

Interactive comment on “Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget” by S. Dusanter et al.

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First, I would like to congratulate the authors on this nice work. In this comment I would like to strength on the fact that “constraining” or “unconstraining” a photochemical model is a complicated and very critical issue.

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

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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: $A + B \rightarrow DCB + MGLY \rightarrow RCO_3 \rightarrow \rightarrow HO_x$, 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 HO_x 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 HO_x 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 HO_x radical concentrations.

2. Line 20, page 9838, the authors stated that “Simulations performed using short or large VOCs set led to similar HO_x 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

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a larger VOC set) but OH not.

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