

## Reply to Anonymous Referee #2

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) According to this study, heterogeneous reaction of  $\text{NO}_2$  with semivolatile organics is the most important source of HONO (about 75%) and yet authors devote it only a brief paragraph and provide no justification of their approach. It appears that authors assume that a fraction of 0.023 of the  $\text{NO}_x$  is converted to HONO. However, the latter value has been measured for diesel exhaust and may not apply to other  $\text{NO}_x$  sources such as emissions from gasoline engines and biomass burning. It will be more appropriate to use the value of 244 mg of secondary HONO per kg of diesel fuel burnt as given by Gutzwiller et al., 2002. I reiterate that only the contribution from diesel fuel can be considered here while extrapolation of this value to other combustion sources is not justified.

We have added discussions 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  $\text{NO}_2$  on time scales of hours, much longer than the time scale of the  $\text{NO}_2$  to HONO conversion on freshly soot particles, which is in the order of one minute (Kalberer et al., 1999). Therefore, using the fraction of  $\text{NO}_x$  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  $\text{NO}_2$  from other sources, such as gasoline engines and biomass burning. Considering the emission contributions from diesel engines and the variation in the fraction of  $\text{NO}_2$  in  $\text{NO}_x$  emissions in Mexico City, the fraction of 0.023 used in the study is likely an upper limit for the HONO formation from  $\text{NO}_2$  heterogeneous reaction with semivolatile organics. Furthermore, it needs to be emphasized that further studies need to be conducted to more appropriately parameterize the  $\text{NO}_2$  reaction with semivolatile organics.”* and in Section 3.1: *“As the most important HONO source in the surface level, the  $\text{NO}_2$  reaction with the semivolatile organics is highly parameterized in the simulations, using a fraction of 0.023 of the  $\text{NO}_x$  emitted to calculate the HONO formation. Based on the experiment of Gutzwiller et al. (2002), the semivolatile organics in diesel exhaust react with  $\text{NO}_2$  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.”*

(2) It appears that soot- $\text{NO}_2$  reaction is considered as instantaneous in the model, i.e.,

1.3e17 molecules of NO<sub>2</sub> are immediately converted to HONO per each mg of freshly emitted soot. This approach may significantly overestimate the rate of HONO formation when sharp changes in soot concentration occur, such as during the rush traffic hours. To avoid this, both the HONO generation capacity and the uptake coefficient should be implemented in the model.

The reaction rate of NO<sub>2</sub> with freshly is dramatically reduced within one minute, less than the chemical integration time step, so the reaction is considered as instantaneous in simulations. We have clarified in Section 2.2: *“We employ the value of  $1.3 \times 10^{17}$  HONO mg<sup>-1</sup> of freshly emitted soot to calculate the conversion of NO<sub>2</sub> to HONO based on the black carbon emissions in the WRF-CHEM model, considering that the reaction rate of NO<sub>2</sub> with freshly emitted soot is dramatically reduced after the first seconds (Kalberer et al., 1999), which is less than the chemical integration time step in simulations.”*

(3) Authors conclude that the impact of additional HONO sources on H<sub>2</sub>SO<sub>4</sub> production is negligible because the gas phase reaction of SO<sub>2</sub> with OH plays a minor role. If formation of H<sub>2</sub>SO<sub>4</sub> through the gas-phase reaction of SO<sub>2</sub> with OH radical is not efficient, how does sulfate form? I doubt that oxidation of SO<sub>2</sub> in cloud droplets has a major impact on sulfate production in Mexico City. In the top paragraph on page 4164 before Conclusions, do authors imply that “other sources” directly emit sulfate?

The oxidation of SO<sub>2</sub> in cloud droplets play a major role in the sulfate production and the other sources include the formation in cloud droplets and the direct emissions of sulfate. We have clarified in Section 3.3.2: *“Other sources, such as the oxidation of SO<sub>2</sub> in cloud droplets as well as the transport of direct emissions of sulfate from the Tula industrial complex and the volcano, may play a key role in the sulfate concentrations in Mexico City (de Foy et al., 2009).”*

(4) Authors conclude that significant overestimation of ozone in the afternoon is caused by the slow movement of the simulated plume and overestimation of the photolysis rate. Wouldn't the same apply to all photochemically generated species?

The long-lived photochemically generated species, such as HNO<sub>3</sub>, are also influenced by the slow movement of the simulated plumes. We have clarified in Section 3.3.2: *“In the early morning, the E-case and H-case reproduce well the observed slow accumulation of HNO<sub>3</sub> concentrations from about 0.01 ppb to 1 ppb, but in the afternoon, the WRF-CHEM model overestimates the observation, which is partially caused by the slow movement of the simulated plume.”*

(5) There is also evidence of a potential heterogeneous reaction of HONO on sulfate aerosols (i.e., Zhang et al., J. Phys. Chem. 100, 339, 1996). Such a potential sink for HONO needs to be evaluated by their model or discussed in the paper.

We have added discussions in Section 1: *“In the stratosphere, when the temperature is below 230 K, heterogeneous reactions of HONO on sulfate aerosols have been observed with an uptake coefficient ranging from 0.03 to 0.1, dependent on the sulfuric acid*

*content (Zhang et al., 1996). However, considering the high temperature in the troposphere, the heterogeneous loss of HONO on sulfate aerosols can not constitute a potentially important HONO sink.”*

Minor points:

Page 4158, line 19: replace “remains” with “remain” Page 4162, line 19: replace “ammonia” with “ammonium” Page 4163, line 16: replace “Figure 10b” with “Figure 11b” Page 4163: I think it would be more appropriate to use “particle-phase nitrate and ammonium” instead of “nitrate and ammonium aerosols” because those aerosols contain many other components.

We have corrected the errors.