sites name in mainland Chinese appeared in this paper are unified in the same format by "Guangzhou" and "Xinken". The sites name in Hong Kong appeared in this paper are unified the standard spelling by "Yuen Long", "Tuse Wan", and "Tap Mum". See the updated Figure 1 here.

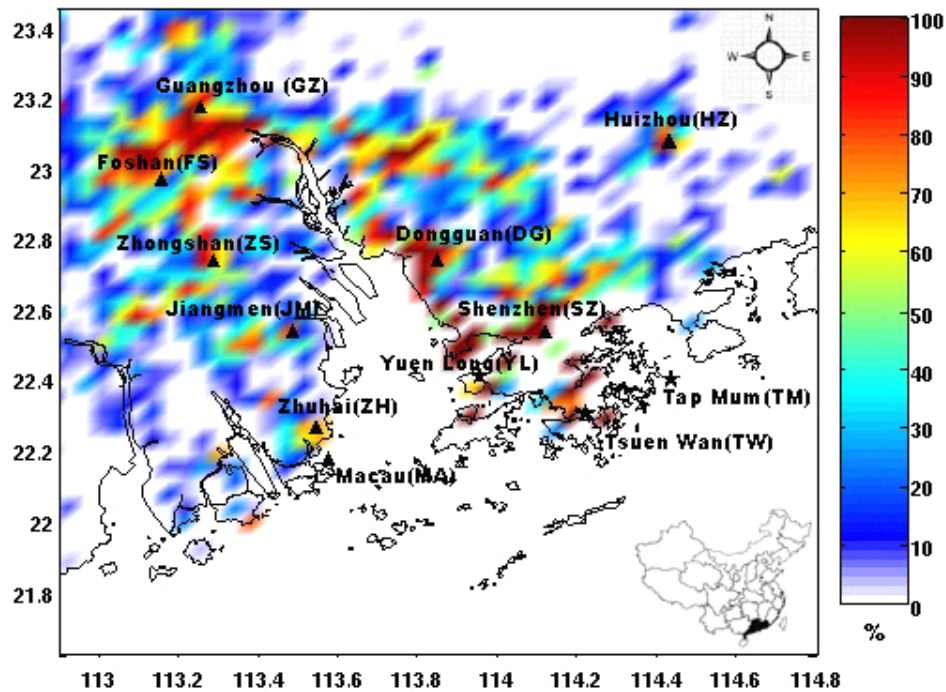


Fig 1. The geographic coverage of CMAQ model overlapped with urban density fraction (scaled from 0% to 100%) over Pearl River Delta region, China. ▲ represents the locations of urban cities over this region, in which the star sites Yuen Long (YL), Tsuen Wan (TW) and Tap Mum (TM) are there ambient air quality monitoring stations in Hong Kong with hourly continuous observation data for criteria pollutants.

Page 15110, Fig. 3: Better use two different coloured lines for model and measurements to better follow the diurnal variations (the symbols look like “noise”, but which is a nice diurnal variation). In addition, in the caption it should be “blue symbols” (not blue lines) and “red lines” (not green ...).

Response:

Some period of observation data during Oct 2004 is missing, so that if the line instead scatter dot is used to plot the monthly observation variation, some sudden jump will appear, which makes the figure looks weird.

The caption of the figure is change to “Fig. 3. Comparison of modeled and observed (a) NO_x, (b) SO₂, (c) O₃, (d) PM₁₀, (e) aerosol sulfate, and (f) aerosol nitrate concentration at Yuen Long (YL) station in October 2004. (The blue dots are the EPD observation, while the red lines are the CMAQ model results) ”

Page 15111, Fig. 4: The hatching of the bars for “CB05+EM” for Guangzhou is different compared to the legend and to that for Xinken.

Response:

Re-plotted the Fig. 4 to make sure the hatching of bars for different simulation cases at Xinken and Guangzhou site are the same. See the new Fig. 4 below.

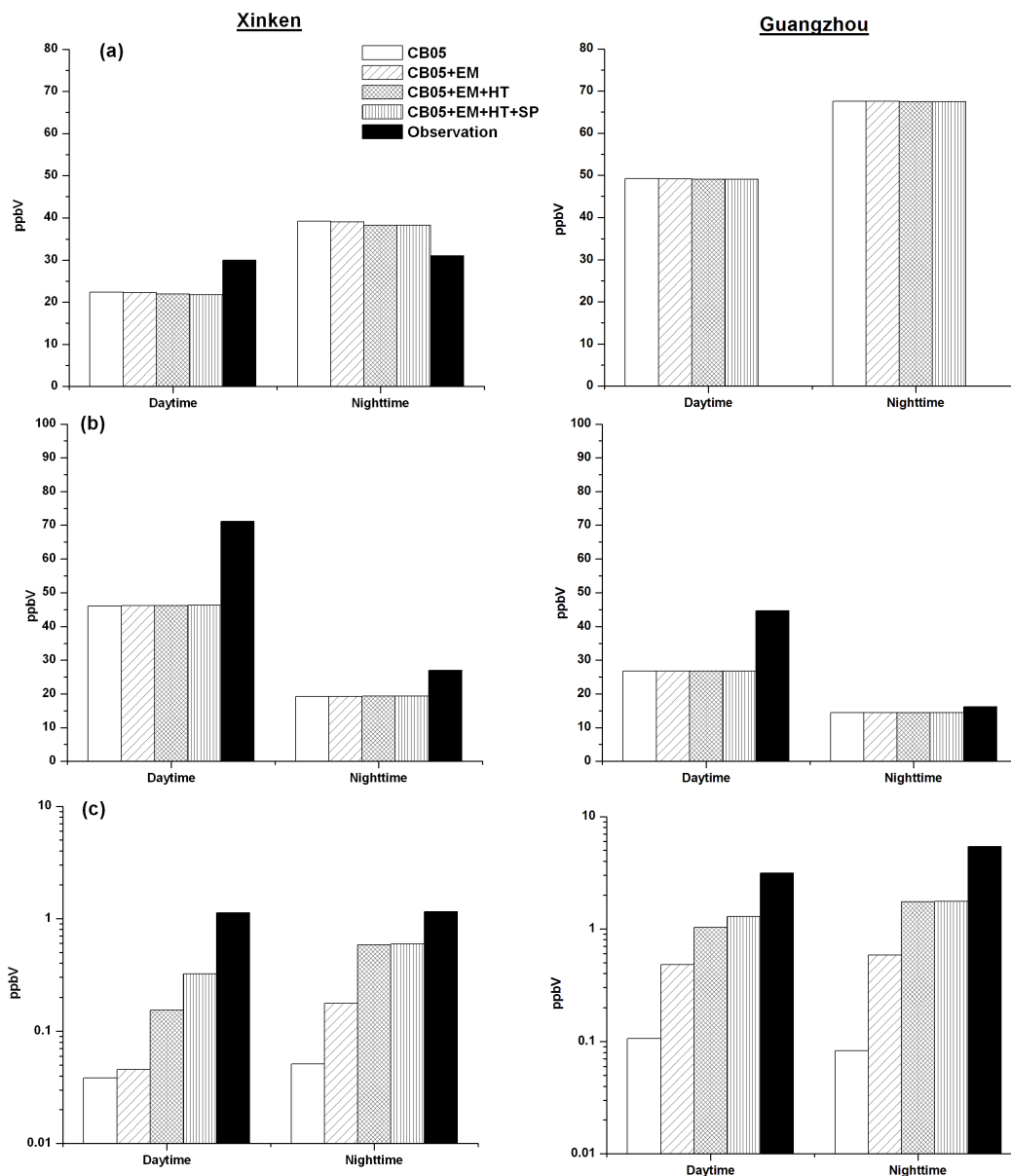


Fig. 4. Model validations after incorporation of different HONO chemistry at Xinken (XK) and Guangzhou (GZ) site for (a) NO₂, (b) O₃ and (c) HONO simulation.

Page 15112, Fig. 5: The quality of the figures should be improved. Even when zoomed in, the names in the figures (e.g. Guang Zhou) are nearly not visible.

Response:

Re-plotted the Fig. 5, especially to make sure the names in the figures is visible. Unified the name spelling for mainland China observation site, i.e. Guangzhou and Xinken. See the new Fig. 5 below.

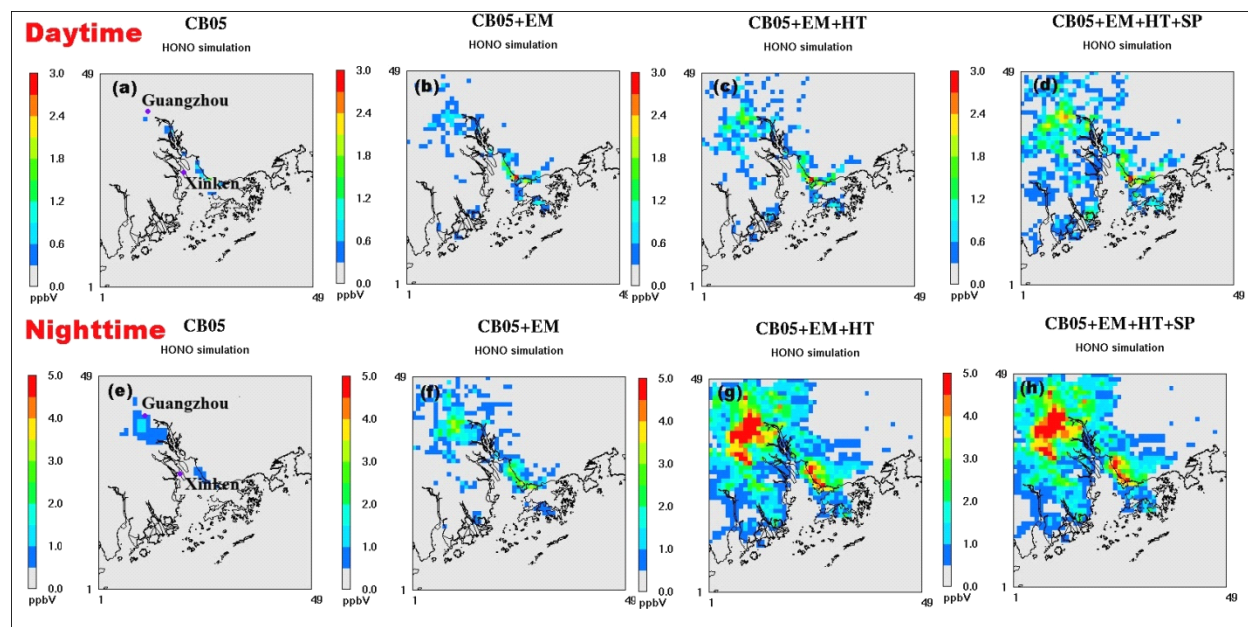


Fig. 5. Spatial distribution of simulated HONO through homogeneous reactions, direct emission, heterogeneous reaction, and surface photolysis formation pathway at daytime (a-d) and nighttime (e-h).

Page 15114, Fig. 7: The diurnal variation of the contribution of HONO emissions in Xinken is unclear. Are there zero HONO emissions during daytime and no rush hour peak in the model?

Response:

Direct HONO emission over PRD region is estimated from on-road and off-road vehicle sources as a fraction of NO_x vehicle emission, hence the emission rate of HONO at certain location is proportional with the vehicle miles traveled amount. Xinken is chosen as a rural site (also see Fig.1 in Page 15108, the urban density fraction is nearly 0% and Fig. 5 in Page 15112 for the location of Xinken) by comparison with the condition in urban site Guangzhou. From Fig 2. (a) in Page 15109, it can be also demonstrate that the average daily HONO emission rate at Xinken site is trivial compared with the Guangzhou site

(noticed that the Fig 2. (b) just give the 'typical' HONO emission diurnal profile, which may exclude the condition in Xinken). Hence, no rush hour peak for HONO emission is expected around Xinken site and the contribution of HONO emission to predicted HONO is negligible in Xinken during daytime afternoon (i.e. 12:00-16:00 LST). Please also notice that during the daytime, the contribution of surface photolysis pathway to predicted HONO concentration is dominate with the weighting around 55%~67%.

Page 15116, Fig. 9: In the captions for (e) it should be “aerosol ammonia” and not “daily mean organic matter”, see Figure. In addition, explanation for figures a-1 and b-1 are missing.

Response:

The caption of Fig. 9 is changed to “Spatial distribution of the maximum enhancement due to HONO chemistry during the entire simulation period for (a)* daily 8h maximum ozone, (b)* daily mean PM_{2.5}, (c) daily sulfate, (d) daily mean nitrate, (e) daily mean aerosol ammonia, and (f) daily mean SOA.

***(a-1) and (b-1) is the spatial distribution of base case simulation *CB05* while (a-2) and (b-2) is the spatial distribution of difference between simulation case *HONO_SV* and *CB05* (see Table 1).”**

Some Typos (but not carefully checked):

Page 15077, line 17 and Page 15078, line 9, page 15079, line 3: Should be “Kleffmann”

Response:

Changed the wrong spelling of “Kelfmann” to “Kleffmann”. Thanks for the correction.

Page 15081, line12: Should be “Ammann”

Response:

Changed. Thanks for the correction.

References:

Acker et al.: Möller, Plass-Dülmer,

Alicke et al. 2002: Impact of Nitrous Acid Photolysis...

Alicke et al. 2003: Pätz, H.-W., Schäfer

Ammann et al.: Rössler, Gäggler, : : :

Please check all reference again (I stopped here...).

Response:

Changed. The authors will go through all the name spelling of the citation in this paper and make sure the all of the European name appeared in references will follow the original publication format. Thanks for the correction.