Oxidative capacity of the Mexico City atmosphere – Part 2: A ROx radical cycling perspective” by P.M. Sheehy et al.

Response to Referee comments

General Response:

We have made considerable changes to the manuscript. It has been simplified and clarified where appropriate to minimize confusion without sacrificing the complexity of the topics discussed. The major difference is in the length of the paper; about 14 pages have been moved to a new Supplementary Information section. The abstract has been improved and clarified, the introduction has been shortened, the sequence of sections has been modified for clarity following suggestions from one reviewer, and the discussion section has been compressed as suggested by both reviewers. Also, we have moved large parts of the model description, and some results that appeared less attached to the central theme of the paper to a separate Supplemental Information section. This has shortened the manuscript considerably and improved its readability. The Supplementary Information section now provides readers with more detail regarding the model construction, the investigation of some other parameters in which missing reactivity may be apparent (but not as convincing as the ones presented in the manuscript), and more information on individual day modeling. We believe this change improves the focus of the paper on the two central themes of radical cycling and observed missing reactivity. Where appropriate, we have updated the manuscript with references that are relevant to this topic that have been published in the (long) period between the submission of the *Discussion* manuscript (ACPD) and this *Final* manuscript (ACP). Similarly, due to the considerable amount of time between the manuscript submissions, we have provided outlines of the previous manuscript and the current manuscript below to make the changes transparent.

Parts of the model description and some results are now provided as supplementary information. No new information was added other than that requested by the reviewers.

Previous Outline of Paper

Abstract
1. Introduction
2. The mechanism and the model
   ~~2.1. Alkanes~~ *
   ~~2.2. Alkenes~~ *
   ~~2.3. Aromatics~~ *
   ~~2.4. Oxygenated VOC~~ *
   2.5. Dilution
   2.6. Photolysis rates of reactions
3. Results and discussion
   ~~3.1. Individual day modeling~~ *
   3.2. OH reactivity
   3.3. HOx: measured vs. modeled
   3.4. HO2/OH vs. NO
   3.5. Predicting RO2
   3.6. Chain length
   ~~3.7. OH production and loss: Measurement imbalance~~ *
   3.8. Ozone production
      ~~3.8.1. VOC_R and NOx~~ *
      3.8.2. Missing OH reactivity
4. Comparison to other studies
   4.1. Radical budgets
   4.2. Missing HOx reactivity
   4.3. Defining chain length
   4.4. Ozone production
5. Conclusions

54 pages in ACPD format

Current Outline of Paper

Abstract
1. Introduction
2. The mechanism and the model
   2.1. OH reactivity: First order loss of OH
3. Results and discussion
   3.1. Missing OH reactivity
   3.2. HOx: measured vs. modeled
   3.3. HO2/OH vs. NO
   3.4. Predicting RO2
   3.5. Chain length
   3.6. Ozone production
4. Comparison to Other Studies
   4.1. Radical budgets
   4.2. Missing HOx radicals
   4.3. Defining a chain length parameter
   4.4. Ozone production
5. Conclusions

40 pages in ACPD format

* *Supplemental Information*
1. Model Constraints
   a. Alkanes
   b. Alkenes
   c. Aromatics
   d. Oxygenated VOC
2. OH production and loss: Measurement imbalance
3. Individual day modeling
4. VOC_R and NOx

13-14 pages in ACPD format

Responses to Referee #1
Specific Comments

1. 5366, line 3+. The HOx 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.

Response (see Supplemental Information): The average daily HOx concentrations from 07:00-13:00 have been added to Table 2 in the Supplemental Information section.

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?

Response (see Supplemental Informationk, p2 and on): There appears to be a misunderstanding here. In response to (i), we'd like to point out that the approach we employed is not simply a speciated emissions inventory for alkenes. We employed highly time-resolved measurements of alkene reactivity towards ozone by a Fast Isoprene Sensor (FIS), and attributed this reactivity to concentrations of individual alkenes following the method described in detail in Velasco et al., 2007. In particular, this method does reflect the ambient concentration of alkenes. As we note in part 1 of this paper series, further alkene speciation will be of interest for future studies.

In response to (ii) (see Supplemental Information, p 2 and on), the uncertainties are a combination of measurement precision/uncertainty and the methodology used to determine the speciation. These were determined based on comparisons between canister data and FIS sensor data, and more information is available in Velasco et al., 2007.

3. 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.

Response (text revised throughout the manuscript e.g., p9, line 1+ or p22, line 22+): We have clarified and minimized the use of the term "reactivity" where appropriate. We are now more explicit and specific in each section regarding the chemical processing we are referring to, rather than using the generic term "reactivity". In particular, we now refer to OH loss rate (section 2.1, p9), missing HOx radicals (section 4.2, p22), etc.. We maintain the use of the term 'missing reactivity', but we have added explanation about the specific

ROx sources and sinks we believe can make up this missing reactivity. Note that Figure 9 and the discussion of VOC reactivity has been moved to the Supplemental Information section.

4. In the 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?

Response (see p 11, line 13 and on): We have included discussion of the Lewis et al., 2000 results in the context of missing OH losses. Indeed we feel that there is at least some overlap between the parameterized IVOC and the larger compounds identified by Lewis et al, as oxygenated C6 to C14 aromatic and aliphatic molecules. We have clarified this in the revised text.

5. 5371. The discussion of the comparisons between measured and modeled radical concentrations is a little confusing, because of some seeming inconsistencies e.g., the discussion of HO2 in the first and second paragraphs.

Response (text revised in Section 3.2, p 12, line 1+): We have rewritten this passage in an attempt to clarify.

6. 5375+ The discussion of chain lengths is central to the paper, but is rather length. 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(ROx) is already a product.

Response (see p19, line 12 and on): We have simplified the text in an attempt to clarify this discussion. (i) and (ii) The definition of ω as a chain length parameter has been clarified and any reference to the ‘wheel’ has been deleted. Note that the wheel value was a term that the authors were using in internal discussions before opting to refer to both n(OH) and ω as chain length parameters – the wheel value was not meant to appear in the manuscript and was an editing error. (iii) Thank you for pointing this out. The product sign is indeed redundant and has been removed (see p19 line 13).

7. 5380. The discussion on P(OH) and L(OH) presumably refers to measured OH and HO2, since modeled OH would necessarily obey detailed balance. This becomes clear later in the section, but should be pointed out at the start.

Response: This discussion has been clarified and moved to the Supplemental Information section.

8. 5388. This discussion on chain lengths is 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.

Response (see Sec 4.3, p24, line 3+): Our proposed viewpoint/definition of chain length is not intended to be the only one; however, it is to our knowledge the first systematic attempt to reduce the complexity that the reviewer is referring to as “multiple points of initiation and termination”. Notably, by expressing the production of ROx radicals in terms of OH-equivalents, we in fact compress the multiple points of initiation into a single parameter. Note that the determination of n(OH) (see eq 1, p16 line 11) does not rely on considerations of radical sinks, and thus the complexity in terms of multiple points of termination is not relevant for this parameter. Thus we do not see what would be missing in our determination of n(OH) to capture atmospheric complexity. Conversely, the ω parameter is defined based solely on considerations of radical termination (see eqs 10-12, p19, lines 13-15). It does not depend on radical production, but accounts for the multiple points of termination. Thus we feel that both of our chain length parameters capture the complexity of the atmospheric ROx cycle. We have modified the text to make the case that our analysis is the first attempt to address directly the complexity of the atmospheric system in the determination of the chain length. We have also compressed our discussion of other methods of calculating chain length, and the difficulties in comparing them quantitatively. While not the only viewpoint, we attempt to quantify chain length (using the n(OH) and ω parameters) in a manner that will facilitate more useful comparisons between air masses hopefully also in future studies.

Responses to Referee #2
Major Comments

1. The paper as it stands, in my opinion, is too long. There are some sections that could be summarized or even dropped-out. For example, the introduction section is too long. The authors list several studies that have addressed HOx modeling/measurement issues (page 5361, line 25 and on). Then, they proceed to discuss several of them, though it is not clear why they go into details in some of them. I believe that these paragraphs could be summarized into a brief discussion of the fallbacks of the studies and challenges that are being addressed by the paper at hand. Another example is Table 2. This table takes a lot of space, but little is said about it and the values presented. It seems that a summary table with value ranges would be more appropriate.

Response: The length of the paper has been reduced by 14 pages. The model description and some results that we found less pertinent to the central themes of radical cycling and missing reactivity have been moved into a Supplementary Information document, which includes Table 2 and Figure 9. Also, the Introduction section has been shortened.

2. Explain how the uncertainty ranges for the input variables were estimated, particularly for those species were no corresponding measurements were available (e.g., alkenes were assigned a 25% uncertainty based on speciation profiles, still is not clear why they were assigned this uncertainty level). Are these values consistent with what others have used? Are the estimates a function of the particular urban area being analyzed? Can these estimates represent an important source of overall uncertainty and influence the overall result?

Response (see Supplemental Information, p2 and on): See response to Reviewer #1, number 2 above. These uncertainties are consistent with estimates in Velasco et al., 2007. While derived independently for alkenes (see Velasco et al., 2007), they also compare – for good reasons or not – with uncertainties estimated in other modeling efforts e.g., RACM modeling. These estimates are not an important source of uncertainty in the overall result. We use Figure 2 to demonstrate this.

3. Revise sequence of the manuscript. Figure 1 is first cited on page 5375, after Figures 2-5. In Table 2, presented in section 3.1, values for the "chain length" are listed. However, the definition of chain length is presented in section 3.6.

Response: The sequence of the manuscript has been revised and is now consistent – please see the outline provided for an overview.

4. Page 5381, line 6: What are the implications of having most of the cases that fall outside the experimental uncertainty as P(OH) less than L(OH)?

Response (see Supplemental Information, p 5, line 10+): The implication is that a model that is constrained for both OH and HO2 measurements is not a balanced model. Only a model that is constrained for either OH or HO2 is balanced. For the modeling of chain length, however, this does not present a fundamental limitation, because our two chain length parameters are either only based on the production term (n(OH)), or on the branching ratio of radical loss versus propagation (ω). Neither chain length parameter convolutes radical initiation and termination processes.

5. Page 5383-5384, starting from line 25. The paragraph lacks of support. Only the idea of an expanded LN/Q parameters is mentioned, but no real insight is presented. The paragraph should be eliminated.

Response (see Supplemental Information, p 7, line 24+): We agree with the reviewer and have moved this paragraph to the Supplemental Information section so as not to confuse the reader. However, notably, in the context of LN/Q we discuss the effect of the internal inconsistency of the HOx measurements (the reviewer's previous comment). Hence, rather than deleting this paragraph we feel some information is contained for the interested reader.

6. In the conclusions section there are ideas that were not discussed in any other part of the manuscript, and thus lack of support o be included in this section. For example: page 5392, lines4-8, and lines 26 and on.

Response (see Conclusions, p26, line 16+): This has been revised and updated in the current manuscript.

Minor comments:

1. Page 5360; lines 16-18: It might not be clear what is meant by "chemical uncertainty", should it be uncertainty in chemical mechanism?

Response: Changed, see p 2, line 26.

2. Revise the use of semi-colons (";") in sentence constructions; there seems to be an "abuse" in its use. Also revise the use of the word "uncertainty". It seems that in some cases the word "error" might be a better selection. There is no need to clarify figure characteristics in the text (e.g., page 5369, lines 23-24, remove "(left)" and "(right)"; this should be in the figure caption). In the same spirit, do not use the figure captions to discuss them, it is redundant with respect to what is included in the text (e.g., Figure 5, Figure 6)

Response: We have revised the use of semi-colons throughout the manuscript. Some of the figure captions have been simplified. We have minimized the redundancy between figure captions and the body of the manuscript. However, we find it difficult to remove them entirely and think that limited cross-talk between the figures and the text enhances the message of the paper, in particular because readers often scan a manuscript with very limited time to read it thoroughly. We have moved a significant portion of the manuscript into the Supplementary Information section in an effort to use publication space in ACP responsibly.

3. Page 5361: NO and NO2 are defined in lines 3 and 4; there is no need to redefined them in lines 5 and 6 (from Introduction section).

Response: Changed.

4. Page 5361; line 11. Remove "kick" (from Introduction section)

Response: Changed.

5. Page 5361; line 20: I do not agree with the statement. Please clarify.

Response: Discussion changed and clarified.

6. Page 5361; line 26: There is a comma missing after Birmingham (from Introduction section).

Response: Changed.

7. Page 5373; line 25: Should say "missing reactivity".

Response: Changed, see p14, line 15.

8. Page 5374; line 4: Should say "... chemistry and ...".

Response: Changed, p14, line 22..

9. Page 5375; line 1: Should say "... Fig. 5B ..."

Response: Noted, section changed, and there is no longer a specific reference to Fig 5B.

10. Page 5377; line 8: It says ",... as it is OVOC...". Revise wording.

Response: Revised to read " … because OVOC is formed …", p17, line 20.

11. Table 1. Provide full reference for EPA document. In the Table caption letters A, B and C are assigned but other definitions are added in the table foot note that cause confusion.

Response: The full reference for the EPA document (online material) is included in the updated manuscript. Regarding the caption letters, I think the confusion stems from the use of a), b), and c) in the Table 1 caption, and the use of A, B, C, etc. in the body of the table. We have changed the lower case letters to numerals, i), ii), and iii).

12. Table 2. "hrs" is missing; define VOC-reac.; define chain length

Response: It is unclear where "hrs" is missing from. The reference to time has been changed to 07:00-13:00. Perhaps that addresses the reviewer's comment. Please advise. The caption has been changed to clarify VOC-reac. and chain length.