

Interactive comment on “Oxidative capacity of the Mexico City atmosphere – Part 2: A RO_x radical cycling perspective” by P. M. Sheehy et al.

Anonymous Referee #1

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This is an interesting and potentially important paper that seeks to examine radical budgets, overall photochemical efficiency and ozone production in the Mexico City Metropolitan Area experiment (MCMA) in 2003. MCMA encountered very high concentrations of NO_x and VOCs and represents the most extreme set of conditions subjected to a study of this sort. The paper uses the master chemical mechanism (MCM) to examine the chemical processes in detail, using a range of constraints, including constraining OH and HO₂, both separately and together. Using this approach, they identify what they term a missing reactivity, which is particularly significant in the morning, and substantially affects ozone formation.

The paper is detailed and, in some places, quite hard to follow. A number of ideas are developed, sometimes without a full explanation. The authors might consider the

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clarity of the paper; a few comments on this issue are made below.

Comments: 5366, line 3+. The HO_x constraints are based on median values across the campaign. The uncertainty introduced through this methodology, arising from the variability of the diurnal profiles, is commented on, but it would be good for the reader to have some idea of this variability. Table 2 is already quite crowded, but it would be useful, for the reason raised here, but also to interpret other aspects of Table 2, if the average values of OH and HO₂ over the 07 to 13 period were given for each day listed in Table 2.

5367. A key issue in modeling of this sort, especially in an intensely urban region, is the determination of VOC concentrations. The method is discussed in some detail. A couple of questions: (i) The alkane to total alkane ratios were checked, but how accurate is it to use speciated emissions inventories for more reactive species such as alkenes? Did the authors assess whether the ambient concentration ratios will differ from the emission ratios under the conditions studied, where OH is high at midday. (ii) What do the uncertainties refer to and how were they determined?

5370. The authors use the term reactivity in a number of senses. In this section, I presume that it corresponds to the first order rate constant for loss of OH, which is assessed against the measured values from Shirley et al. In other parts of the paper, e.g. the abstract, I presume that missing reactivity refers to missing radical sources. It would be helpful to define the terms used clearly. Fig. 9 refers to VOC reactivity, which again I take to be the first order rate constant for loss of OH by reaction with VOCs, although I understand the desire to use VOC(r) within the context of ozone isopleths. Some clarity is needed!

In this same context, the authors later on discuss the possibility of SVOC and IVOC as sources of OH reactivity. Have they considered the possible contribution from undetected species that are not in current inventories, as discussed by Lewis et al some time ago? (A larger pool of ozone-forming carbon compounds in urban atmospheres,

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A C Lewis, et al., Nature, 2000, 405, 778)

5371. The discussion of the comparisons between measured and modelled radical concentrations, is a little confusing, because of some seeming inconsistencies, e.g. the discussion of HO₂ in the first and second paragraphs.

5375+ The discussion of chain lengths is central to the paper, but is rather lengthy. It could be compressed, with maybe some material placed in appendix. The discussion on p 5379, by contrast, I found to be rather impenetrable. (i) I presume that the exponential treatment is in terms of probability; if you like in terms of probability of transmission through the chain. Is this correct? An explanation would help. (ii) What is a wheel value?(iii) The product sign in eq 12 is presumably redundant, since gamma(RO_x) is already a product.

5380. The discussion on P(OH) and L(OH) presumably refers to measured OH and HO₂, since modelled OH would necessarily obey detailed balance. This becomes clear later in the section, but should be pointed out at the start.

5388. This discussion on chain lengths is again perhaps over-lengthy. The exact definition of a chain length only really works with a single point of initiation and termination. Atmospheric systems are more complex, because they have multiple points of initiation and termination. The present paper largely follows the approach of Wagner, with some differences, and it is an appropriate point of view, but not necessarily the correct or only viewpoint, because of the nature of the process. The points made are worth saying, but could be compressed.

Overall, a good paper, that should be published, but it should be worked on to improve clarity.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5359, 2008.

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