Reply to Anonymous Referee #1

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following their suggestions as is described below.

(1) The interaction of NO_2 with soot producing HONO has been recently revisited, finally showing that it is catalytic (see Monge et al, PNAS, 2010). How would these recent findings alter the outcome of this modeling study? Would the HONO impact still increase?

Monge et al. (2010) reported a NO_2 reactive uptake coefficient of 2×10^{-6} on soot particles if their experimental results are extrapolated to the solar irradiance in the 300—420 nm range. We used a larger daytime uptake coefficient of 5×10^{-6} on aerosol surfaces to include the catalytic effect of soot particles. Since the contribution to the HONO formation due to the NO_2 heterogeneous reaction on aerosol surfaces is insignificant, the recent finding by Monge et al. (2010) does not alter the outcome of this modeling study. We have included the reference Monge et al. (2010) in Section 2.2: "*We use a low value of* $r_a = 1\times10^{-6}$ *during the nighttime (Aumont et al., 2003) and increase it to* 5×10^{-6} *during the daytime with the assumption that aerosols are mixed or covered with organic compounds, humid acids, soot or dust, which significantly enhance the HONO formation when sunlight is available (George, 2005; Stemmler et al., 2007; Monge et al., 2010; Ndour et al., 2008).*"

(2) Kleffmann and coworkers also showed that the photochemistry of some gaseous aromatic compounds do produce HONO. This is not discussed here, why? Maybe you could justify slightly more the HONO sources you selected. Would this gas phase photochemistry be the artificial photolytic HONO source that had to be introduced to improve the HONO simulations during daytime?

We have conducted a sensitivity study to estimate the upper limit of the HONO production from the photolysis of different *ortho*-nitrophenols. As such, a paragraph is added in Section 1: "*Recently, gas-phase production of HONO has been observed during the photolysis of different ortho-nitrophenols (Bejan et al., 2006; Kleffmann, 2007), with a noontime HONO production of 100 pptv* h^{-1} *in the urban regions. In addition, the gas-phase photolysis of methyl-substituted nitroaromatics is also prosposed to produce HONO (Kleffmann, 2007).*" And the sensitivity results are discussed in Section 3.1: "*Additionally, in the HONO parameterization, we do not include the HONO production from the photolysis of different ortho-nitrophenols (Bejan et al., 2006; Kleffmann, 2007), because all nitrophenols are represented by one lumped species (NPHE) in the SAPRC 99 mechanism and the absorption cross section of ortho-nitrophenols is not available yet. In order to evaluate the possible HONO contribution from the photolysis of different ortho-nitrophenols, we have conducted a sensitivity study in the E-case, assuming that all nitrophenols are photolyzed to form HONO and the photolysis frequency is interpolated from* $J[NO_2]$ *as suggested by Bejan et al. (2006). The study provides an upper limit of the HONO production from the photolysis of different ortho-nitrophenols. The enhancement of HONO concentrations due to the photolysis of nitrophenols is less than 3 ppt on average during daytime, which probably due to the low level of predicted nitrophenols* *(less than 0.3 ppb) in the simulation. Therefore, the photolysis of ortho-nitrophenols is less likely a significant HONO source in the Mexico City.*"

(3) The authors mention the study of Ndour et al (2008) which is related to dust chemistry. Does this mean that the impact of dust has been considered here? Finally, going one step further, building and roads are covered of dust – would the interaction between NO_2 and this road- or building-dust be an additional HONO source?

Yes, we have considered the dust impact on the HONO formation on aerosol and ground surfaces by using a large uptake coefficient of $r_a = 5\times10^{-6}$ in Section 2.2: "*We use a low value of $r_a = 1\times10^{-6}$ at the nighttime (Aumont et al., 2003) and increase it to 5×10^{-6} at the daytime with the assumption that aerosols are mixed or covered with organic compounds, humid acids, soot or dust, which significantly enhance the HONO formation when the sunlight is available (George, 2005; Stemmler et al., 2007; Monge et al., 2010; Ndour et al., 2008).*", and "*Stemmler et al. (2006) showed that NO_2 is effectively reduced to HONO on light activated surfaces containing humic acids, soils or selected sythetic aromatic compounds. The dust and soot particles deposited on the ground surface also enhance the HONO production when the sunlight is available (Ndour et al., 2008; Monge et al., 2010).*"

(4) Finally, I'm slightly confused about the distinction made of the four additional sources. In fact, the semivolatiles studied by Gutzwiller et al. were derived from soot particles. Therefore, how does this differs from HONO being produced from soot directly?

We have added discussions about the HONO source from the NO_2 reaction with semivolatitle organics in Section 2.2: "*It is worthy to note that the fraction suggested by Gutzwiller et al. (2002) was obtained in diesel exhaust. It might be more appropriate to use the value of 244 mg of secondary HONO formation per kg of diesel fuel burnt as suggested by Gutzwiller et al. (2002). However, in the experiment of Gutzwiller et al. (2002), the semivolatile organics in diesel exhaust react with NO_2 on time scales of hours, much longer than the time scale of the NO_2 to HONO conversion on freshly soot particles, which is in the order of one minute (Kalberer et al., 1999). Therefore, using the fraction of NO_x or diesel fuel burnt to calculate the HONO formation is a highly parameterized method based on the experiment of Gutzwiller et al. (2002). In Mexico City, diesel vehicles contribute almost all the organic aerosol emissions (Zavala et al., 2009) and very high levels of organic aerosols have been observed (Aiken et al., 2009), indicating a large amount of semivolatile organics are emitted from diesel vehicles, which could participate in the conversion of NO_2 from other sources, such as gasoline engines and biomass burning. Considering the emission contributions from diesel engines and the variation in the fraction of NO_2 in NO_x emissions in Mexico City, the fraction of 0.023 used in the study is likely an upper limit for the HONO formation from NO_2 heterogeneous reaction with semivolatile organics.*"

(5) Also light enhancement seems to apply both to soot (see Monge et al, PNAS, 2010) and to the semivolatils (George et al., 2005). As the latter is one of the major sources, would a light enhancement be significant here?

Please refer to (1). Although we have used a large reactive uptake coefficient of 5×10^{-6} during the daytime to consider the light enhancement effect on HONO formation, the HONO production on aerosol surfaces is still insignificant.

(6) The authors should point out which S/V values (aerosol surface) they are using in their simulations. As this is a key point for the importance of heterogeneous chemistry.

We have clarified in Section 3.1: "The simulated maximum aerosol surface to volume ratio (*S/V*) exceeds 1.0×10^{-3} m^{-1}, due to the heavy pollution in Mexico City."

(7) How are these findings limited to Mexico City? Can these findings be transposed to moderately polluted locations? Would the author state that simulating urban quality (in general) would require implementing these HONO sources in all air quality models? Is there an NOx concentration threshold which activates the importance of these HONO sources?

We have added discussions in Section 3.1: "*As the most important HONO source in the surface level, the* NO_2 *reaction with the semivolatile organics is highly parameterized in the simulations, using a fraction of 0.023 of the* NO_x *emitted to calculate the HONO formation. Based on the experiment of Gutzwiller et al. (2002), the semivolatile organics in diesel exhaust react with* NO_2 *within hours in the condition of sufficient water content. Considering the massive emissions of semivolatile organics from diesel vehicles in Mexico City and the high relative humidity due to convective activities during the simulation period, the fraction of 0.023 used is reasonable, which is demonstrated by the comparison of the simulations in the E-case with the observations at T0. However, the parameterization of the* NO_2 *reaction with the semivolatile organics in the study might not be fit for moderately polluted areas where the emissions of semivolatile organics are not high enough. Further studies are needed to directly parameterize the* NO_2 *reaction with semivolatile organics in models. The uncertainty of the effective surface used in the WRF-CHEM model may also considerably influences the simulated HONO levels because the ground surface plays an important role in the HONO formation in the surface layer. In addition, the HONO formation from* NO_2 *reaction with freshly emitted soot remains highly uncertain, ranging from* 1.3×10^{17} *to* 10^{18} *HONO molecules* mg^{-1} *freshly emitted soot and also depending on the water content (Kalberer et al., 1999; Arens et al., 2001).*", and in Section 4: "*Generally speaking, the HONO sources play an important role in the photochemistry in the morning through enhancing the OH concentration in Mexico City. If the air quality in the morning is much concerned in urban regions, it may be necessary to include these HONO sources in air quality models. However, except the gas-phase gas phase reaction of NO with OH, the other four HONO sources are all associated with* NO_2*, so the importance of these four HONO sources is dependent on the* NO_2 *level, i.e., there is a* NO_x *threshold to activate the importance of these HONO sources.*"

(8) How sensitive are the HONO levels to the input parameters, which are partly unknown or have been highly parameterized?

Please refer to (7) and we have also included the results of three sensitivity studies in Section 3.1: "*We have performed three experimental studies to evaluate the sensitivities of HONO concentrations to the parameters in the above three sources based on the E-case. In the first study, we have used a fraction of 0.013 of the emitted* NO_x *to parameterize* NO_2 *reaction with semivolatile organics in the E-case. The simulated HONO concentrations are decreased by about 0.67 ppb or 34% on six-day average at T0 when the fraction of the emitted* NO_x *is reduced from 0.023 to 0.013. In the second study, when only the effective surface is increased 50% in the E-case, the HONO concentrations are increased by 0.16 ppb or 8% on average at T0, and the simulations in the afternoon are improved but overestimations frequently occur in the morning. When the value of* 10^{18} *HONO* mg^{-1} *of freshly emitted soot is used to calculate the conversion of* NO_2 *to HONO in the E-case, the HONO concentrations is enhanced by about 0.13 ppb or 7% on average at T0, and the* NO_2*-soot reaction become a non-negligible HONO source.*".

(9) On page 4161, the authors should explain more how they parameterized the SOA formation. It is unclear to me which conditions have been used here.

We have re-organized this part in Section 3.3.1: "*In the WRF-CHEM model, a traditional 2-product secondary organic aerosol (SOA) module is applied to predict the aerosol distribution and variation. The SOA module accounts for the SOA formation from the oxidation of six primary organic groups (POG): alkanes, alkenes, cresol, high-yield aromatics, low-yield aromatics, and monoterpenes. Ten semi-volatile, gaseous SOA precursors (hereafter referred as to SVOC) are produced via these reactions - two each for olefins, monoterpenes, and aromatics, and one each for alkanes and cresol.*

$$POG + oxidant \rightarrow \alpha_1 SVOC_1 + \alpha_2 SVOC_2 \qquad (R18)$$

The oxidants mainly include the OH radical, the nitrate radical NO_3*, and* O_3*. The saturation vapor pressures and mass-based stoichiometric yield coefficients (*α_i*) of semi-volatile precursors are obtained from either smog chamber experiments or from published estimates in cases where smog chamber data are unavailable. The SOA is calculated using the method developed by Schell et al. (2001), which was based on the absorptive partitioning model of Pankow (1994) that was extended by Odum et al. (1996).*"