

Interactive comment on “Oxidative capacity of the Mexico City atmosphere – Part 1: A radical source perspective” by R. Volkamer et al.

Anonymous Referee #2

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The paper presents an analysis of radical sources in the 2003 Mexico City Metropolitan Area (MCMA) field campaign. The analysis is based on a box model using the master chemical mechanism v3.1 (MCMv3.1). Various methods of constraining variables to field measurement values are used. The aim of the paper is to understand the radical sources throughout the day and the night. The analysis is detailed and the conclusions both valuable and interesting. It is shown that secondary sources, deriving from radical precursors formed photochemically, dominate radical production during the day; Photolysis of ozone, HCHO and other OVOCs are the major sources. The analysis focuses on OH as the principal radical, presumably because it is the main chain carrier. HO₂ and RO₂ yields are converted into OH yields by assessing losses of these radicals in the chain cycle. It is regrettable that the authors have decided to treat the various parts

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of the radical chemistry in separate publications, because it is less easy to obtain an overview of all the processes involved. It is a natural consequence of the decision to treat the material in such detail.

Detailed comments: P5369 et seq. The paper suffers from its selectivity in the presentation of measurement methods. Details are given for those techniques used directly by the authors, but there is not even a reference in section 2.1 to the methods used for OH, HO₂ and RO₂. It would be useful to be able to see those data - presumably via a referenced paper. Similarly there is little information on concentrations of NO_x, hydrocarbons etc. It is difficult to interpret the data, as a result, and one is left very much in the hands of the authors. Some information should be contained in this paper (e.g. campaign diurnal averages, or some other concise method of presentation.) References to the sources of data would also help. At present, the paper doesn't really stand on its own.

P5373 line 11. The match between calculated and measured HCHO is used to assess dilution. What are the timescales of HCHO formation and decay? Can the authors assure us that this procedure is appropriate

P5373 line 27. More information should be given on the constraints applied. What is meant by average and median? What are the averaging times used for the constraining concentrations - are they all the same or are they related to the measurement frequency.

P5374, section 2.3. The contributions to HCHO production from different VOCs is determined by treating each VOC separately and constraining to the measured radical concentrations. This would be fine if there were no non-linearities in the propagation cycles. For example, can the authors assure us that the competition between RO₂ + NO and RO₂ + HO₂/RO₂ is properly captured with this approach. Is [NO] sufficiently large that this competition is insignificant. At present this is difficult to assess because we don't have any [NO] data. More explanation and justification is needed. The fi-

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nal sentence in this section also needs more explanation. It is clear from Table 1 that modelled OVOCs make a substantial contribution to radical formation. This is difficult to understand given the claim that HCHO derives almost exclusively from first generation processes. Does none of this OVOC chemistry lead to HCHO, either directly or indirectly? This issue is examined again in section 3.5 and on p5389

P5376 line 10. The use of the word dominated is questionable, since less than half derives from OH sources.

P5377 Section 3.2 This section is particularly difficult to interpret without more data on species concentrations.

Overall, it is a good paper, but more information is needed to allow the reader to think about the analysis and assess its validity.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 5365, 2007.

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