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Interactive comment on "Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget" *by* S. Dusanter et al.

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We are grateful to Dr. Y. Elshorbany for this careful analysis. For clarity, the comments are reproduced below with a bold font, followed by our replies

1. In line 9, page 9837, the authors stated that the "predicted concentrations (i.e of Glyoxal (GLY)) were higher than that observed by a factor 5-20". In line 3, page 9839, they stated that "it is likely that the same overprediction occurs for other dicarbonyl species such as and Methyl Glyoxal (MGLY) and unsaturated dicarbonyl (DCB)". In line 25, page 9838, the authors stated that both OH and

HO2 are consistently overestimated throughout the day when DCB species are not constrained. In line 18, page 9839, the authors stated that "when MGLY and DCB are constrained in the model, the agreement between the model and the observation is improved" and finally used these results to show the important contribution of the secondary OVOCs to the radical initiation. photolysis of the photochemical adducts, unsaturated dicarbonyl (DCB) and Methyl Glyoxal (MGLY) lead to the formation of RCO3, which then mainly react with NO to give RO2 which recycle to OH radical: A + B → DCB + MGLY → RCO3 →→ HOx, The production of DCB and MGLY results in loss of the radicals and/or species A and B while their photolysis and subsequent recycling results in the production of HOx radicals. Having the concentration of DCB and MGLY typically overpredicted by the model, then constraining the model with their concentrations (5-20 times lower levels of DCB and MGLY) will lead to a net loss of species (A, B) and thus artificially lower OH radicals. That is because A and B will react anyway in the model to form DCB and MGLY but the model will use only the much lower constrained values to apply the subsequent photolysis reaction which will led at the end to lower HOx radicals. Thus the lower OH concentrations (in good agreement with the measurement) obtained by the authors is only an artificial modelling error that reflects only the nature of above reaction. Instead you could have switched off all formation and destruction channels of DCB and MGLY. Alternatively, I would also suggest that the authors perform an additional model run where ([DCB]+[MGLY])*2, similar to what they have done with aldehydes (ALD) and ketones (KET) which showed that they have a minimal impact on the HOx radical concentrations.

The procedure employed to constrain MGLY and DCB in our model is necessary to deal with an incomplete description of the dicarbonyl chemistry, likely due to a missing sink (2'):

(1) A + B → DCB + MGLY

(2) DCB, MGLY → RCO_3

(2’) DCB, MGLY → Loss
(3) $RCO_3 \rightarrow\rightarrow HO_x$

Steady state concentrations of DCB and MGLY depend on the reaction rates of (1), (2) and (2’), with Rate(1) = Rate(2) + Rate(2’). The model does not incorporate (2’) and as a consequence overestimates [DCB], [MGLY] and Rate(2). Constraining the concentrations of DCB and MGLY species by lower values allows correcting Rate(2) while keeping Rate(1) the same. Not doing it would lead to erroneous predictions of the concentrations of RCO_3 radicals and thus HO_x radicals. Complementary modeling, performed by adding an additional sink of MGLY and DCB (2’) in the model was performed as stated P9839 L22. The similar concentrations of RO_x radicals predicted by RACM using two distinct procedures to account for the missing pathway (2’) support the validity of our approach.

2. Line 20, page 9838, the authors stated that “Simulations performed using short or large VOCs set led to similar HOx concentrations”. I would expect only similar OH concentrations but RO2 and HO2 should increase as a result of the oxidation of the additional estimated hydrocarbons!?. Then, I would also agree using any of these two VOC sets. In addition, this run shows that DCB and MGLY does not have any impact on the OH levels because their production rates have essentially also increased using a larger VOC set) but OH not.

Although estimated concentrations of VOCs are significant for the surrogates HC8 (+76%), ALD (+10%) and OLT (+8%), the total OH reactivity increases by only 8% on a median campaign basis. As a consequence, simulations performed with the large and short sets of VOCs led to predicted concentrations of RO_x that are similar within 10%.

Comparing the runs performed with the short and large sets of VOCs does not allow one to gauge the impact of dicarbonyl species on the total RO_x initiation rate since these species are mainly produced during the oxidation of aromatic species in the MCMA. No additional aromatic species were added to the large set of VOCs, and as a result the rate of production of dicarbonyl species is likely to be similar between the two simulations.

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

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