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Atmospheric Chemistry and Physics Discussions

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

R. Volkamer et al.

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We like to thank the reviewer for the detailed comments.

Detailed response to the reviewers comments:

C1) 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 NOx,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

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of data would also help. At present, the paper doesn't really stand on its own.

R1) We have added the following text in the introduction to Section 2: "An overview of typical pollutant concentrations at the CENICA site is compiled in (Molina et al., 2007); campaign median concentrations were 86 ppb NOx during morning rush hour, 20 ppb NOx during afternoons, median peak concentrations of 115 ppb O3, 0.4 ppt OH, and 40 ppt HO2 shortly after noon, 120 s-1 OH-reactivity during morning rush hour. Of the calculated contributions to the OH reactivity, 12% was due to NOx, 7% to CO, 4% to HCHO and 72% to VOCs (Shirley et al., 2006). A complete list of measurements used to constrain the MCM model is given in Table 1 of (Sheehy et al., 2008)."

C2) 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

R2) A sentence was added in Section 3.5 about the atmospheric lifetime of HCHO, which is on the order of few hours during mid morning, noon time, and the early afternoon. The reviewer could have been a bit more specific in what aspect he/she would like additional assurance that the procedure followed is appropriate. The following reply might hence not be very specific in addressing the rather diffusely stated concerns.

HCHO concentrations peak around 9am, and decreasing HCHO concentrations after 9am are partly the result of increasing sink reactions (photolysis and OH radical reactions), and efficient venting from the MCMA; decreasing concentrations are observed despite the HCHO production rate is increasing. The reviewer is referred to Figure 7 in Garcia et al. 2006, where it is demonstrated that HCHO formation rates from photochemical sources actually peak between 10am and noon. Photochemical sources clearly dominate over emission sources around noon time (70-80%), and the balance between photochemical HCHO formation and destruction rates determines largely the atmospheric HCHO burden (as is shown in Fig. 5 of this manuscript). Given that the photochemical formation rate is well constrained by the model (section 3.6), and HCHO loss rates by photolysis and OH-radical reactions are measured and assimilated into the model, the dilution can be traced from the difference in HCHO burden.

C3) 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.

R3) A statement has been added to refer the reader to part 2.

C4) 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 do not have any [NO] data. More explanation and justification is needed.

R4) The branching ratios for the fate of RO2 radicals is shown in Figure 6 of part 2. The fate of peroxy radicals is consistently determined to more than 80% by reactions with NO at any time of day (90% during mid morning). A sentence, and reference to Figure 6 in Sheehy et al. 2008 has been added.

C5) The final 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

R5) It is not true that "none of this OVOC chemistry leads to HCHO formation". In fact, the paper quantifies that about 16% of HCHO forms from OVOC precursors. This number applies for mid morning conditions, which we chose for the HCHO source

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apportionment based on the fact that photochemical activity peaks during mid morning, and hence the photochemical HCHO formation rate is largest then.

We have expanded on the meaning of the last sentence of section 2.3, and added some further explanation in section 3.5 (now section 3.6 in the revised manuscript)

C6) P5376 line 10. The use of the word dominated is questionable, since less than half derives from OH sources.

R6) We have rearranged the text in this section and give radical sources now in order of the relative contributions (most important first). The language was changed as part of these updates.

C7) P5377 Section 3.2 This section is particularly difficult to interpret without more data on species concentrations.

R7) See above our reply to the first comment.

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