

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.

Anonymous Referee #1

Received and published: 15 June 2009

This is a very good paper describing field measurements of OH and HO₂ radicals made in Mexico City during the MCMA 2006 campaign. A comparison is made with predictions from a constrained box model using the RACM mechanism. Although this is a lumped mechanism, the authors do a very good job of clearly stating the limitations of such a mechanism, and where possible, looking at comparisons with the Master Chemical Mechanism, which is a much more detailed mechanism. I think this discussion of the merits and outputs of two models is a highlight of the paper – rather than focussing on one model and rather overlooking model deficiencies.

There is a good set of measurements over quite a few days. The HO₂ measurements

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are of good precision, and although the OH measurements are well above the detection limits, the relative precision compared with HO₂ is not as good, reflecting the lower concentrations of OH. There is sufficient overlap of the HO_x measurements and the supporting measurements to enable a meaningful analysis of the discrepancies between measurements and model calculations. Another thing I really liked about the paper is the diagnosis of the discrepancies between model and measurements, and trying various strategies and scenarios to try to reconcile the differences. Ultimately, although in this case it was not possible to put their finger on the precise reason for the differences, some good ideas were discussed and reasons speculated. Clearly, there are still some unknowns about the fast photochemistry of very polluted regions such as Mexico City. The concentrations of NO_x and particularly of VOCs are immense, the chemical environment is incredibly rich with very high fluxes for production and loss of OH and HO₂. The main conclusion is that there are missing sources of radicals during morning hours when NO_x is really high, and also that the predicted HO₂/OH ratio is underestimated for high NO, but it is not clear in which direction (HO₂ to OH or OH to HO₂, or a combination of both) the error is located. This piece of work does not include measurement of the OH reactivity (something that was present in the earlier study in Mexico City involving Brune's group) which provides an additional constraint for the model.

The paper also provides an excellent and balanced review of the previous literature, together with a rate of production and destruction analysis for HO_x, OH and HO₂, which helps to show what the main processes are controlling these species (with the caveat that some of these may be missing or under/overpredicted). Interestingly O(1D)+H₂O only provides 6% of the source of the radicals.

I recommend publication of the manuscript in ACP, subject to a discussion of the following points:

Abstract. It is a little confusing saying that the predicted HO₂/OH ratios were underestimated. (underestimated by what? the measurements presumably but this is not

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explicit). Better to say that the model underestimated the measured ratio HO₂/OH ratio – this is clearer.

Although there are no measurements in this campaign, it would be worth making the point that OH reactivity measurements in this study would have been useful.

The reference Sheehy et al appears to be missing at the end in the references.

I was pleased to see some discussion together of the RACM and the MCM mechanisms. There needs to be a lot more of this, and someday, an exhaustive comparison of the OH and HO₂ predictions of each mechanism for the same input parameters of supporting measurements needs to be done for real campaign data.

Sander and not Sanders page 9830, line 18.

It is stated that chemiluminescence measurements of NO₂ are prone to interferences from various NO_y. Perhaps be more specific, as there are several ways to convert the NO₂, e.g. by photolysis to NO, or by heating with a Mb catalyst to form NO. I assume you were using the latter or are both methods prone to problems in very polluted conditions? Using instead the DOAS with the attendant spatially averaging issues is not ideal.

Page 9833 line 20, large fraction of VOCs not measured. Seems a good place to reference some indirect evidence for this, namely missing OH reactivity, thought to be from VOCs, references from the e.g. Brune, Kajii, Heard groups.

I like the section on uncertainties associated with RACM very much.

There is a big discrepancy between predicted and measured glyoxal, which suggests a deviation from photochemical equilibrium. Also heterogeneous loss of glyoxal is mentioned as a possible uncertainty in the model and a reference given. Can some more details be given?

Page 9389, line 16 and surrounding section. This scaling is a bit messy by the ap-

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proach is justified in the absence of other data being available.

With such a rich chemistry expected in this environment, is the lack of predictive ability for dicarbonyl species the only likely problem? It is likely there are problems predicting many other species.

Page 9845, line 2, does Mao et al 2009 cover discussion of OH reactivity measurements? If so, explicitly say so.

Again, repeating my earlier point, on page 9847, line 13, it is good to see a comparison of the RACM and MCM mechanisms, and incorporation of some MCM 3.1 updates into the RACM.

Page 9849, line 12. Again, I like the approach, not dodging the issues, rather being realistic about the model that is being used.

Page 9851, line 8. the incomplete mixing between HO₂ and NO (an anthropogenic emission) is analogous to a hypothesis put forward from the Suriname GABRIEL campaign, which suggested OH and isoprene (a biogenic emission) were not mixed properly either, as the new OH source necessary being postulated (Lelieveld et al, Nature 2008) to bring modelled and measured OH into agreement then gave the models problems in calculating isoprene. Perhaps discuss this link between the two studies.

Page 9854. Line 18. A further investigation is mentioned – is this via a paper in preparation?

Page 9855. It is likely that the electronically excited NO₂ plus water vapour reaction being a source of OH is erroneous. There is a new paper in Science (Carr et al. 2009) which throws doubt on this new source of OH, in agreement with measurements by Crowley's group in Mainz, and also by Christa Fittschen in Lille. It is worth leaving the section in though as the conclusion is that this source of OH is not important, even using the initial results (Li et al., 2008). However, it should be pointed out that there are new results (see above) which cast doubt on this source of OH.

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References. Sheehy et al 2008 is not on the list.

Fig 1, 2, 3 need to be bigger, hard to see when I printed out (OK on screen is blown up).

Figure 8. Can you split up the OH loss as well to RO₂?

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