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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign" *by* G. Li et al.

Anonymous Referee #2

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This modeling study attempts to identify unaccounted sources of HONO in the urban atmosphere. Four heterogeneous HONO sources are included in the WRF-CHEM model in addition to the well-known gas-phase reaction. The contribution of these sources to the photochemistry in Mexico City, including formation of secondary gas and aerosol pollutants, is investigated. Heterogeneous reaction of NO2 with semivolatile organics appears to be the strongest HONO source. Enhanced photochemistry caused by additional HONO noticeably enhances production of ozone and secondary organic aerosols. This study is interesting and focuses on a very important topic. The manuscript can be accepted for publication, after the following issues have been resolved.

(1) According to this study, heterogeneous reaction of NO2 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 NOx is converted to HONO. However, the latter value has been measured for diesel exhaust and may not apply to other NOx 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.

(2) It appears that soot-NO2 reaction is considered as instantaneous in the model, i.e., 1.3e17 molecules of NO2 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.

(3) Authors conclude that the impact of additional HONO sources on H2SO4 production is negligible because the gas phase reaction of SO2 with OH plays a minor role. If formation of H2SO4 through the gas-phase reaction of SO2 with OH radical is not efficient, how does sulfate form? I doubt that oxidation of SO2 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?

(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?

(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

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HONO needs to be evaluated by their model or discussed in the paper.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 4143, 2010.