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Interactive comment on "Impact of nitrous acid chemistry on air quality modeling results over the Pearl River Delta region" *by* R. Zhang et al.

Anonymous Referee #1

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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 3 D 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/NOx 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

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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.

R5 is also an extremely slow second order reaction (<10-21 cmˆ3 sˆ-1), which needs not to be taken into consideration, besides deposition and photolytic losses.

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.

R8 and R9 are also not properly used here. Whereas gamma values between 10ˆ-7 - 10ˆ-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 10ˆ-6 (see studies by Gutzwiller et al., Arens et al., Ammann et al,. . .). However, later the higher value of 10ˆ-6 is used incorrectly for reaction R8. In addition, R9 is used here for two different reactions a) NO2+soot and b) NO2+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 NO2 with semivolatile VOCs. I suggest here to use humidity dependent gamma values (10ˆ-7 - 10ˆ-8) for R8 (see Finlayson-Pitts) and a gamma value of 10ˆ-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

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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...).

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 gammas values for heterogeneous HONO formation of <10^-10 were published (Kleffmann et al., 2004).

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.

For R11 a parameterisation (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...).

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 parameterisation (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.

And finally, in the sensitivity runs the conversion of NO2 on semivotatile hydrocarbons studied for diesel engine emissions by Gutzwiller et al. is used. For this run an additional fraction of 2.3 % HONO/NOx is used in the model. Although the average

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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 NOx levels near 2 ppm (40 ppb HONO / 0.023 emission ratio), the main NOx component will be NO (something around 90 %). But NO is not reacting, see Gutzwillers study. Thus, only the NO2 should be used for this reaction, see above (gamma ca. 10ˆ-6 derived in several lab studies).

2) Presentation of the results

Form 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. 3x10ˆ-6 during daytime (which should be ca. 6x10ˆ-6, see above), but only of 1x10ˆ-6 during night-time (which should be 10ˆ-7 - 10ˆ-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).

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 $>5 \times 10^7$ OH cm^{-3} 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 at 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.

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.

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.

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

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

Page 15078, line 14: Whether the PSS daytime concentration of HONO is only several ppts (as mentioned) or several hundred ppts 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".

Page 15078, NO2E+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).

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

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.

Page 15079, line 8: The field study by Stutz et al. can not proof any humidity depen-

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dence (may give some hint) but only lab studies. Again the reference to Finlayson-Pitts et al. is recommended.

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.

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

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 <10ˆ-3 but not to model uptake on ground surfaces. Only when gamma values are very small (<10ˆ-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 easy 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 paramerizations 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.

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

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

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missing here and also later in the discussion.

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

Page 15085, line 24 and also Figure 2: The unit is wrong. Should be mol sˆ-1 areaˆ-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].

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 please 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...).

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).

Page 15089, line 23 and Fig. 1: Is PM2.5 or PM10 measured? In the text and Fig. it is PM2.5, in the figure caption PM10?

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 N2O5 to get more closer to the measurements and is not overestimating but underestimating.

Page 15091, first paragraph: It would be nice to see the agreement between model

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.

Page 15092, first paragraph: The modelled OH concentrations (1.5-2.5x10ˆ6 cmˆ-3) are at least a factor of two lower than those directly measured at PRD in Hofzumahaus et al. (ca. 5x10ˆ6 cmˆ-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.

Page 15092, second and third paragraph: The numbers of the modelled HONO concentrations (2 ppb, <500 ppt and 800 ppt) are significantly different compared to those shown in Fig. 4 (ca. 1.3 ppb, <50 ppt, <100 ppt). Any reason?

Page 15094, lines 13-15: 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 10ˆ-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).

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 (5x10ˆ7 cmˆ-3 sˆ-1, see above), I would expect much stronger increase.

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.

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. . .).

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.

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.

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?

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.

Some Typos (but not carefully checked):

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

Page 15081, line12: Should be "Ammann"

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...).

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 15075, 2011.

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