

## ***Interactive comment on “Measurements of OH and HO<sub>2</sub> concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget” by S. Dusanter et al.***

**S. Dusanter**

sdusante@indiana.edu

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We are grateful to the second anonymous reviewer for these valuable comments which helped us to improve our manuscript. For clarity, the comments are reproduced below with a bold font, followed by our replies.

**P9828-9829, the description of LIF for OH and HO<sub>2</sub> measurements and its calibration can be removed because they have been described in the companion paper (Dusanter et al., 2009).**

All the conclusions reached in this manuscript were assessed from the measurements

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of HO<sub>x</sub> radicals. We believe that it is important for readers – including those more interested in the modeling aspect of the HO<sub>x</sub> chemistry rather than instrumental development - to know how these measurements were performed without having to read the companion paper. We have thus decided to leave this short paragraph in the revised manuscript.

**P9832, L5, a factor of 1.04 was applied to reflect roof surface albedo. A brief explanation is needed (why 1.04).**

There were no collocated measurements of the downward flux during MCMA-2006. However, surfaces usually exhibit albedos on the order of 2-10% and we decided to use a factor 1.04 for a dark brown roof. For comparison, Sheehy et al. (2008) used a factor 1.08 to correct for surface albedo when the HO<sub>x</sub> instrument was located on a small tower (6 meters) on the roof of the CENICA building in Mexico City. This has been clarified in the revised manuscript.

**P9833, bottom, the sentence “A reference VOC measured during both MCMA-2003 and 2006 exhibiting a similar rate constant with OH than an unmeasured VOC was selected to calculate the scaling factor.” is not clear to me. Which VOC species is selected as a reference VOC? Also, as the authors have stated that quite a lot of VOC species might not be measured in field studies, even with the combined suite of VOC measurements in both MCMA2003 and MCMA2006, it is possible that there are still missing VOC species (e.g., oxygenated species) which are not included in the model and may be partially responsible for the over-prediction of OH in the afternoon. The author should include this possibility somewhere in the paper.**

The procedure used to estimate concentrations of unmeasured VOCs during MCMA-2006 is based on averaged ambient concentrations reported for MCMA-2003 (Velasco et al., 2007) from several urban sites (Table 4 in Velasco et al.). For instance,

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while 3-methyl hexane (3MH) was measured in 2003, no ambient concentrations were reported for 2006. The bimolecular rate constant for OH + 3MH ( $7.20 \times 10^{-12}$  cm<sup>3</sup>/molecule/s, 298K, 1 atm) is similar to that recommended for n-heptane ( $7.15 \times 10^{-12}$  cm<sup>3</sup>/molecule/s, 298K, 1 atm), which was measured during both campaigns. The concentration ratio 3MH/n-heptane observed during 2003 was used to estimate ambient concentrations of 3MH for 2006 using measured concentrations of n-heptane. Different reference compounds were used to estimate ambient concentrations of other chemical species for 2006, providing that the rate constant with OH was similar for both compounds.

Missing OH reactivity from saturated chemical species cannot account for a large overestimation of OH around noon due to a rapid recycling of OH from RO<sub>2</sub> + NO and HO<sub>2</sub> + NO (see Fig. 8). An increase of the constrained concentrations for HC3+HC5+HC8 by a factor two only leads to 8-13% decrease of OH (see Table S6, supplementary material), while the measured concentrations are a factor 1.5 lower than predicted. In addition, missing reactivity from unsaturated species would lead to a larger disagreement between measured and predicted OH concentrations around noon as shown by a simulation performed with a 2-fold increase of OLT and OLI in the model (see Table S6, supplementary material). OH increases by 11-23% in the latter simulation. These points have been added in the revised manuscript.

**I noticed that the authors limited the comparison within the period between 8:40am and 6:40pm (CST). Any reasons for this? Were OH and HO<sub>2</sub> only measured during this period? I am not sure when the morning rush hour is in Mexico City, but according to Shirley et al. (2006), the maximum NO<sub>x</sub> appeared between 5am and 8 am (CST) and apparently a period with richest chemistry is missing in this study. By the way, are there any nighttime OH and HO<sub>2</sub> measurements?**

Unfortunately, the rush hour period is missing from the dataset. This study presents HO<sub>x</sub> concentrations measured during the first deployment of the IU-FAGE instrument

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and due to experimental difficulties, nighttime and early morning HO<sub>x</sub> concentrations were not measured.

**P.9844, L.2, change “the measurements” to “the measurements of HO<sub>2</sub>”**

This has been changed as suggested.

**P.9850, L.6-7, I would suggest adding “on average” or something like that when the authors state good agreement between observed and modeled HO<sub>2</sub>/OH ratios when NO was 1-5 ppb. The measured HO<sub>2</sub>/OH ratios are quite scatter as a function of NO while I assume the modeled HO<sub>2</sub>/OH ratios are much tighter.**

We have added the term “on average”.

**P.9853, bottom, the authors pointed out the differences in the contribution of different RO<sub>x</sub> production processes. I wonder if the different locations (thus different chemical conditions) of MCMA2003 and MCMA 2006 could be partly the reason for these differences.**

The different locations are likely the reason for the differences observed in the radical budget. For instance, O<sub>3</sub> photolysis is of minor importance during MCMA-2006 while it contributes to 21% of the total RO<sub>x</sub> initiation rate in 2003. This is mainly due to high NO<sub>x</sub> concentrations observed at T0 (median morning peak of 250 ppb) compared to CENICA (86 ppb). During the morning and early afternoon, O<sub>3</sub> is efficiently titrated by NO at T0 and peaks around 2:00 – 2:30 p.m. (Dusanter et al., 2009) while J(O<sup>1</sup>D) peaks sooner around 12:30 p.m. (CST). Note that at 2:30 p.m. J(O<sup>1</sup>D) is half its peak value and the production of OH from O<sub>3</sub> photolysis is already declining. In 2003, the similar timing between J(O<sup>1</sup>D) and O<sub>3</sub> (12:00 – 12:30 p.m.) leads to higher production rates of OH from O<sub>3</sub> photolysis. The higher NO<sub>x</sub> concentrations observed at the T0 site may also explain the higher concentrations of HONO observed and hence the higher contribution of HONO photolysis to the total initiation rate of RO<sub>x</sub> radicals.

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There is a body of growing evidences which suggests that an unknown source of HONO is operating in the troposphere, likely due to light-enhanced heterogeneous reactions of NO<sub>2</sub> on surfaces (Kleffmann, 2007). This has been clarified in the revised manuscript.

**Figure 7, in the OH figure, the order of green-orange-red lines (from large to small) is consistent with the order of the additional HO<sub>2</sub> production rates (i.e., green=2.2, orange=1.1 and red=0.7 x10<sup>8</sup> molecule cm<sup>-3</sup> s<sup>-1</sup>). However in the HO<sub>2</sub> figure, this order is red, green, and orange (from large to small). Is this an error?**

Figure 4 is correct. The red line displays a simulation performed with the lowest additional production rate of HO<sub>2</sub> but also a reduction of the effective rate constant for HO<sub>2</sub> + NO. This is why the order is not similar between the two panels.

**In Figure 8, I noticed that there are at least two processes are not included in the termination: HO<sub>2</sub>+HO<sub>2</sub> and HO<sub>2</sub>+RO<sub>2</sub> to form peroxides (might be part of Figure 7, L(RO<sub>x</sub>) others). I also noticed that the total initiation rate and termination rate are slightly not in balance (e.g., P(RO<sub>x</sub>) = 11.4 + 5.7 + 2.8 + 11.7 =31.6 and L(RO<sub>x</sub>) = 6.5 + 4.6 + 19.7 = 30.8). Can these missing processes account for this discrepancy? Also the authors should mention that modeled RO<sub>2</sub> (and modeled OH and HO<sub>2</sub> I assume) concentrations are used in the calculation, although other species are from measurements.**

On an average basis (8:40 a.m.-6:40 p.m.), the radical terminations due to HO<sub>2</sub> + HO<sub>2</sub> (4.0x10<sup>5</sup> molecule/cm<sup>3</sup>/s) and HO<sub>2</sub> + RO<sub>2</sub> (2.7x10<sup>5</sup> molecule/cm<sup>3</sup>/s) were of lower importance at the T0 site. This is a consequence of the fast radical cycling initiated by NO. As a consequence, we omitted them in Fig. 8 for clarity. As mentioned by the reviewer, the slight imbalance between P(RO<sub>x</sub>) and L(RO<sub>x</sub>) is due to these missing processes. For completeness, we will include them in Fig. 8 in the revised manuscript.

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We will also indicate that model predicted concentrations of radicals are used in these calculations.

#### References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9823, 2009.

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